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Environmental Perspective on the Emerging Oil Shale Industry

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ENVIRONMENTAL PERSPECTIVE ON THE EMERGING OIL SHALE INDUSTRY

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati is engaged in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report provides a preliminary overview of environmental considerations related to the emerging oil shale industry. The report and similar ensuing reports are intended to develop the technical basis for eventual regulations.

The recently announced national synfuels program relies on development of the oil shale industry. We believe that providing information on environmental concerns and developing control technology in concert with development of oil shale technology will enable the establishment of a mature oil shale industry compatible with national environmental goals without unnecessary delay.

Further information on the subject of this report can be obtained through the authors and offices responsible for preparation of each topic or from the Oil Shale and Energy Mining Branch, Energy Pollution Control Division, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268.

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PREFACE

This document originated as a result of the U.S. Environmental Protection Agency (EPA) concern that the development of oil shale as an alternative energy source not be constrained by uncertainties about environmental standards. The EPA intent is to insure that technology-specific environmental goals are identified and achieved during the course of oil shale technology development. The concurrent development of control technology and oil shale technology will result in the undelayed establishment of a mature oil shale industry compatible with Federal, State, and local environmental goals.

This document is intended as part of a series leading toward the establishment of regulatory standards for the oil shale industry. The entire series is supported by the EPA oil shale research program and is expected to serve several purposes. First and foremost, it will communicate EPA regulatory policies to oil shale developers on a comprehensive basis. Second, the series will update the state of knowledge with respect to known oil shale pollutants and their potential effects. Third, the series will describe state-of-the-art control technologies as they evolve and will describe the remaining needs for which technologies are not sufficient. Fourth, the series will describe methods for monitoring and for sample collection and analysis applicable to the oil shale industry. Finally, it will suggest ranges of discharge and emission limits within which the oil shale industry should strive to operate. Ideally, as more information becomes available, each document in the series will offer more definitive limits and more demonstrated confidence in available control technologies.

This document presents general information relevant to oil shale pollution problems and their control as they are viewed today. It should be kept in mind that the present data base is meager and that attempts to define problems and their control precisely are incomplete. The purpose here is to present a first approximation to EPA's environmental expectations and thereby to generate, through their publication, the proper perspective, concern, and approach for the environmental aspects of oil shale development.

ABSTRACT

Oil shale deposits in the United States are among the richest and most extensive in the world. Estimates place total identified resources of medium and rich shales in the United States at 2 trillion equivalent barrels of oil. About 600 billion barrels are considered recoverable with present technology. This report summarizes the anticipated regulatory approach taken by the EPA toward oil shale development and is designed to serve as a reference and guide to EPA offices, Federal agencies, and private developers involved with the emerging oil shale industry.

The document conveys EPA's understanding and perspective of oil shale development by providing (1) a summation of available information on oil shale resources, (2) a summary of major air, water, solid waste, health, and other environmental impacts, (3) an analysis of applicable pollution control technology, including limitations, (4) a guide for the sampling, analysis, and monitoring of emissions, effluents, and solid wastes from oil shale processes, (5) suggestions for interim objectives for emissions, effluents, and solid waste disposal, and (6) a summary of oil shale technology, emissions, and effluents. The report provides a brief yet thorough discussion of the environmental problems of oil shale development.

For readers who wish further information on the topics covered in this volume, a list of Appendices referred to in the text, as well as ordering instructions, is included following the list of Tables.

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National Technical Information Service
U.S. Department of Commerce
Springfield, Virginia 22161

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ABBREVIATIONS

AA	—atomic absorption
AAS	—atomic absorption spectroscopy
ADA	—anthraquinone disulfonic acid
adits	—access tunnels
API	—American Petroleum Institute
ANFO	—Ammonium Nitrate Fuel Oil
ARCO	—Atlantic Richfield Corporation
ASTM	—American Society for Testing and Materials
BACT	—best available control technology
BaP	—benzo(α)pyrene
BAT	—Best Available Technology
BATEA	—best available technology economically achievable
bbl	—barrels (159 litres or 42 gallons)
BEJ	—Best Engineering Judgment
BLM	—Bureau of Land Management
BMP	—best management practices
BOD	—biochemical oxygen demand
BPT	—best practical technology
BTU	—British Thermal Units
cfm	—cubic feet per minute
CFR	—Code of Federal Regulations
CI	—chemical ionization
cmm	—cubic meters per minute
COD	—chemical oxygen demand
COED	—char-oil-energy development
Comm. Dev. Phs.	—commercial development phase
COS	—carbonyl sulfide
CRA	—compression/refrigeration/absorption
CRC	—compression/refrigeration/condensation
CWACOG	—Colorado West Area Council of Governments
DDP	—detailed development plan
DDT	—dichlorodiphenyltrichloroethane
de novo	—starting from scratch
DMEPG	—dimethyl ether of polyethylene glycol
DO	—dissolved oxygen
DOC	—dissolved oxygen content
DOE	—Department of Energy
DOI	—Department of Interior
dscf	—dry standard cubic foot
EDF	—Environmental Defense Fund
EDXRF	—energy dispersive x-ray fluorescence spectroscopy
EI	—electron impact
EIS	—environmental impact study
EPA	—Environmental Protection Agency
Eh or EH	—oxidation-reduction potential
FID	—flame ionization detector
FWPCA	—Federal Water Pollution Control Act
gal	—gallon

GC/MS	—gas chromatograph/mass spectrometer
GCR	—gas combustion retort
GPM	—gallons per minute
GPT	—gallons per ton
ha	—hectare
IFP	—Institute Francais de Petrok
IGT	—Institute of Gas Technology
in situ	—in the original location
in vitro	—outside the organism in an artificial apparatus
IPA	—Intergovernmental Personnel Act
IR	—Infrared
kmph	—kilometers per hour
kW	—kilowatt
kWh	—kilowatthour
LC	—liquid chromatography
LETC	—Laramie Energy Technology Center
LPG	—low pressure gas
M	—molar
MBAS	—methylene blue active substances
MCi	—megacuries
MDP	—Modified Development Phase
mill	—tenth of a cent
MIS	—modified *in situ*
MMC	—Multi-Mineral Corporation
Mod. Dev. Phs.	—modular development phase
mph	—miles per hour
MSSS	—Mass Spectral Search System
MTB	—methylthymol blue
NAA	—neutron activation analysis
NAAQS	—National Ambient Air Quality Standards
NAS	—National Academy of Sciences
NDIR	—nondispersive infrared
NESHAP	—National Emission Standards for Hazardous Air Pollutants
NEPA	—National Environmental Policy Act
NIH	—National Institute of Health
NMHC	—non-methane hydrocarbons
NOx	—oxides of nitrogen
NPC	—National Petroleum Council
NPDES	—National Pollutant Discharge Elimination System
NSPS	—New Source Performance Standards
NWS	—National Weather Service
ORNL	—Oak Ridge National Laboratory
OSHA	—Occupational and Safety Hazard Act
OXY	—Occidental Oil Shale, Inc.
PAD	—perchloric acid digestion
PAH	—polycyclic aromatic hydrocarbons
PCB	—polychlorinated biphenyls
pCi	—picocurie
PDU	—Process Development Unit
PES	—proton-electron spin spectrometer
PMC	—potency of the mixture complex
POM	—polycyclic organic matter
PON	—program opportunity notice
ppb	—parts per billion
ppbv	—parts per billion by volume
ppm	—parts per million

ppmv	—parts per million by volume
PSD	—prevention of significant deterioration
psig	—pounds per square inch (mercury scale)
PTCM	—potassium tetrachloromercurate
PUV	—pulsating ultraviolet
RBOSC	—Rio Blanco Oil Shale Development Corp.
RCRA	—Resource Conservation and Recovery Act
RSH	—sulfhydryl compounds
scf	—standard cubic foot
scfd	—standard cubic feet per day
scfm	—standard cubic feet per minute
scm	—standard cubic meter
scmd	—standard cubic meters per day
SCOT	—Shell Claus Off-gas Treating
SGR	—steam gas recirculation
SIC	—Standard Industrial Classification
SNG	—synthetic natural gas
SO_x	—oxides of sulfur
SSMS	—spark-source mass spectrometer
STORET	—storage and retrieval system
TCM	—tetrachloromercurate
TDS	—total dissolved solids
THC	—total hydrocarbons
TIC	—Total Inorganic Carbon
TKN	—Total Kjeldahl Nitrogen
TLC	—thin layer chromatography
TLV	—threshold limit values
TOSCO	—The Oil Shale Corp.
TRS	—Total Residual Sulfur
TRW, Inc.	—Thompson-Raymo-Woolridge
TSCA	—Toxic Substances Control Act
TSP	—Total Suspended Particulates
TSS	—total suspended solids
UBAG	—Uinta Basin Association of Governments
UIC	—underground injection control
UOC	—Union Oil Company
USBM	—U.S. Bureau of Mines
USFS	—United States Forestry Service
USGS	—U.S. Geological Survey
UV	—ultraviolet
VTN	—Voorheis-Trindle-Nelson
WATSTORE	—water data storage and retrieval system (USGS)
WRSP	—White River Shale Project
XRF	—x-ray fluorescence spectroscopy

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SECTION I
INTRODUCTION

The introductory section describes oil shale resources in the United States, with emphasis on the rich shales contained in the Green River Formation in Colorado, Utah, and Wyoming. It provides a status report on developmental activity and technology, and summarizes applicable current environmental control laws.

This report defines and evaluates oil shale on the basis of stratigraphy, mineralogy, and recoverability of oil. It presents detailed information on the rich shales, those that yield 62 to 125 l/tonne or 15 to 30 gal/ton of the Green River Formation, which is believed to contain 80 percent of all commercially attractive deposits.

The two general methods of recovering oil or gas from shale are mining plus surface retorting and *in situ* (in the original place) processing. The first section of this report describes these methods, discusses the status of mining retorting technology as it applies to the recovery of oil from shale and presents a short history of development during recent years.

A review of current Federal and State pollution control requirements applicable to oil shale facilities follows the technology discussion. Federal legislation generally establishes the framework for State environmental regulations. Therefore, the document discusses Federal laws dealing with air and water pollution, solid wastes, noise, and radiation with less emphasis on the State regulatory process.

PURPOSE OF DOCUMENT

The purpose of this document is to provide preliminary environmental guidance on the emerging oil shale industry. The report is intended to serve as a reference, summary, and guide to regulators, developers, and others who are or will be involved with the oil shale industry.

This report conveys the Environmental Protection Agency's (EPA) understanding and perspective of oil shale development by providing (a) a summation of available information on oil shale resources; (b) a summary of major air, water, solid waste, health, and other environmental impacts; (c) a brief overview of applicable pollution control technology; (d) suggestions for the sampling, analysis, and monitoring of emissions, effluents, and solid wastes from oil shale processes; and (e) suggestions for interim objectives for emissions, effluents, and solid waste control. The report contains a brief summary discussion of the environmental problems of oil shale development. For the reader not acquainted with oil shale technology, Section 7 presents a summation of the major retorting methods and their probable emissions, effluents, and solid wastes.

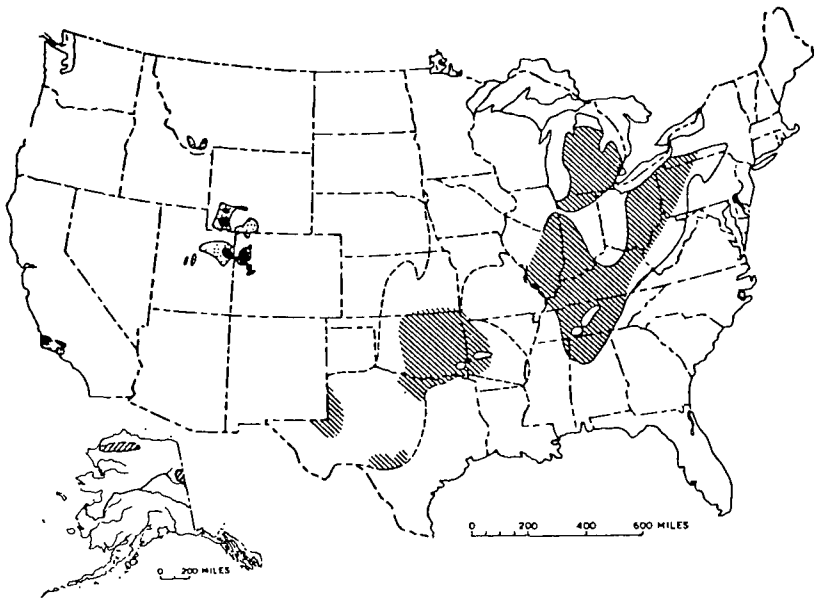
Government agencies and private developers will find this document useful as a source of basic information as well as for identifying EPA concerns and interests relative to oil shale development. The report discusses those environmental impacts and control technologies likely to be of importance. Oil shale developers will find Appendices D and F particularly useful; these appendices provide a discussion of Federal, State and local laws and permits applicable to oil shale development.

OIL SHALE RESOURCES

Charles Prien

Oil shale is commonly defined as a fine-grained sedimentary rock containing organic matter that is essentially insoluble in petroleum solvents, but that yields substantial quantities of oil upon pyrolysis (1). Though oil shale deposits occur throughout the world, those in the United States are among the highest grade, most extensive, and best explored.

U.S. oil shales (Figure 1-1) occur in four general locations: (a) the Tertiary period (Eocene) deposits of the Green River Formation in Colorado, Utah, and Wyoming; (b) the late Devonian and early Mississippian period marine shales of the central and eastern United States, stretching from Michigan and Pennsylvania southward through Indiana and Kentucky to Texas; (c) the early Cretaceous and upper Triassic marine shales in Alaska; and (d) the small Tertiary shale deposits of Montana, Nevada, Idaho, and California. Estimates place total known U.S. oil



Explanation

Tertiary deposits: Green River Formation in Colorado, Utah, and Wyoming, Monterey Formation, California; middle Tertiary deposits in Montana Black areas are known high-grade deposits.

Mesozoic deposits: Marine shale in Alaska.

Permian deposits: Phosphoria Formation, Montana.

Devonian and Mississippian deposits (resource estimates included for hachured areas only). Boundary dashed where concealed or where location is uncertain.

Figure 1-1. *Principal United States Oil Shale Deposits.* (Source: Reference 2)

shale resources in place, for oil shales yielding 42 l/tonne (10 gal of oil per ton of shale), at well over 270 billion tonnes or 2 trillion barrels (bbl) (2). The Green River Formation oil shales of the western United States accounts for an estimated 90 percent of this total resource, or some 250 billion tonnes (275 billion tons), and are thus generally regarded as being the most important commercially.

The Devonian marine black shales of the central and eastern United States are estimated to contain at least 54 billion tonnes, or 400 billion bbl of equivalent oil in place, but they are not currently considered to be commercially attractive. The Alaskan marine shales and the Tertiary shales of California and elsewhere have received little attention to date and are likewise not considered to be commercially attractive.

Green River Formation Oil Shale

Description of Resources—

The oil shale deposits of the Green River Formation occur in a 44,000-km^2 (16,988 mi^2) area in northwestern Colorado, northeastern Utah, and southeastern Wyoming (Figure 1-2). Total identified shale oil resources in place, which average 63 l/tonne (15 gal/ton) or more in strata up to 600 m (2,000 ft) thick, are estimated to be 163 billion tonnes (179 billion tons) in Colorado's Piceance Creek Basin, 44 billion tonnes (48 billion tons) in Utah's Uinta Basin, and 44 billion tonnes (48 billion tons) in the combined Green River, Washakie, and Sand Wash basins of Wyoming (Table 1-1). The three-state total is thus 251 billion tonnes (1,842 billion bbl).

The total in-place resource is not presently recoverable, but it is estimated by the U.S. Geological Survey (USGS) that approximately 80 percent of the known shale that yields 104 l/tonne (25 gal/ton) or more, or some 80 billion tonnes (88 billion tons) of shale oil are frequently located and of adequate thickness to be reasonably regarded as the potentially recoverable resource base. Different development

TABLE 1-1. TOTAL IN-PLACE SHALE OIL RESOURCES OF THE GREEN RIVER FORMATION[a,b]

	Type of shale (yield/tonne)					
	62.6 l/tonne (15 gal/ton) or more		104.3 l/tonne (25 gal/ton) or more		125.2 l/tonne (30 gal/ton) or more	
Location	Billions of tonnes	Billions of equivalent barrels of oil	Billions of tonnes	Billions of equivalent barrels of oil	Billions of tonnes	Billions of equivalent barrels of oil
Colorado	163.2	1,200	82.6	607	48.3	355
Utah	43.7	321	8.7	64	6.8	50
Wyoming	43.7	321	8.2	60	1.8	13
Total	250.6	1,842	99.5	731	56.9	418

[a] Source: Reference 3.
[b] In beds at least 3 m (10 ft) thick.

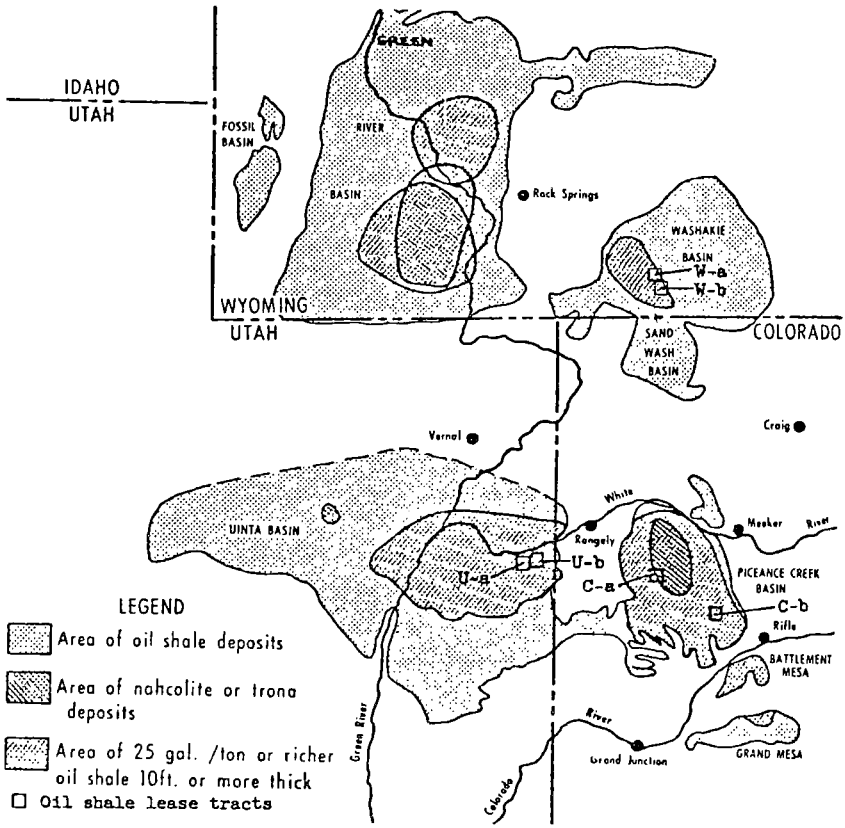


Figure 1-2. Green River Formation oil shale deposits. (Source: Reference 2)

schemes would result in various recovery percentages from this resource base. If 50 percent of the 104 l/tonne (25 gal/ton) or more resource could be recovered, it would be large enough to produce 270,000 tonnes/day (2 million bbl/day), or one-fourth the present daily imports, for more than 400 years. Table 1-1 shows that 80 to 85 percent of the in-place, 104- to 125-l/tonne (25- to 30-gal/ton) oil shale resources are in Colorado's Piceance Creek Basin, with the remainder divided between Utah's Uinta Basin and Wyoming.

Resource Ownership—

Oil shale ownership is summarized in Table 1-2. Oil shale resources occur on 4.5 million hectare (ha) (11 million acres) of land in the three-State Green River Formation oil shale region. Approximately 72 percent of this land is Federally owned and administered by the U.S. Department of the Interior (DOI). This Federal land contains 79 percent of the total in-place resource. The remaining 28 percent of the oil shale land is owned by the State, private individuals, and American Indians. This non-Federal land contains 21 percent of the total in-place resource. Of the total in-place resource of 252 billion tonnes (1,842 billion bbl), 65 percent is located in Col-

orado, 17 percent in Utah, and 17 percent in Wyoming. Of the 389 billion barrels of in-place resource on non-Federal lands throughout the region, 54 percent is in Colorado, 17 percent in Utah, and 29 percent in Wyoming.

Numerous legal proceedings are currently pending that cast doubt on title to oil shale lands, particularly in Colorado and Utah. As the various cases are decided in future years, overall ownership percentage will no doubt change.

One of the most significant cases at present concerns ownership of some 64,000 ha (157,000 acres) of oil shale land in Utah, an area that includes Federal lease tracts U-a and U-b. The state of Utah sued the DOI for title to these lands to complete the state's acquisition of lands pursuant to legislation which led to statehood. Federal courts at the district and appellate levels have ruled in favor of Utah, but the Federal Department of Justice has appealed the case to the U.S. Supreme Court. Thus a final decision is not expected until sometime in 1980.

The other principal type of pending litigation concerns title to hundreds of unpatented oil shale mining claims. Some of these cases have been underway for nearly 20 years. Specific details differ, but each case essentially involves private party or company attempts to obtain outright ownership of numerous claims originally staked under the 1872 Mining Law. The Department of the Interior has contested most of these claims on grounds varying from failure to perform assessment work to lack of discovery of valuable minerals. All unpatented mining claims are included in the Federal lands columns in Table 1-2.

Stratigraphy and Mineralogy—

A knowledge of the general stratigraphy and mineralogy of the Green River Formation is important for an understanding of both the mining and surface processing of the oil shale resource and associated minerals, and of problems that may be encountered during *in situ* processing. The following description is based largely on the Piceance Creek Basin, since it contains more than 80 percent of the commercially attractive Green River Formation oil shale.

A continuously identifiable zone of 104 l/tonne (25 gal/ton) or more of Green River Formation shale extends throughout all three States. It is known as the Mahogany Zone in Colorado and Utah, and the Le Clede bed in Wyoming. The zone averages a thickness of some 30 m (100 ft) in Utah and Colorado, but less in Wyoming. In many places the zone is exposed at the surface in easily accessible escarpments, but in other locations it is covered by overburden varying in thickness from a few to several hundred meters. Below the Mahogany Zone in the central portion of the Piceance Basin, there are seven additional shale-bearing zones (called R-6 through R-0, in order of descending depth) totaling 330 to 400 m (1,100 to 1,300 ft) in thickness. Zones R-6 through R-2, together with the Mahogany Zone, constitute the complete Parachute Creek Member of the Green River Formation. Zones R-1 and R-0 are in the Garden Gulch.

The R-6 zone roughly corresponds to what is frequently referred to as the "leached zone," an aquifer of saline water. The R-5 and R-4 oil shale zones commonly contain bedded and/or disseminated nahcolite (sodium bicarbonate). Zone R-5 downward through zone R-2 also normally contain dawsonite (a sodium aluminum hydroxy carbonate). Below the Parachute Creek Member, the shale bearing zones R-1 and R-0 continue into the Garden Gulch and Douglas Creek members of the Formation. Below zone R-0, the shale beds become too lean to be of any significance.

Green River oil shale consists essentially of dolomite, calcite, illite, and quartz, plus a solvent-insoluble organic material called kerogen. A typical composition of Mahogany Zone oil shale is shown in Table 1-3. The mineralogy is basically consistent throughout the Basin, except for 1,300 km^2 (500 mi^2) in the central part of the Basin (Figure 1-2), where substantial quantities of saline minerals (nahcolite, halite, and dawsonite) are present, in contrast to their virtual absence along the periphery of the Basin.

TABLE 1-2. GREEN RIVER FORMATION OIL SHALE OWNERSHIP[a]

Item	Colorado			Utah			Wyoming			Total		
	Federal	Non-Federal[a]	Total	Federal	Non-Federal	Total	Federal	Non-Federal	Total	Federal	Non-Federal	Total
Amount of land:												
Thousands of hectares	570	160	730	1,540	445	1,985	1,090	650	1,740	3,200	1,255	4,455
Thousands of acres	1,400	400	1,800	3,800	1,100	4,900	2,700	1,600	4,300	7,900	3,100	11,000
As % of total	13	4	16[c]	35	10	45	25	15	39[c]	72	28	100
As % of total Federal or non-Federal	18	13	—	48	35	—	34	52	—	100	100	100
Amount of in-place resource:[d]												
Billions of tonnes	135	29	164	35	9	44	28	16	44	198	54	252
Billions of barrels	990	210	1,200	254	67	321	209	112	321	1,453	389	1,842
As % of total	53	12	65	14	4	17[c]	11	6	17	79	21	100
As % of total Federal or non-Federal	68	54	—	18	17	—	14	29	—	100	100	100

[a] Source: References 3 and 4.
[b] Non-Federal land includes private, State, and Indian lands.
[c] Figures do not add because of rounding.
[d] Resource expressed as in-place oil shale assaying 63 l/tonne (15 gal/ton) or more, at least 3 m (10 ft) thick.

TABLE 1-3. TYPICAL COMPOSITION OF 104-l/TONNE GREEN RIVER FORMATION OIL SHALE[a]

Constituent	Wt.%[b]
Kerogen:	14
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1.0
Oxygen	5.8
Inorganic Minerals	86
Dolomite	32
Calcite	16
Quartz	15
Illite	19
Albite	10
K Feldspar	6
Pyrite	1
Analcime	1

[a] Source: References 5 and 6.
[b] Note: All percentages on dry basis.

Six principal stratigraphic units are usually identified (see Figure 1-3). They are as follows: (1) an overburden layer, the Uinta Formation, which is comprised mainly of quartz-bearing sandstones and siltstones with minor dolomitic marlstone and is overlain by alluvium in valleys dissecting the Formation; (2) the Upper Part of the Parachute Creek Member of the Green River Formation, which is comprised of oil shale containing the minerals dolomite, calcite, quartz, and albite, and together with the Uinta Formation forms the "Upper Aquifer"; (3) the Mahogany Zone of the Parachute Creek Member, containing moderate-to-high grade oil shale and generally exhibiting very low permeability except in areas of intense fracturing; (4) the leached zone of the Parachute Creek Member which is comprised of oil shale devoid of most saline minerals and encompasses the "Lower Aquifer" and associated saline waters; (5) a saline zone which, in addition to oil shale, contains halite, nahcolite, and dawsonite; and (6) the Garden Gulch zone of low-to-moderate grade oil shale with low permeability.

The oil shales of the Uinta Basin are stratigraphically similar to those in the Piceance Creek Basin, although the oil shale strata are leaner, thinner, less continuous, and do not contain commercially attractive quantities of saline minerals. The highest grade of oil shale in the Uinta Basin is located in the east-central portion near the Colorado border (Figure 1-2), where the deposit attains a maximum thickness of approximately 185 m (600 ft) and contains interbedded intervals with oil yields as high as 200 l/tonne (50 gal/ton). The range in overburden thicknesses in the Uinta Basin are comparable to those in the Piceance Basin.

In the Green River Basin of Wyoming, oil shale occurs in thin and geographically widely dispersed beds distributed in the Tipton, Wilkins Peak, and Laney members of the Green River Formation. The Wilkins Peak Member contains thick, commercially exploitable beds of trona. In the Washakie Basin, oil shale occurs primarily in the Laney Member, with leaner and thinner shales in the Tipton Member. The shales in the Sand Wash and Great Divide basins are too poor to be commercially significant.

Geologic Unit	Unit subdivisions		Lithologic description	Hydrologic unit	Water-yielding properties
Valley alluvium 0' - 140'			Sand, gravel, clay	Alluvial aquifer	Limited in areal extent and thickness. 1,500 gpm maximum
Uinta Formation 0' - 1230'	–		Mainly sandstone and siltstone with minor amounts of low-grade oil shale and barren marlstone.	Upper aquifer	Well yields about 100 gpm. locally more where unit is fractured TDS from 250 to 1800 ppm.
Green River Formation	Parachute Creek Member 500' - 1600'	Upper Part Parachute Creek Member	Low-to-high-grade oil shale		Thickest in southern portion of Piceance Creek Basin
		Mahogany zone	Moderate-to-high-grade oil shale	Aquitard	Low permeability. Limited percolation through vertical fractures is important in regional ground water flow.
		Leached zone	Low-to high-grade oil shale.	Lower aquifer	Best developed in north central part of basin. Confined aquifer. Wells may yield 1000 gpm. About 2,000 ppm TDS near edges to 45,000 TDS near center.
		High-resistivity or saline zone	Saline minerals and moderate-to high-grade oil shale.	Aquitard	Relatively impermeable.
	Garden Gulch member 0' - 900'		Mainly clayey shale and low-to-moderate-grade oil shale.	Aquitard	Relatively impermeable.
	Douglas Creek member 0' - 800'		Mainly sandstone with minor amounts of limestone.	Minor aquifer	Relatively impermeable About 350 gpm well yields. TDS from 3,000 to 12,000 ppm.
	Anvil Points member 0' - 1670'		Shale, sandstone, marlstone.	Minor aquifer	Relatively impermeable
Wasatch Formation				Aquitard	Relatively impermeable.

Figure 1-3. Detailed stratigraphy of Green River Formation.

Various trace elements have been identified as being associated with Green River Formation oil shale. A selected list of typical elements and their concentrations, found in various locations in the Piceance Creek Basin are provided in Section 3 under Trace Elements. Attention is directed particularly to the amounts of fluorine, boron, arsenic, and molybdenum present.

Regional Description—

The 44,000-km^2 (17,000-mi^2) oil shale region of Colorado, Utah, and Wyoming (Figure 1-2) is a semiarid land receiving 18 to 50 cm (7 to 20 in.) of precipitation annually. Elevation ranges from 1,500 to 3,000 m (4,920 to 9,840 ft) within the high plateaus of the Upper Colorado River Basin and the equally high plains of Wyoming. The region is characterized by sparse vegetation, immature soils, and stark topography. The terrain varies from deeply dissected wooded plateaus bordered by high oil shale cliffs to poorly vegetated plains with low escarpments. The oil shale deposits are located in large, well-defined topographic basins with distinctive surface drainage: the Piceance Basin in Colorado, the Uinta Basin in Utah, and the Green River, Washakie, and Sand Wash basins in Colorado and Wyoming. The entire region lies within the Upper Colorado River Basin and is drained by the Colorado River and its tributaries.

Most of the region's precipitation is received as snow during the winter months (December through April). Rain occurs intermittently during the summer, often as storms of high intensity. Precipitation varies with elevation, increasing approximately 8 cm (3 in.) for each 500-m (1,640-ft) increase in elevation above 300 m (984 ft)—hence, the wide range for precipitation mentioned earlier.

Temperatures may reach 38 °C (100 °F) during midsummer at lower elevations, and as much as -34 °C (-29 °F) at the higher elevations during winter, with 50 to 125 frost-free days annually. Wind patterns vary in the Piceance and Uinta basins, being generally westerly during the day with drainage winds down the canyons and gullies at night. Mild temperature inversions are common in the Piceance and Uinta basins.

Existing air quality throughout the oil shale region is generally acceptable. Ambient concentrations of sulfur dioxide, nitrogen oxides, hydrogen sulfide, and carbon monoxide are very low. In both the Piceance and Uinta basins, however, natural concentrations of particulates, total oxidants (measured as ozone), and nonmethane hydrocarbons occasionally exceed the National Ambient Air Quality Standards (NAAQS), even in the absence of any significant activity at present.

Population density is low, averaging about 3 persons/km^2 (1 person/mi^2) throughout the entire region but considerably lower in many large areas of the region. For example, it was reported in 1967 that a 6,500-km^2 (2,510 mi^2) area in the southeast portion of the Uinta Basin had a population of only 250, or a density of only 0.04 persons/km^2 (.015 persons/mi^2). Total population in the entire region is about 120,000, of which 62 percent are in Colorado, 17 percent in Utah, and 21 percent in Wyoming. Major communities include Grand Junction, Rifle, Meeker, Craig, and Rangely in Colorado; Vernal, Utah; and, Green River and Rock Springs in Wyoming. The region's economy is currently based on agriculture (cattle and sheep ranching), petroleum and other mineral production (oil, gas, uranium, trona, and coal), and tourism.

Piceance Basin—The Piceance Basin in Colorado is a structural entity wherein groundwater moves from recharge areas at the margins and along the Piceance Creek and Parachute-Roan Creek Divide to discharge areas in the northeastern part of the basin and along the Southern outcrop by way of secondary permeability (mainly fractures and joints). Elevations vary from 1,600 m (5,200 ft) along the White River on the north to 2,740 m (9,000 ft) on the south. The northern part of the basin is drained by Piceance and Yellow Creeks, both of which discharge into the White River, which joins the Green River in Utah. The southern part of the basin is drained by Parachute and Roan Creeks which flow into the Colorado River.

Groundwater accounts for about 80 percent of the annual water discharge from the basin. Total dissolved solids in the groundwater varies from about 250 mg/l (2.09×10^{-3} lbs/gal) in the Upper Aquifer to 63,000 mg/l (0.525 lbs/gal) in the Lower Aquifer. Sagebrush, serviceberry, scrub oak, pinyon, juniper, mountain mahogany, and other shrubs dominate the vegetation, except for cultivated areas of alfalfa and other crops on valley floors.

Uinta Basin—The Uinta Basin encompasses some 17,200 km^2 (6,650 mi^2) in Utah and 900 km^2 (350 mi^2) in Colorado, and is separated structurally from the Piceance Basin by the Douglas Creek Arch. Elevations vary from 3,000 m (9,840 ft) atop the Roan Cliffs on the basin's southern boundary to 1,310 m (4,300 ft) on the valley floor of the Green River, 29 km (18 mi) northwest of the Roan Cliffs. The basin contains deposits of gilsonite, natural gas, petroleum, and tar sands, in addition to oil shale.

Groundwater in the Uinta Basin ranges from fresh (350 mg/l or 2.92×10^{-3} lbs/gal total dissolved solids) to briny (72,000 mg/l or 0.60 lbs/gal), but supplies are much more limited than in the Piceance Basin. The Green River flows from the northeast to the southwest through the region, cutting through the major oil shale deposits. The White River flows westward from Colorado and joins the Green River near Ouray, Utah.

The basin is semiarid, with 18 to 38 cm (7 to 15 in.) of precipitation annually, 45 percent of which is received as snow. Desert shrub, salt desert shrub, pinyon juniper, and sagebrush dominate the vegetation. The terrain is deeply dissected and therefore difficult to traverse.

Wyoming Basins—Oil shales in the Green River and Washakie Basins of Wyoming are leaner and less continuous than in either Colorado or Utah. Oil shale in Wyoming occurs over an extensive area of approximately 23,300 km^2 (9,000 mi^2), bounded on the west by the Wasatch Mountains, on the north partly by the Wind River Range, on the east by the Medicine Bow Range, and on the south by the Uinta Mountains. Elevations range from 1,500 to 2,450 km (4,920 to 8,000 ft). Hills and ridges frequently have a steep incline on one side and a gently facing slope on the other. Drainage in the area flows into the Green River and the Big Sandy River. Dissolved solids in surface streams range from 150 to 855 mg/l (1.25×10^{-3} to 7.13×10^{-3} lbs/gal). Groundwater quality in the region varies from 450 to 7,000 mg/l (3.75×10^{-3} to 5.84×10^{-2} lbs/gal); it occurs primarily in the Laney Member of the Green River Formation, but also in the Bridger, Wasatch, and Fort Union Formations.

Principal types of vegetation include sagebrush, mountain shrub, juniper, greasewood, and salt desert shrub. The climate is semiarid, with 18 to 53 cm (7 to 21 in) of precipitation annually, mostly as snow. Temperature ranges are extreme, from -40° to 32°C (-40° to 90°F), with 50 to 120 frost-free days. High winds are typical of the region.

Devonian Shales

The vast deposits of the western Green River Formation lacustrine oil shale have long diverted attention from the black marine shales of the Mississippian/Devonian periods in the Eastern and Central States. These shales, part of an original shallow inland sea, occur over an area of more than 1 million km^2 (400,000 mi^2) in Ohio, Kentucky, Tennessee, Indiana, Michigan, Alabama (the Appalachian, Illinois, and Michigan basin areas), and even extend as far southwest as Oklahoma and Texas.

Description of Resources—

The thickness of black shale deposits varies, but it is seldom more than 60 m (200 ft). Strata are exposed at the surface in portions of the Appalachian, Illinois, and Michigan basins, but gradually dip to the west to a depth of some 915 m (3,000 ft). Some of the deposits in the 400,000-km^2 (160,000-mi^2) Appalachian Basin are associated with significant quantities of potentially recoverable natural gas. Other deposits, such as the Antrim Shale of Michigan, are being investigated as potential candidates for *in situ* gasification.

The Devonian shales are lean by western shale standards, with an average Fisher assay of only 42 l/tonne (10 gal/ton); however, the carbon content of Devonian shales is typically about 14 percent, or approximately the same as Green River shale assaying 125 l/tonne (30 gal/ton). The difference in Fischer assay is due to the higher carbon to hydrogen weight ratio of the 42-l/tonne Devonian shale (11.2 to 1) as compared with the 125-l/tonne Green River shale (7.2 to 1). If, however, the 42-l/tonne Devonian shale is retorted in the presence of hydrogen (i.e. hydroretorted), oil yield can be increased to 104 l/tonne (25 gal/ton), according to research conducted by the Institute of Gas Technology (IGT) (7).

The higher oil yields possible with hydroretorting can, of course, have an influence on defining the Devonian shale resource base. The USGS estimate of equivalent oil in place in Devonian shales is 54 billion tonnes (400 billion bbl), without considering the effect of hydrogen in retorting. With hydroretorting, this value could easily increase to 136 billion tonnes (1 trillion bbl), or 250 percent of conventional Fischer assay.

The Institute of Gas Technology has surveyed the three principal Devonian shale basins (Appalachian, Illinois, and Michigan) and estimated that some 58 billion tonnes (423 billion bbl) of oil could be recovered from the 16,000 km^2 (6,200 mi^2) of outcrops and relatively shallow deposits in these basins alone if hydroretorting were employed. Their criteria for a recoverable resource required that a shale deposit have an organic content of more than 10 percent by weight, a unit rock thickness of at least 3 m (10 ft), an overburden thickness of less than 60 m (200 ft), and a stripping ratio of less than 2.5 to 1. The study assumed hydroretorting yields of 85 percent of the organic carbon present, and strip mining at 90 percent recovery of in-place shale.

Stratigraphy and Mineralogy—

The stratigraphy and mineralogy of Devonian shales has not been completely examined. The rock matrix is primarily illite, with little mineral carbonate (0.5 percent) compared with Green River shale (48 percent). Many Devonian shale deposits contain small amounts of uranium, vanadium, and phosphates.

The Antrim shales of Michigan have probably been studied as much as any of the Devonian shales. Humphrey and Wise (8) have described Antrim shale as a very fine-grained, dense (2,323 kg/m^3, 145 lb/ft^3), impermeable, laminated structure composed primarily of illite (45 percent), quartz (30 percent), mineral carbonates (5 percent), pyrite (5 percent), miscellaneous mineral (5 percent), and organic material (10 percent) as a finely dispersed amorphous binder. Fischer assay oil yields range from 8.3 to 62.6 l/tonne (2 to 15 gal/ton).

Because the Devonian shales are largely located in highly industrialized areas of the United States, interest in their potential as an energy resource is higher than might otherwise be the case. Current research programs are aimed at investigating both *in situ* and aboveground retorting of Devonian shales, and also at procedures for stimulating and recovering associated natural gas.

Other Shales

Among other U.S. shale deposits are the thin strata of carbonaceous shales associated with coal beds, particularly in the Appalachian coal region. It is estimated that perhaps 8 billion tonnes (60 billion bbl) of equivalent oil may be present there in high grade shales assaying from 104 to 417 l/tonne (25 to 100 gal/ton). In California, the Miocene marine shales are believed to constitute a 10-billion tonne (70-billion bbl) resource in shales varying from 21 to 104 l/tonne (5 to 25 gal/ton). In southwestern Montana, beds of Permian black shale, ranging from 21 to 63 l/tonne (5 to 15 gal/ton), may total up to 1.4 billion tonnes (10 billion bbl) of equivalent oil in place. As with the Appalachian coal shales, however, neither the Alaskan, Californian, nor the Montana shale are considered to be of near-term commercial importance (2).

CURRENT STATUS OF INDUSTRY DEVELOPMENT

Charles Prien

The two general methods for the production of oil or gas from oil shale are: (a) mining followed by surface retorting and (b) *in situ* processing. Both are under active investigation at the present time. Surface retorting may follow either underground room-and-pillar mining or other underground mining methods, or open pit mining.

In situ processing, in which the majority of a target oil shale zone is retorted in place, may be true *in situ* or modified *in situ*. True *in situ* consists of hydraulically and/or explosively fracturing shale in place to create permeability for retorting. In modified *in situ* procedures, a portion of the shale (perhaps 15 to 40 percent) is mined and removed to the surface, while the remaining shale in place is explosively rubblized to fill the void created by mining. The result is, in effect, an underground

rubblized to fill the void created by mining. The result is, in effect, an underground retort filled with fragmented oil shale with a void volume and permeability adequate for retorting.

A brief summary of mining and retorting activities and current project status is presented in the following pages. Most of the discussion concerns development of Green River Formation oil shale in Colorado, Utah, and Wyoming. Particular attention is given to the individual field programs where experimental and commercial activities are now scheduled through 1985. Overall project schedules are summarized in Figures 1-4 and 1-5. Technical details of the processes mentioned are described in greater depth in Section 7.

Mining and Surface Retorting

Industry and government research and development concerning U.S. oil shales, primarily during the past 30 years, has led to a processing sequence most often involving room-and-pillar underground mining. Commercial-scale room-and-pillar mining of oil shale has been demonstrated by the U.S. Bureau of Mines (USBM) and Paraho Development Corporation at Anvil Points near Rifle, Colorado, and by Colony Development Operation, Union Oil Company, and Mobil Oil Corporation on their respective properties along Parachute Creek north of Grand Valley, Colorado. Though these mines were not intended to produce oil shale in quantities sufficient to feed commercial-scale retorting complexes, they are nevertheless commercial-scale in all other respects, in that full-size rooms and pillars were created by full sized equipment. In all of the existing demonstration mines, access to target oil shale intervals has been gained via horizontal access tunnels (adits) along cliff faces. Although this is possible at the southern edge of the Piceance Basin where the oil shale deposit terminates in an abrupt escarpment, access at other margins and in the interior of the basin would have to be by vertical or inclined shaft.

In room-and-pillar mining, a series of rooms is created underground, with 25 to 45 percent of the interval left in place as pillars for roof support. In the USBM mine, for example, rooms and pillars are squares, 18.3 m (60 ft) on a side; total room height is 22.3 m (73 ft) in two levels of 11.9 m (39 ft) and 10.4 m (34 ft). Pillar and room dimensions, and thus percent recovery of in-place oil shale, are functions of the thickness of overburden present at a given site. Because oil shale is a very competent rock, little or no surface subsidence is expected during the life of the mine from well designed room and pillar mining.

Groundwater might pose problems in some locations, but more data are still needed to determine the exact nature of these potential problems. As mine development progresses at a given site, a point could be reached where as much as 70 to 85 percent of the spent shale resulting from surface retorting could be returned to the mine. This would further reduce the possibility of surface subsidence, would reduce the amount of spent shale disposal required at the surface, and might provide for additional resource recovery.

While open pit oil shale mining has been proposed for certain locations in the Piceance Basin, it has not yet been demonstrated. The technology, however, would be basically the same as that employed in open pit copper mining. Open pit mining would result in greater resource recovery than underground room and pillar mining, unless restricted to a very small surface area.

Surface oil shale technology was initiated over 60 years ago. Much of the early work came on the heels of World War I. In 1925, at least 28 pilot plants were operating in Oregon, California, Utah, Colorado, Montana, Kentucky, Pennsylvania, and New York. By 1930, all of these operations had ceased. Renewed interest in oil followed World War II and for the most part provided the atmosphere which led to the development of five surface retorting processes which have been developed to a stage of potential industrial scale-up on Green River Formation Oil

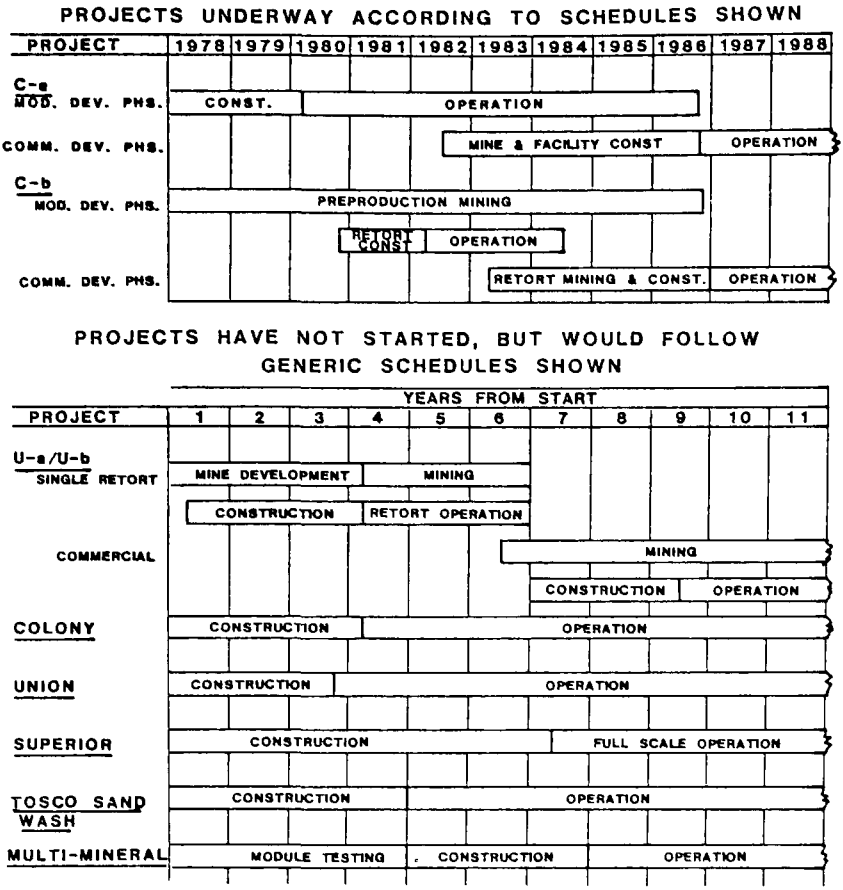


Figure 1-4. Project schedules for commercial oil shale projects.

Shale. These are: The Oil Shale Corporation (TOSCO) II and Lurgi Ruhrgas processes, which employ recycled hot solids for heating; the Paraho Direct Mode process, a gas combustion type process in which heat is furnished by an internal combustion zone within the retort; and the Union B Retort and Superior Oil processes, which have external, fuel-fired furnaces as heat sources.

The TOSCO II process has been tested at a throughput capacity of some 900 tonnes/day (1,000 ton/day) at the Colony semi-works plant on Parachute Creek, and the Paraho process has been operated at a capacity of 365 tonnes/day (330 ton/day) at Anvil Points. Both could be considered amenable to early scale-up to commercial modules of as great as 9,000-tonne/day (10,000-ton/day) capacity. This is also true of the Union B retort, which is based on an earlier retort design; a 1,100-tonne/day (1,210-ton/day) retort of the earlier design was successfully operated 20 years ago at Union property on Parachute Creek.

A Lurgi Ruhrgas pilot plant of 14.5- to 22.7-tonne/day (15.6- to 25.0-ton/day) nominal capacity has been used in West Germany to process Colorado shale, and based on that experience, a 3,600-tonne/day (3,960-ton/day) demonstration unit has been designed. Superior Oil Company has operated a 2,200-tonne/day (2,420-ton/day) pilot plant in Cleveland and has proposed a 2,200-tonne/day (2,420-ton/day) commercial plant.

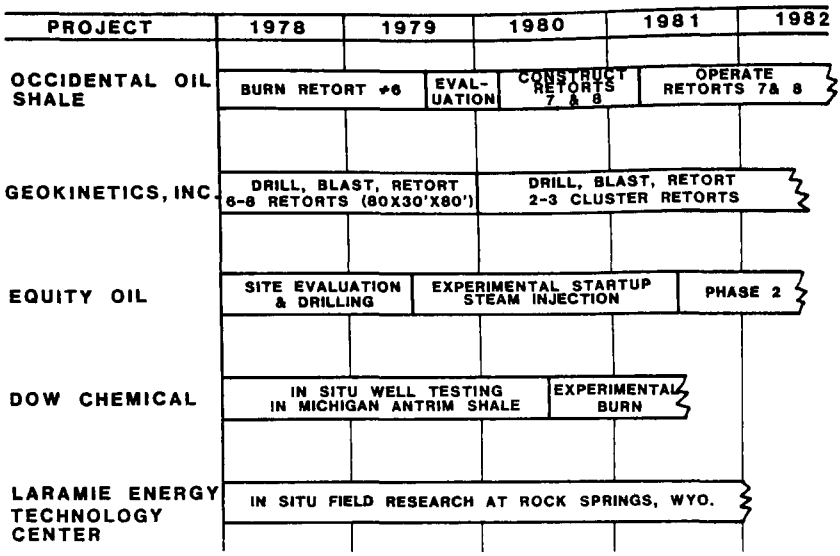


Figure 1-5. Project schedules for field test oil shale projects.

In addition to these five processes, a 0.9-tonne/hour (1.0-ton/hour) hydrogasification pilot plant has been operated for several years by the Institute of Gas Technology in Chicago. The unit has been operated on both Green River and Devonian shales.

In Situ Processing

The retorting of oil shale *in situ* has always been an attractive alternative to surface retorting since it eliminates the need for: the construction and operation of a large surface retorting facility; other attendant facilities such as crushing, handling, and oil shale feed storage systems; and, the material handling and surface disposal of spent shale. Depending on market conditions for product shale oil from *in situ* processing, on site upgrading facilities could be required.

In situ processing generally falls into one of two categories: True (borehole) *in situ* or modified *in situ*. True *in situ* generally involves the drilling of injection and production holes from the surface into the oil shale strata to be retorted. These holes are also used to fracture (hydraulic and explosive) and create permeability in the oil shale. Other variations include using the injection and production holes to inject fluids for the dissolution of soluble saline minerals. Once permeability is established, hot fluids or fire fronts are passed from injection wells to production wells where the retorted product shale oil is pumped to the surface. Modified *in situ* differs from true *in situ* in that mining is utilized to remove a volume of the oil shale (perhaps 15 to 40 percent). The remaining oil shale in-place is explosively expanded (rubblized) into the void created by the mining. In effect, an underground vertical or horizontal retort is prepared through which hot fluids or a fire front may be passed to produce shale oil.

Research along the line of true or borehole *in situ* was initiated by private industry 26 years ago. Field tests were performed by Sinclair Oil and Gas Company in 1953-54 and again in 1965. From 1965 to 1971, Equity Oil conducted tests in a naturally fractured zone in the Piceance Basin. Between 1964 and 1970, two nuclear *in situ* experiments (Project Bronco and Operation Utah) were proposed, but never conducted. Within the past 10 years, additional *in situ* field experiments have been conducted in the Piceance Basin by Mobil Oil (at shallow depth), by Exxon (in lower zone shales) and by Shell Oil (with hot miscible fluids). All of these efforts have now been discontinued.

In 1975, Geokinetics began field tests of its true *in situ* process at a site in the Uinta Basin of Utah. This work is currently being conducted under a Program Opportunity Notice (PON) contract with the Department of Energy (DOE). Some 20 retorts have been constructed and 11 have been tested to date, all at relatively shallow depths. Geokinetics' Retort No. 18, for example, is 55 by 48 by 5 m thick (180 by 156 by 17 ft), with 6 m (20 ft) of overburden. Blasting and burning of two three-retort clusters is planned from 1980 to 1982.

The Federal government became interested in true *in situ* oil shale retorting in the early 1960's. A series of true *in situ* field experiments was begun by the U.S. Bureau of Mines, Laramie Energy Research Center (now DOE, Laramie Energy Technology Center) in 1965 at a site near Rock Springs, Wyoming, where experimentation continues today. Also in 1965, the Laramie Energy Research Center constructed a 9-tonne (10-ton) batch retort to simulate underground conditions expected from the detonation of a nuclear device in oil shale. A much larger unit, a 136-tonne (150-ton) batch retort, was constructed in 1969 for the same purpose. These two retorts are still used today and over the years have provided useful engineering data for both *in situ* and surface retorting research.

Modified *in situ* research was initiated only seven years ago. In 1972, Occidental Oil Shale, Inc. began field experimentation of its vertical, modified *in situ* process at Logan Wash near Debeque, Colorado at the southern edge of the Piceance Basin. To date, six experimental retorts of increasing size have been rubblized and retorted at this site, and additional tests are planned through 1982. Part of these tests are being financed under a DOE PON contract. The Department of Energy has recently proposed a horizontal modified *in situ* project at a site in Cowboy Canyon near Bonanza, Utah.

Shale Oil Production

Shale oil production over the years has been largely undocumented. Data compiled from literature searches and shale oil producers reveal the limited quantities of shale oil that have been produced over the years. Table 1-4 lists various operations which have produced shale oil. Production is listed for each of the operations in which quantity could be determined as well as shale oil disposition and number of barrels currently in storage.

Current Project Status

In 1972, Colony Development Operation (now composed of Atlantic Richfield Corporation (ARCO) and TOSCO) completed operations on its 900-tonne/day (1,000-ton/day) TOSCO II semi-works plant on Parachute Creek and prepared a design for a 6,392-tonne/day (47,000-bbl/day) commercial plant.

A final environmental impact statement for the project was approved in 1977. Colony is now in the process of applying for the permits necessary to construct a commercial project on their Davis Gulch site. The Environmental Protection Agency issued a conditional Prevention of Significant Deterioration (PSD) permit in July 1979, and Colony is awaiting approval of a State Mined Land Reclamation Permit. Definite plans to proceed with plant construction have not yet been announced.

In 1974, Paraho began a 3-year, industry-sponsored demonstration program on the Paraho vertical kiln retorting process at Anvil Points. This work was completed at the end of 1976. During operation of the demonstration plant, the U.S. Navy signed a contract with Paraho for production of 100,000 barrels of crude shale oil which was subsequently refined at Sohio's Cleveland refinery. Paraho has since proposed construction of a 10,400-tonne/day (11,500-ton/day), $90 million commercial module. Funding for the $3 million engineering design phase of this project is currently being sought. Also, an Environmental Impact Study (EIS) is being developed by the DOE.

Union Oil Company has for several years tested the Union B and steam gas recirculation (SGR) surface retorting processes in a 3-tonne/day (3.3-ton/day) pilot plant in Brea, California. These are successors to Union's A retort, which was successfully operated at a rate of 1,100 tonnes/day (1,210 tons/day) in a semi-works plant near Grand Valley, Colorado, in 1957 and 1958. Union announced plans in 1978 for construction of a 9,000-tonne/day (10,000-ton/day) commercial module using the Retort B design at its Long Ridge site near the location of the earlier semi-works plant. Union hopes to begin construction during 1980 and operate the plant through 2000. All required permits for this project have been secured, but Union has stated that the project is contingent on approval of a $3/barrel income tax credit.

The Superior Oil Company is continuing its efforts to exchange 1,041 ha (2,572 acres) of its private lands at the north edge of the Piceance Basin for 828 ha (2,045 acres) of adjacent Federal land to block up a more manageable tract for development. The lands in question contain substantial quantities of sodium minerals such as nahcolite and dawsonite. A draft EIS covering the land exchange was prepared by the U.S. Bureau of Land Management (BLM) in July 1979. Superior proposes to develop a 23,700-tonne/day (26,200-ton/day) multi-mineral project at the site that would produce shale oil, nahcolite, and alumina.

The State of Utah has permitted TOSCO Corp. to unitize 5,900 ha (14,000 acres) of noncontiguous state oil shale leases in the central portion of the Uinta Basin. In return, TOSCO has agreed to spend a minimum of $8 million by 1984 for predevelopment activities on what is referred to as the Sand Wash Unit. Site exploration, environmental monitoring, and shaft sinking are currently underway on the unit.

On April 30, 1979, Multi Mineral Corporation (MMC), U.S. Bureau of Mines and U.S. Bureau of Land Management signed an agreement which permits MMC to conduct a one-year experimental mining program at the U.S. Bureau of Mines Horse Draw Facility. The Multi Mineral Corporation has developed the Integrated *In Situ* process which would produce raw nahcolite, shale oil, fuel gas, alumina, and soda ash in one integrated operation. Upon completion of the experimental program, MMC hopes to enter into a three-year cooperative agreement with DOE and DOI to construct and test a full scale module of the Integrated *In Situ* process. Upon successful completion of this phase, MMC would bring the plant to commercial production of 4,500 to 9,000 tonne/day (5,000 to 10,000 ton/day) raw nahcolite, 6,800 tonne/day (50,000 bbl/day) shale oil, 900 tonne/day (1,000 ton/-day) alumina, and 4,500 to 9,000 tonne/day (5,000 to 10,000 ton/day) soda ash by 1986.

In 1974, the U.S. Department of the Interior issued Federal leases on four 2,065-ha (5,100-acre) tracts of oil shale land—Tracts C-a and C-b in Colorado and Tracts U-a and U-b in Utah. Original lessees on the tracts were as follows: Tract C-a, Gulf Oil Company and Standard of Indiana; Tract C-b, ARCO, Ashland Oil, Shell Oil, and TOSCO; Tract U-a, Phillips Petroleum and Sun Oil; and Tract U-b, White River Shale Oil Corporation, owned equally by Sun, Phillips, and Sohio. Detailed development plans (DDP's) were filed by the original lessees in early 1976.

TABLE 1-4. SHALE OIL PRODUCTION AND DISPOSITION[a]

Dates	Producer-location	Retort type	Production (bbls)	Shale oil disposition	In storage (bbls)
May 1947-June 1951	Bureau of Mines-Anvil Points, CO	N-T-U	20,300	Refined in shale oil refinery of BuMines at Rifle. Products used in passenger cars, buses, diesel trucks and other equipment at the plant. Residuals used on roads.	None
Jan 1950-July 1955	Bureau of Mines-Anvil Points, CO	Gas combustion	11,000	Same as above	None
1957-1958	Union Oil Co.-Parachute Creek, CO	Union A	20,000	Concurrent with mining and retorting tests, refining tests were conducted on product of retort in Brea, California. In 1961, 15,000 barrels of this shale oil was refined in the American Gilsonite Co. refinery at Fruita, Colorado and the products marketed in the Grand Junction area.	None
July 1959-Dec 1966	The Oil Shale Corp/ Denver Research Inst. Zuni Street, Denver, CO	TOSCO I	7,500 ±	Some used for laboratory research and the remainder was incinerated.	None
1962	Mobil-Rio Blanco Cty. Colorado, Beaver Bluff *in situ* project	*In situ* (2 burns)	23	Laboratory testing	None
May 1964-Sep 1967	Six Company* Group-Anvil Points, CO	Gas combustion	25,000	Distributed to six participants for research purposes. Final disposition unknown.	None None

[a] Source: The PACE Company Consultants & Engineers, Inc., 1980.

TABLE 1-4. (continued)

Dates	Producer-location	Retort type	Production (bbls)	Shale oil disposition	In storage (bbls)
	*Mobil, Humble, PanAm, Sinclair, Continental & Phillips, with CSMRF assistance				
1966-1967 1971-1972	Colony Development Company-Parachute Creek, CO	TOSCO II demonstration plant	180,000	Industrial fuel, incinerated, small quantities to refinery feed.	20
1966-1968	Equity Oil Co.-Rio Blanco County, CO	"Bx" Experimental *in situ*	Unknown	Unknown	Unknown
1968-1971	Equity/ARCO Rio Blanco County, CO	"Bx" Experimental *in situ*	Unknown	Unknown	Unknown
Apr 1969-May 1970	Laramie Energy Research Center (BuMines)—Laramie, WY	*In situ* test sites 4 & 7	570	Tested in laboratory and characterized	Unknown
Oct 1969 to present	Laramie Energy Research Center (BuMines)—Laramie, WY	150-Ton & 10-Ton batch reports	1,000 + E	—	Unknown
1970-1972	Shell Oil Co.—Piceance Creek Basin	Leaching & *in situ* retorting	420	—	None
1974-Aug 1976	Seventeen Company Group-Anvil Points, CO	Paraho	10,000 +	9,956 barrels processed into NATO gasoline, JP4, JP-5/Jet A, DFM/DF-2 and heavy fuel oil, 5756 bbls of products, by Gary Western Refining at Fruita, CO. Products disposed of by U.S. Navy.	Unknown

TABLE 1-4. (continued)

Dates	Producer-location	Retort type	Production (bbls)	Shale oil disposition	In storage (bbls)
Dec 1975 to present	Occidental Oil Shale, Inc. Logan Wash, CO	Modified *in situ* retorts 1-6	99,500 and continuing	Internal use for steam generation, commercial boiler tests (Consumers Power, Kalamazoo, Michigan) boiler fuel for small refinery, Mich.	40,000
July 1975 to present	Geokinetics, Inc. Kamp Kerogen, UT	*In situ*	12,000 +	3,500 bbls sold to Plateau Refinery, Roosevelt, Utah. Some used as boilder fuel. Remainder blended with normal feedstock refined to diesel fuel and gasoline, marketed locally.	8,500
1976-1979	IGT, Chicago, IL	HYTORT (1 ton/hr.)	24.5	2.7 bbls for Air Force upgrading tests.	21.8
1976; 1978	Sunoco-Toll Processed Brea, CA	Union B	25	Comprehensive analytical examinations, rheology, crystallography, and upgrading studies	Unknown
	Anvil Points, CO	Paraho	24		
1977-Sep 1978	U.S. Navy/Development Engineering Corp. Anvil Points, CO	Paraho	100,000	Refined at Standard Oil Company's (Ohio) Toledo OH, refinery under contract to U.S. Navy for the Department of Defense and Department of Energy joint program. Refine fuels distributed to various government and contractor facilities for testing in early 1979.	Unknown
June 1979-contin.	Equity Oil Co.-Piceance Creek, CO	*In situ*	None at this time		

E = estimated by Pace-Rocky Mountain Division

The original DDP for Tract C-a proposed an open pit mine with surface retorting. For various reasons, including the nonavailability of off-tract land for solid waste disposal, the lessees (now doing business as Rio Blanco Oil Shale Company) submitted a revised DDP in early 1977 describing plans to use vertical modified *in situ* processing on the tract rather than open pit mining. Shaft sinking and other preparations for construction of five experimental retorts are currently underway. The process involves removing some 40 percent of the underground void space and retorting that on the surface using Lurgi Ruhrgas technology. A decision concerning a full-scale commercial project will be made on completion of a 4-year modular development phase program. Commercial efforts would lead to a production level of 10,340 tonnes/day (76,000 bbl/day) by 1987.

The original lessees of Tract C-b proposed that it be developed using underground room and pillar mining followed by TOSCO II retorting. Further studies indicated that serious mining problems would probably be encountered. Participation in the project subsequently changed, and in early 1977, the newly formed C-b Shale Oil Venture (composed of Occidental and Ashland) submitted a revised DDP outlining plan to use the Oxy modified *in situ* process on Tract C-b. The schedule provided in the second DDP was further revised in 1978. In early 1979, Ashland withdrew from the project, leaving Occidental as the sole participant. However, in September 1979, Tenneco joined Occidental in the Tract C-b venture, renamed the Cathedral Bluffs Shale Oil Company, as a 50 percent partner. Shaft sinking for a series of retorts is currently in progress. Occidental, as operator, and Tenneco intend to continue project development to a commercial scale of 7,750 tonnes/day (57,000 bbl/day) by 1987.

The 1976 DDP for the White River Shale Project (combined Federal Tracts U-a and U-b) proposed the use of underground mining plus surface retorting (TOSCO II, Union and Paraho Direct Mode processes) for development. Two clouds to lease title, involving pre-1920 oil shale claims and an overfiling for State leases, resulted in suspension of lease terms in May 1977 pending court resolution of the conflicts. At present it is not known when or on what basis future development of Tracts U-a and U-b will proceed.

In May 1979, the DOE issued a PON inviting proposals for the design and planning of a surface oil shale retorting demonstration module. The PON solicitation stems from a $15 million appropriation approved by Congress in 1978. Work resulting from any contracts awarded under the PON would not begin until late 1979. The goal of the proposed program is to demonstrate one or more surface retorting technologies at a scale necessary to prove commercial feasibility. The program will be composed of two phases. Phase I (approximately 18 months) will include engineering design of the commercial module and planning for Phase II. Phase II, which is optional at this point, would include a construction period of approximately 30 months and an operating period of about 24 months. The May 1979 PON covers Phase I only. The Department of Energy will wait until completion of Phase I before deciding whether or not to proceed with Phase II. The form of award under the PON will be a cost sharing cooperative agreement. Planning on the PON by DOE has been based on government/contractor cost sharing at the rate of 50/50.

This, then, is the current (late-1979) status of industrial oil shale developments in the United States. The technology of mining, the present major surface retorting processes, and the *in situ* processes that are currently under investigation are described in more detail in Section 7. Appendix A describes in more detail specific plans of oil shale development mentioned herein.

APPLICABLE FEDERAL AND STATE POLLUTION CONTROL LAWS

Terry L. Thoem

In general, environmental legislation and regulations established by the U.S. Congress provides a framework for State legislation and implementation of Federal and State regulations. State legislation and regulations can be more (but not less) stringent than Federal requirements if a State is delegated responsibility for administering the program in a given media. The Federal government retains an oversight/reviewing role for those programs that are delegated to the States. State legislation in general parallels Federal legislation in form and substance. A compilation of Federal and State legislation is provided in Appendix D. The following discussion highlights the major aspects of the legislative mandates of EPA as applied to an oil shale industry. These mandates are: to protect air and water quality, to insure a safe drinking water supply, and to provide for an environment conducive to the enjoyment of man. To accomplish these goals, EPA and the States are involved in a partnership with State and local environmental agencies in the planning, implementation, and enforcement of environmental policies.

Clean Air Act

Under the Clean Air Act (PL 95-95) shale developers must: (a) employ Best Available Control Technology (BACT), (b) insure that National Ambient Air Quality Standards (NAAQS) are not violated, (c) not violate the prevention of significant deterioration (PSD) ambient air quality increments (40 CFR 52.21), (d) not significantly degrade visibility in mandatory Class I areas (40 CFR 51), and (e) obtain as much as up to 1 year of baseline data before applying for a PSD permit to construct and operate. The BACT has been defined in the form of allowable emissions limits and control device operational characteristics. Source monitoring, ambient monitoring, record keeping and reporting requirements are also part of the PSD permit (40 CFR 60.7). Also EPA is authorized to request monitoring data, to take enforcement actions, and to take administrative and judicial actions if there are any emergency episodes of pollutants that present an imminent and substantial endangerment to public health.

Clean Water Act

The Clean Water Act (PL 95-217) established goals of: (a) no discharge of pollutants into navigable streams by 1985; (b) attainment by July 1, 1983, of water quality suitable for protection and propagation of fish, shellfish, and wildlife and for recreational use; and (c) prohibition of discharges of toxic amounts of toxic pollutants. The Act contains requirements in Sections 402 and 404 for potential permits for an oil shale developer. A National Pollutant Discharge Elimination System (NPDES) permit must be obtained under requirements of Section 402 if water is discharged to a navigable stream (defined as waters of the United States and, in fact, could be a dry creek bed which flows during runoff). Neither effluent guidelines (Section 304) nor New Source Performance Standards (NSPS) (Section 306) have been promulgated for an oil shale industry. However, in their absence, NPDES effluent limits are established on a best engineering basis. A Section 404 permit must be issued by the Army Corps of Engineers and concurred upon by EPA if any dredge and fill operations take place in a navigable stream (defined for 404 purposes as stream flow greater than 85 l/sec or 3 cfs). Section 303 of the Act provides the mechanism for establishing water quality stream standards. Plans developed by State Water Pollution Control Agencies must define water courses within the State as either effluent-limited or water-quality-limited. Best management practices (BMPs) to control nonpoint source runoff may be defined via Sections 208 and 304 (e) of the Act.

Safe Drinking Water Act

Underground injection control (UIC) regulations proposed on April 20, 1979 (Title 40 of the Code of Federal Regulations [CFR], Part 126) and portions promulgated in the May 19, 1980, Federal Register under the Safe Drinking Water Act will govern the injection or reinjection of any fluids. Permits (40 CFR 122.36) will be required for *in situ* operations and for mine dewatering reinjection. The State of Colorado requires reinjection permits under existing regulations. The basic thrust of the UIC program is to require containment of reinjected fluids. Monitoring (40 CFR 146.34) and mitigation measures (40 CFR 122.42) to prevent the endangerment of the groundwater system are requirements under these UIC regulations.

Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) will govern the disposal of solid and hazardous wastes generated by an oil shale facility. Criteria for the identification of hazardous wastes were proposed by EPA on December 18, 1978 at 40 CFR 250. Final regulations were promulgated in the May 19, 1980, Federal Register at 40 CFR 261-265. It appears that processed shale will not be considered a hazardous waste. Instead, it will be subject to requirements at 40 CFR 257 (September 13, 1979, Federal Register). A concept of Best Engineering Judgment will govern the disposal of hazardous wastes such as American Petroleum Institute (API) separator sludge.

Toxic Substances Control Act

Testing of effects, record keeping, reporting, and conditions for the manufacture and handling of toxic substances are defined under the auspices of the Toxic Substances Control Act (TSCA) of 1976. A tentative inventory of all commercially-produced chemical compounds was published in May 1979. If a substance is placed on the inventory, it is "grandfathered" from the TSCA premarket notification requirements. Ten synthetic fuels including shale oil were identified on this list of 43,000 compounds. Being on the list does not "protect" a product from possible control requirements included in Section 8. If a material is found to be a hazard, certain restrictions including labeling, precautionary handling requirements or even a ban on its production may be imposed by EPA.

National Environmental Policy Act

The final piece of environmental legislation in which EPA participates and which is relevant to the production of oil shale is the National Environmental Policy Act (NEPA). The Environmental Protection Agency reviews, and in limited cases writes, the EIS when a project involves a major Federal action. The Agency's role as a reviewer is to comment on the environmental aspects of the project.

Legislation as described above normally provides a permit process mechanism. Companies wishing to construct and operate an oil shale facility must receive a permit from EPA or from the State which permits the facility to be operated. A description of the permits required for an oil shale facility is provided in Appendix F.

APPLICABLE FEDERAL AND STATE POLLUTION CONTROL REGULATIONS

Terry L. Thoem

Federal and State legislation generally prescribes the establishment of National and State environmental standards for a given media (i.e. air, water, solid waste, etc.). Regulations designed to control emissions/effluents from an individual facility are promulgated to achieve the stated environmental standards. This section

briefly describes this concept of standards/regulations. In almost all cases, the standards/regulations concept requires an oil shale developer to obtain a permit to construct and operate his facility. It is the intent of EPA to delegate the permit programs to the State. Table 1-5 summarizes the current status of these delegations for oil shale states.

Air

Regulations to protect air quality exist in two forms—ambient air quality standards and stack emission standards. All EPA regulations are codified in Title 40 of the Code of Federal Regulations. Applicable parts are referred to in discussions of the various regulations below. Pursuant to Section 109 of the Clean Air Act, EPA has established NAAQS for seven criteria pollutants (40 CFR 50). Primary standards are designed to protect public health, secondary standards (which are more restrictive) are to protect public welfare (vegetation, materials corrosion, aesthetics, etc.). States may also establish ambient air quality standards.

The prevention of significant deterioration of air quality concepts provided for in the Clean Air Act is designed to protect clean air areas (40 CFR 52.21). Class I areas include national parks larger than 2,428 ha (6,000 acres), national wilderness areas greater than 2,023 ha (5,000 acres), international parks, and national memorial parks that exceed 2,023 ha (5,000 acres). Areas in the United States that presently have lower ambient air quality than that specified in the NAAQS are designated as nonattainment areas Class III; the remainder of the United States is designated Class II. Redesignation of Class II areas to either Class I or Class III by the state is possible.

A second ambient air quality consideration is the visibility protection afforded to Federal Mandatory Class I areas via Section 169A of the Clean Air Act (40 CFR 51). Regulations are to be promulgated by EPA (November 1980) and the States (August 1981) that are designed to prevent visibility impairment in the Federal Mandatory Class I areas. Since there are many issues to be resolved, it is too early to delineate the potential implications of the visibility regulations. Proposed

TABLE 1-5. STATUS OF EPA REGION VIII DELEGATIONS TO OIL SHALE STATES

	Delegation to States		
Type of permit	Colorado	Utah	Wyoming
NPDES	Yes	No	Yes
Drinking water (UIC)	No	No	No
Hazardous waste (RCRA)	No	No	No
Construction grants	Yes	Yes	Yes
Dredge & fill permit (Sec. 404)	No	No	No
NESHAP (beryllium, asbestos, mercury and vinyl chloride)	Yes[a]	Yes	No
Noise	No	No	No
Radiation	No	No	No
PSD	No	No	Yes

[a] States have partial delegations, depending on their need for authority.

regulations appeared in the May 22, 1980 Federal Register at 40 CFR 51-300. An EPA Report to Congress on visibility was published in November 1979.

Limitations on the amounts of pollutants emitted from an oil shale facility are the enforceable mechanism to assure that the NAAQS and PSD increments are not violated. The Environmental Protection Agency establishes New Source Performance Standards (NSPS) (40 CFR 60); States establish emission standards; and EPA (or the State) must define emission limits that reflect the BACT. NSPS have not been defined for oil shale facilities, but BACT has been defined for five oil shale facilities via the PSD permit process. These are further described in Section 6 and in Appendix D. Also, Colorado has an emission limitation specifically for oil shale production and refining. Utah and Wyoming do not have oil shale-specific emission limits.

Water

Water pollution control requirements exist in the form of Water Quality Criteria, State Water Quality Standards, Drinking Water Standards, National Pollutant NPDES limits, and effluent guidelines. The following discussion summarizes the major aspects of surface water and groundwater quality standards. A complete discussion of the enforceable mechanism to attain these standards, that is, the NPDES and VIC permits system, is found in Appendix D.

Surface Water Quality Standards—

Water quality standards are addressed in Section 303 (Water Quality Standards and Implementation Plans) of the Clean Water Act. Excerpts and summaries of requirements for establishment and implementation of water quality standards of that section are presented below:

> Water quality standards shall be reviewed at least every 3 years by the Governor or State Water Pollution Control Agency and shall be made available to the EPA Administrator.
>
> State revised or adopted new standards shall be submitted to the EPA Administrator for approval. Such revised or new water quality standards shall consist of the designated uses of the navigable waters involved and the water quality criteria for such waters based upon such uses. Such standards shall be such as to protect the public health or welfare, enhance the quality of water, and serve the purposes of the Act (FWPCA). Such standards shall be established, taking into consideration their existing or intended potential use and value for public water supplies, propagation of fish and wildlife, recreational purposes, agricultural, industrial, and other purposes, while also taking into consideration their use and value for navigation.
>
> Each State shall identify those waters for which existing or proposed effluent limitations are not stringent enough to attain established water quality standards and establish waste load allocations for those waters. Regulations promulgated at 40 CFR 131.11 and further discussed in the December 28, 1978 Federal Register describe the Total Maximum Daily Load concept.
>
> Each State shall identify those waters or parts thereof within its boundaries for which controls on thermal discharges are not sufficiently stringent to assure protection and propagation of a balanced indigenous population of shellfish, fish, and wildlife.

Colorado Water Quality Standards—

Water quality standards for the State of Colorado were promulgated pursuant to Section 66-28-202 (b) and Section 66-28-204 C.R.S. 1963, as amended, and were most recently amended by the State on January 15, 1974 to become effective June 19, 1974. The Colorado Water Quality Control Commission is in the process of revising these standards via a document entitled *Regulations Establishing Basic*

Standards and an Antidegradation Standard and Establishing a System for Classifying State Waters, for Assigning Standards, and for Granting Temporary Modifications on May 22, 1979 (effective July 10, 1979). The 1974 standards and these 1978 regulations are the subject of litigation at the present time. Ten public hearings are being held during 1979 and 1980, following which, the Commission will establish stream classifications and numeric standards designed to protect a stream's designated use. The 1974 standards entitled "Water Quality Standards and Stream Classifications," as promulgated by Colorado, were approved by EPA on August 13, 1974, with the exceptions stated below.

1. The salinity control policy, procedures, and requirements for establishing water quality standards for salinity control in the Colorado River System are those established by Federal promulgation on December 18, 1974, as set forth in 40 CFR 120.104(b)(9). (It should be noted that the salinity litigation has recently been decided.) A more complete discussion on salinity is found in Appendix D.
2. In the Flow Criteria and Exceptions section of the Water Quality Standards and Stream Classification document, EPA has excepted from its approval on August 13, 1974, the following sentence of the Colorado Standards: "Exceptions on specific parameters may be allowed through discharge permits."

There are general criteria that apply to all Colorado "State Waters," one of which is an antidegradation statement that specifies:

> Waters of the State, whose quality exceeds the limits set in these standards, shall be maintained at existing quality unless and until it can be demonstrated to the State that a change in quality is justified to provide necessary economic or social development. In that case, treatment to the extent necessary to protect the current classification of such waters shall be required.

This 1974 statement has been revised in the 1978 regulations. Due to the litigation on the 1978 regulations, the 1974 standards are the ones in effect. In Colorado, streams may be classified as one of four designations under the 1974 standards: A1, A2, B1, or B3. The general differentiation is between groups A and B:

> Class A1 or A2 waters are suitable for, or can become suitable for, customary raw water purposes *including primary contact recreation.*
> Class B1 or B2 waters are suitable for, or can become suitable for customary raw water purposes *except primary contact recreation.*

A1 and B1 relate to cold waters and A2 and B2 to warm waters. The 1978 regulations changed the classification system. Streams will now be classified as: (1) recreation (primary contact Class I and secondary contact Class II); (2) agriculture; (3) aquatic life (Class I - cold water, Class I - warm water, and Class II-cold water and warm water); (4) domestic water supply (Class I and Class II); or (5) existing high quality waters (Class I and Class II). The 1978 regulations include guidelines for four types of parameters: (1) physical and biological, (2) inorganic, (3) metals, and (4) organics.

The Federal oil shale lease Tracts C-a and C-b are in the Colorado River Basin/White River Sub-Basin. Potential drainage from both tracts will discharge to the reach of the main stem of the White River from the mouth of Piceance Creek to the Colorado-Utah State line. This reach is classified as B2. It should be noted that Piceance Creek is presently undesignated but has been proposed to be classified under the "aquatic life Class I - cold water" classification. Yellow Creek and most of Parachute Creek have been proposed as "agriculture."

Utah Water Quality Standards—

The Utah Board of Health adopted water quality standards on May 19, 1965, and amended in 1967, 1968, and most recently on October 23, 1978. The Environmental Protection Agency approved the 1968 amended document entitled

vironmental Protection Agency approved the 1968 amended document entitled "Code of Waste Disposal Regulations, Part II, Standards of Quality for Waters of the State "on December 13, 1973, with the exception:

> A salinity control policy, procedures, and requirements establishing water quality standards for salinity control in the Colorado River System are those established by Federal promulgation on December 18, 1974, as set forth in 40 CFR 120.104 (b) (10).

The Utah Water Quality Standards (Wastewater Disposal Regulations, Part II, Standards of Quality for Waters of the State) adopted by the Utah State Board of Health on October 23, 1978, was approved by EPA with certain exceptions. The Agency will be promulgating standards to take the place of those identified differences in late 1980 or early 1981. Specific areas disapproved are further discussed in Appendix D.

In specifying Utah's water quality standards the following should be noted:

> "No water quality degradation is allowable which would interfere with or become injurious to existing instream uses "(9).

Utah further has an antidegradation policy stating:

> "Waters whose existing quality is better than established standards for the designated uses will be maintained at high quality unless it is determined by the Committee that a change is justifiable as a result of necessary economic or social development"(9).

Utah also has designated certain raw water sources for drinking water supplies as "antidegradation segments."

Where Colorado has four (under 1974; five under 1978) stream classifications, Utah has six with several subclassifications. The general differentiations in the classifications are presented below. The White River and its tributaries are classified as 3C and 4. Water quality standards associated with these classifications are presented in Appendix D.

Class 1 - protected for use as a raw water source for domestic water systems.

a. Class 1A - protected for domestic purposes without treatment.

b. Class 1B - protected for domestic purposes with prior disinfection.

c. Class 1C - protected for domestic purposes with prior treatment by standard complete treatment processes as required by the Utah State Division of Health.

Class 2 - protected for in-stream recreational use and aesthetics.

a. Class 2A - protected for recreational bathing (swimming).

b. Class 2B - protected for boating, water skiing, and similar uses, excluding recreational bathing (swimming).

Class 3 - protected for in-stream use by beneficial aquatic wildlife.

a. Class 3A - protected for cold water species of game fish and other cold water aquatic life, including the necessary aquatic organisms in their food chain.

b. Class 3B - protected for warm water species of game fish and other warm water aquatic life, including the necessary aquatic organisms in their food chain.

c. Class 3C - protected for nongame fish and other aquatic life, including the necessary aquatic organisms in their food chain. Standards for this class will be determined on a case-by-case basis. (See Appendix D.)

d. Class 3D protected for waterfowl, shorebirds and other water-oriented wildlife not included in Classes 3A, 3B, 3C, including the necessary aquatic organisms in their food chain.

Class 4 protected for agricultural uses including irrigation of crops and stockwatering.

Class 5 protected for industrial uses including cooling, boiler make-up, and others with potential for human contact or exposure. Standards for this class will be determined on a case-by-case basis.

Class 6 - protected for use of waters not generally suitable for the uses identified in Sections 2.6.1 through 2.6.5 above. Standards for this class will be determined on a case-by-case basis.

The 208 Process—

Section 208 of the Federal Water Pollution Control Act (FWPCA) required States to designate areawide waste treatment planning agencies. The Colorado West Area Council of Governments (CWACOG) was so designated for the oil shale area in Colorado. The Uinta Basin Association of Governments (UBAG) was designated for Utah oil shale country. These 208 agencies are to plan, promulgate, and implement a program designed to protect surface water quality. Stream classifications and water quality standards are to be developed. The Colorado Council and UBAG have submitted plans to their respective states. The UBAG 208 plan was certified by the State on November 22, 1978, and approved by EPA on October 2, 1979. The CWACOG 208 plan is anticipated to be certified by the State by April 1980 and approved by EPA by May 1980.

Local input in Colorado on the proposed stream use indicated a desire to assign multiple classifications wherever possible. Although the apparent intent of the proposed State classification system (1978) is simply to identify the criteria applicable to a given stream segment, there is considerable local concern that a single "use" classification may be used later to restrict other uses, particularly agricultural ones. Intermittent streams have not been classified because of provisions made for this situation in the proposed classification system.

The four combinations of multiple use classifications that are proposed for Colorado include:

Class 1: Aquatic Life, Water Supply, Recreation, and Agriculture
Class 2: Water Supply, Recreation, and Agriculture
Class 3: Recreation and Agriculture
Class 4: Agriculture

Proposed classifications and rationale are presented in Appendix D for the Yampa, White and Colorado Rivers.

The proposed water quality standards allow exceptions under certain conditions. Using the guidelines in the proposed criteria, the water quality data base, the proposed water quality criteria, the existing water quality problems, and a subjective analysis of potential effectiveness of potential control measures, three types of exceptions were identified for Colorado:

Permanent exception The current criterion limit is not valid for the drainage area because of natural environmental conditions. It is assumed that, given a return to prehistoric conditions, this parameter would still violate the criterion limit. The parameter should be monitored regularly, and any trend of increasing concentration would require evaluation/investigation of possible causes beyond natural conditions. It is further assumed that it is uneconomical to attempt controlling runoff.

Temporary exception (10 Years) - This exception is requested when a criterion violation is identified as a possible consequence of man's activities in the basin and management strategies are available to improve water quality. Control measures, when funded, may improve water quality, but it will take 10 years to evaluate effectiveness.

Temporary Exception (5 Years) - This exception is requested when a limited data base indicates a problem but more data are required to identify the cause, extent, and correctability of the problem. The 5-year exception should allow sufficient

time for necessary additional data collection and analysis.

Since the Colorado Water Quality Standards and Stream Classification will not be completed until after the CWACOG is approved, the 208 plan will be in effect for a transition period. The plan will subsequently be revised pursuant to the State standards.

Groundwater Quality Standards—

Colorado—Water quality standards for groundwaters in the State of Colorado are not well defined at present . However, groundwaters do fall into the category of "State waters " and therefore should meet the basic standards applicable to all State waters. No specific water quality standards for groundwaters have yet been established. With regard to wastewater disposed of in pits, ponds, and lagoons, no permit is required. However, if upon review it is determined that toxic substances may enter the groundwater system, the State may require sealing of the waste water retention area with an impermeable layer. The State does require a permit for wastewater injection wells.

It should be noted that the State is currently revising water quality regulations with respect to groundwater. Specifically, a limited number of water quality constituents (e.g., radioactivity) will be limited in discharges to groundwaters so that background concentrations are not exceeded. In addition, permits will be required for wastewater disposed of in pits, ponds, and lagoons if there is any possibility of discharges to the groundwater systems.

Utah—The State of Utah also has no specific quality standards for groundwater. However, as in the State of Colorado, groundwaters are part of the State Waters, and therefore general pollution control standards do apply.

The State Department of Health has regulatory and statutory approval authority for all wastewater control facilities. Hence the Department of Health reviews the engineering adequacy and pollution control capabilities of facilities that include wastewater injections wells, pits, ponds, and lagoons. Upon approval of such facilities, a construction permit is issued.

Expected discharges from such facilities to aquifers that serve as potable water sources must not degrade aquifer quality below applicable drinking water standards.

Federal—Federal regulations that may pertain to groundwaters are addressed in the Safe Drinking Water Act. This act has most recently been interpreted as applying to well injection of waste into aquifers that do or that might serve as sources for public drinking water. Such underground drinking water sources, while specified to include aquifers with less than 10,000 mg/l (8.34×10^{-2} lbs/gal) total dissolved solids, must have the potential to be sources of public water supply. Underground injection control (UIC) regulations were promulgated at 40 CFR 126 on May 19, 1980. *In situ* operations will fall into the category of "Class III wells." Drinking water standards are listed in Appendix D. Note that pits, ponds, and lagoons are not identified as underground injection sources at this time. They are covered under the RCRA.

Solid and Hazardous Wastes

The RCRA requires that solid and hazardous waste generators and transporters receive permits and that wastes be disposed of only by safe practices. Regulations have been promulgated at 40 CFR 261 for (1) the criteria to identify solid and hazardous wastes (Section 3001); (2) disposal standards (Section 3004); and (3) permit programs (Section 3005). If a waste is not defined as hazardous (i.e., it is defined only as a solid waste), disposal will be governed by the Section 4004 regulations as promulgated at 40 CFR 257 on September 13, 1979. The promulgated regulations define a waste as hazardous if it is ignitable (flash point F60°C or 140°F), corrosive (extract pH F2 or f12.5), reactive (explosive or oxidizing), or

toxic (extract concentration 10 times greater than drinking water standards). Overburden mine wastes that are returned to the mine are exempt from these regulations. Also, materials ready for further processing are exempt.

RCRA regulations, as promulgated, do affect oil shale facilities due to the following:

1. Tank bottoms, cooling tower sludges, API separator sludges, scrubber sludge are hazardous.
2. Spent catalysts are probably hazardous.
3. Processed shale will probably be treated as a solid waste. Under this classification processed shale shall not be disposed of in environmentally sensitive areas. These include wetlands, floodplains (100-year flood), critical habitats, and the recharge zone of a sole-source aquifer.

Miscellaneous

Hazardous pollutant standards for air may have an impact on oil shale processing facilities but radiation and noise limitations probably have none.

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SECTION 2
RECOMMENDATIONS

One of the purposes of this document is to present a first approximation of EPA's regulatory expectations regarding oil shale development. This section provides a summary of recommendations on regulatory philosophy, pollutants of concern, monitoring programs, and areas which need further research. It should be recognized that both government and industry have certain monitoring and research responsibilities. The Environmental Protection Agency defines various regulatory requirements, but it also is responsible for environmental advocacy. The recommendations in this section attempt to distinguish between requirements and advocacy positions.

An approach to regulating oil shale facilities to minimize environmental impacts from oil shale development is proposed. Emphasis is placed on source characterization and impact assessment. A comprehensive monitoring program for regulated and nonregulated pollutants is recommended. The monitoring program would include baseline studies and operational monitoring. Surface water, groundwater, air and meteorology, solid waste disposal piles, and oil shale residual streams would constitute the ambient and source monitoring coverage.

This section also reviews research needed to improve monitoring and control technology. It recognizes the potential particulate pollution resulting from the mining, transport, and disposal of raw and spent shale on a mass scale never before attempted, and the subsequent possible impact of runoff and infiltration from the above-ground disposal of millions of tonnes of spent shale and other solid wastes.

Though much proven technology is available, the need to demonstrate technology in the combinations and on the scale involved in a commercial oil shale industry is recognized. Much of the concern about the impact of shale disposal results from lack of experience with large quantities of spent shale and disposal piles of the size that would result from a commercial operation.

A known shortcoming is the unreliability of standard sampling and analytical techniques when applied to effluent streams from shale oil recovery processes. Among the research recommendations, therefore, is the development and validation of sampling and analytical methods. These methods must produce reliable measurements and be applicable to monitoring programs with predictive capability.

PROPOSED PRECOMMERCIAL APPROACH TO REGULATIONS

The approach regulating the first oil shale facilities must ensure compliance with existing standards, but more importantly, should emphasize characterization of residuals from an oil shale facility. Both the State of Colorado and EPA Region VIII have expressed their desire to see an oil shale industry develop in a phased orderly manner. Rigorous testing programs and data analyses which would be applicable to a commercial-sized operation should be performed on the first facilities. Comprehensive monitoring of emissions, effluents, and waste materials should be performed. Research programs designed to define the optimum control technology for a given pollutant resulting from an oil shale facility should be conducted. Trade-offs among air pollution, water pollution, and solid waste must be defined. The energy penalty, water consumption, and cost of control must be defined. The

comprehensive monitoring efforts should not be limited to the regulated pollutants only, but should characterize nonregulated pollutants.

Following the characterization of residuals from modules and from a couple of commercial facilities, an assessment could be made as to how large an industry Western Colorado, Northeastern Utah, and Southwestern Wyoming could support. Additional Federal leasing could then be considered.

As previously stated, emphasis should be placed on source characterization. A moderate degree of ambient impact monitoring should be performed to validate predicted impacts and to document trends and changes from baseline. Programs to evaluate effects on receptors should be performed to provide feedback on source and ambient monitoring programs.

The BACT for air pollutants must be employed for any proposed oil shale facility with the potential for emitting 91 tonnes (100 tons) or more per year of any regulated air pollutant. Those facilities which have smaller potential emissions do not need BACT but should perform comprehensive monitoring in order to develop emissions data for potential permit applications. Two primary mechanisms exist to define the BACT. First, several oil shale facilities have received Prevention of Significant Deterioration (PSD) permits. The BACT has been defined on a case-by-case basis for these facilities. Second, air pollution control technology that has been defined as the BACT for oil-shale-related facilities may be considered as transferable to the oil shale industry. It is highly likely that air quality requirements may prove to be the governing constraint to the size of an oil shale industry. Therefore, in order to maximize the amount of oil production capability of oil shale country, it is important to maximize the air emissions control for each oil shale facility.

A no-discharge-of-pollutant concept is being considered by several oil shale developers as a means of handling their wastewater streams. Three types of water should be considered—mine, process, and *in situ* water. A no-discharge-of-process-water concept has been written into water permits. If any water is discharged to surface streams or reinjected into the groundwater system, it would consist of mine inflow (but not process or *in situ* water) or uncontaminated surface runoff. Treatment may or may not be necessary. Effluent limitations will be defined for certain pollutants including toxics for certain oil shale process streams in the NPDES permit. Major concepts to be addressed by regulatory agencies and the oil shale developer are summarized as follows. First, because of the semiarid, water-short condition of oil shale country, it may be environmentally best to encourage treatment if necessary and discharge to a surface stream of mine water. Second, because of salinity considerations, treatment of mine water and/or minimization of water consumption is a desirable policy. Third, disposal of process water onto processed shale piles without treatment may not be desirable, since high organic and salt concentrations in process water may represent too great a risk to groundwater and surface water quality because of potential catastrophic events or unexpected permeabilities or leaching. High organic and salt concentrations also would be a deterrent to successful revegetation. Fourth, maximum recycling and reuse of process and nonprocess water will be encouraged; cost effectiveness must be considered. Finally, land application of untreated mine water may be desirable only for a short period of time because of the potential nonpoint source runoff problems.

Solid and hazardous wastes should be disposed of in a manner that avoids contact with water and subsequent toxic concentrations. Disposal practices should also be designed to preclude (or at least minimize) the potential for the solid material from becoming air-borne as a fugitive dust. Safe disposal practices as defined at 40 CFR 250 apply to oil shale facility hazardous wastes such as spent catalyst, API separator sludge, tank bottoms, cooling tower sludge, and water treatment plant sludge. The principal solid waste from an oil shale industry will, of course, be the processed or raw shale. Surface disposal at a minimum should conform to those

practices found in 40 CFR 257. Special disposal practices for high-volume semihazardous waste materials such as processed shale may need to be defined in individual permit determinations.

REGULATED AND NONREGULATED POLLUTANTS

Terry L. Thoem

Source and ambient monitoring programs will enable developers to characterize oil shale facility residuals and their impacts on the environment. The Environmental Protection Agency has regulatory authority to require inclusion of certain pollutants in an oil shale developer's monitoring program. This regulatory authority is found in Sections 114 and 165 of the Clean Air Act, in Section 308 of the Clean Water Act, and in Section 3005 of the Resource Conservation and Recovery Act. Source monitoring requirements would be covered in NPDES and PSD permits, the discussion of which are in Section 6 and Appendix D. In its environmental advocacy role, EPA has an interest in characterizing quantities of other pollutants released and their resulting impacts. Future standards may result from such characterizations. Responsibility for these characterizations clearly lies with the government.

Summarized below are monitoring program pollutant components categorized according to regulatory requirements, regulatory requirements of primary interest, and advocated characterization. These components are categorized to provide guidance for oil shale developers. Further guidance on monitoring programs, sampling methods, and sampling frequency may be found in Sections 2 and 5 and in Appendices B, C, and E.

Air

Regulatory requirements:

Total suspended particulates (TSP)	Total residual sulfur (including H_2S)
SO_2	Asbestos
NO_x	Be
CO	Hg
NMHC	F
O_3	Vinyl chloride
Pb	H_2SO_4 mist

Regulatory requirements of primary interest:

TSP	Pb
SO_2	H_2S
NO_x	Hg
O_3	F

Advocated characterization:

Inhalable particulate (F15 micron)	SO_4
Fine particulate (F2.5 micron)	NO_3
COS	Cd
CS_2	Radioactivity
RSH	Polycyclic Organic Matter (POM)
NH_3	
AsH_3	
Se	

Water

Regulatory requirements:

"Section 307 " toxic pollutants (65 toxic pollutants listed in January 31, 1978 Federal Register. See also the list of 129 Consent decree pollutants in Appendix D.

"Section 304" conventional pollutants, biochemical oxygen demand (BOD), suspended solids, fecal coliform, and pH).

Regulatory requirements of primary interest:

TSS	Cu
phenols	Cr
pH	Hg
Pb	Se
As	Ag
Cd	

Advocated characterization:

Total dissolved solids (TDS)	Al
SO_4	Fe
F	Mo
B	oil and grease
NH_3	Acid organics (as a class)
Cl	Neutral organics (as a class)
COD	Base organics (as a class)
Temperature	Dissolved oxygen (DO)
Ba	POM

Solid Waste—

Primary authority relates to composition of the hazardous waste and characteristics which may affect water quality. Since Resource Conservation and Recovery Act (RCRA) implementing regulations have not yet been promulgated, the following characteristics and compounds should be considered to be within the regulatory authority of EPA.

Toxicity	POM
Ignitability	MO
Corrosivity	B
Reactivity	F
Permeability	As
Leachability	

PROPOSED MONITORING PROCEDURES

Mike Pearson

Guidelines for an Ambient Air Monitoring Network in Oil Shale Development Areas

A comprehensive air quality monitoring program is required to establish baseline air quality before development and to identify oil shale development impacts. To achieve these goals, a network of air sampling stations capable of repeated simultaneous measurements of the physical and chemical parameters of air quality at very low concentrations is required. The sites selected should be representative of the airshed being sampled. The number and location of sampling sites must be determined on a site-by-site basis after considering local and regional factors related to air pollutant dispersion (climatology, topography, proposed plant characteristics, etc.). Although most stations should be permanent sites, temporary or mobile stations may be used to locate points of maximum impact. Some criteria for selecting monitoring sites can be found in EPA reports 450/2-77-015 and 450/2-78-019 (1,2).

The network of permanent stations should be operated uniformly to permit quantitative comparisons of data from various stations. Sampling should include the air quality parameters listed in Section 2 (Regulated and Nonregulated Pollutants), as well as meteorological parameters. Parameters subject to diurnal or seasonal cyclic behavior should be measured throughout that cycle. Every effort should be made to ensure the measurement of extreme and severe-impact conditions.

Determination of the low baseline concentrations generally found in oil shale regions has proven difficult. Most continuous instruments commonly in use do not have sufficient sensitivity to measure these background levels. To measure these levels, skilled personnel and new methods may be required. Some of the potentially applicable methods for monitoring ambient air are presented in Section 5 of this volume and in Appendix B.

Since permitting and control strategy decisions will ultimately be based on diffusion models, measurement of local and regional meteorological parameters are extremely important. In the rough terrain associated with oil shale areas, local topography and the resulting enhanced turbulence significantly influence air pollutant dispersion. These influences of complex terrain will generally require site-specific model validation. The development of an air quality diffusion model capable of accurately predicting air quality concentrations at distances up to 200 km (124 mi) expected from cumulative emissions of oil shale facilities and urban population centers is critically needed.

Surface and Groundwater Ambient Monitoring—Wesley L. Kinney and Leslie McMillion

Surface Water—

Surface water monitoring programs should be keyed primarily to (a) instream monitoring for purposes of detecting and characterizing pollutants of point and nonpoint origin, (b) the detection of spills and stressed or faulty containment structures or practices that could result in accidental discharges, (c) measurement of flows in streams, seeps and springs for purposes of assessing flow reductions resulting from dewatering operations and consumptive uses, and, (d) measurements of the aquatic biota to determine community changes or biocumulative effects associated with developmental activities.

Monitoring sites should be established on major streams upstream and downstream from anticipated sources of pollution, including impacted tributaries. In addition, stations should be located on the tributaries themselves, including washes and gulches that are designated as disposal sites or are otherwise potentially affected by accidental discharges.

Sampling frequencies for particular parameters should be uniform among stations on mainstream waterways, but all parameters need not be sampled at the same intensities. Sampling on temporary tributaries need only be conducted during periods of runoff when potential for transport of dissolved and suspended materials is greatest. Initially, sampling of perennial streams should be conducted on a fixed schedule to simplify logistics until sufficient data are available to permit the development of a time-stratified sampling schedule that permits maximum sampling intensity during periods of greatest variability in water quality. A schedule designed to yield 25 to 50 samples/station per year for analyses of chemical and physical parameters should provide an adequate data base to permit development of a time-stratified schedule to be implemented as developmental activities intensify. The EPA publication entitled *Surface Water Quality Parameters for Monitoring Oil Shale Development* (3) should provide additional guidance.

Surface water monitoring programs should incorporate biological, chemical, and physical components on an integrated basis to assure maximum program efficiency. Physical and chemical parameters should be selected and assigned priorities on the basis of ambient levels in receiving waters, potential for mobilization and release to surface waters, level of hazard or potential for impairment of beneficial water uses (including aquatic biota and human health), and value of indicator parameters in interpretation of water quality data. Biological parameters should be selected and assigned priorities on the basis of the responsiveness of communities or components to changing conditions, and measurement techniques most appropriate for directly or indirectly measuring such response.

Groundwater—

We recommend that groundwater monitoring systems be related to: (a) potential sources of pollution, (b) geology and hydrology of the site to be monitored, (c) probable movement and dispersion of pollutants in the subsurface, and (d) hydraulic effects of events such as pumping of dewatering wells on the rates and direction of groundwater movement. The EPA report *Monitoring Groundwater Quality: Monitoring Methodology* (4) is suggested as a general guide. Further specific guidance may be obtained in the EPA report entitled *Groundwater Quality Monitoring of Western Oil Shale Development* (5). Monitoring wells should be installed and sampled to provide verification data; even so, their placement and sampling frequency should allow for early detection of pollution so that measures to alleviate the pollution problem can be applied in a timely manner. Parameters to be analyzed should be discreetly selected to reflect the water quality changes that are likely to occur in each situation.

Any recommendations concerning the monitoring of injection wells must take into account that this is a special monitoring situation. The guidance of the EPA report *Monitoring Disposal-Well Systems* (6) is suggested. Important considerations are well design, careful construction measures, inventory of fluids being injected, and continuous monitoring of the well itself.

Modified *in situ* developments pose unique monitoring problems, since little is known about the organic and inorganic pollutants that will be leached from abandoned *in situ* chambers or how the pollutants will behave in the subsurface. It is recommended that close attention be given to the monitoring of groundwater quality in these instances until a reliable body of knowledge can be developed.

Solid Waste—Leslie McMillion

The monitoring of solid wastes is recommended to identify environmental problems in time for corrective measures to be taken. Proposals for such predictive monitoring include: (a) inventory and characterization of wastes that are disposed and the manner of disposal, (b) performance of infiltration tests to gage the probability of leaching from waste disposal piles, (c) performance of regular tests to track the buildup of moisture in disposal piles, (d) the regular monitoring of groundwater quality in near-surface aquifers at points downgradient and close to potential pollution sources, (e) performance of routine determination of sediment and other pollutant loading in surface runoff from facilities, and (f) maintenance of an early warning system with respect to surface runoff.

Programs should be established to regularly inspect the conditions of disposal pile slopes and the integrity of retaining structures associated with solid wastes as a step toward preventing mass movements of disposal piles or catastrophic failure of structures. Instrumentation such as inclinometers could be used in this monitoring effort.

RECOMMENDED RESEARCH

In the course of preparing this document it became apparent to many authors that additional research was needed to better define and resolve environmental issues related to oil shale development. At the request of the editors, each author submitted a list of areas requiring additional research. The following list is intended to exemplify environmental research needs in oil shale. It is not meant to be a complete listing of research needs. Some areas may be suitable for research by either government or industry alone but many will require joint government-industry effort. Active oil shale operations of either pilot or commercial module size are essential for conducting research in many of the subject areas listed.

Air Pollution Control

Complete characterization of emission streams and fugitive emissions resulting from each of the various surface and *in situ* retorting processes.

Regional characterization of baseline air quality (visibility, fine particulates, SO_4, NO_3, trace elements, and precipitation chemistry) prior to development, followed by continued monitoring to determine impacts of development.

Demonstration of the applicability of new and conventional air pollution control technology to emission streams and fugitive emissions from oil shale processing.

Development of predictive techniques for air quality modeling in complex terrain including development of a basin-wide air quality model for the Piceance Basin.

Determination of the cause of high ambient ozone concentrations in the western oil shale regions.

Research to further assess the fugitive dust problem from mining, crushing, transporting, and stockpiling of raw oil shale.

Determination of the quantity of CO_2 generated per unit of fuel product produced.

Complete characterization of atmospheric fugitive emissions from the refining of crude shale oil.

Determination of the effectiveness of monitoring and maintenance in controlling fugitive emissions from the refining of crude shale oil.

Water Pollution Control

Complete characterization of wastewater streams produced by each of the various surface and *in situ* retorting processes.

Demonstration of the applicability and efficiency of conventional water pollution control technology in the treatment of wastewater streams from oil shale processing.

Research and development to ensure that control technology is adequate for boron and fluoride removal from wastewater.

Development of technology for removal of trace organics such as POM, polycyclic aromatic hydrocarbons (PAH), and benzo(a)pyrene (BaP) from oil shale effluents and wastewaters.

Case-by-case analysis for trace metals in process wastewaters to define potential problems and abatement measures.

Research to determine egress routes of groundwater during *in situ* retorting and backflood water following retorting operations.

Determination of detailed mineralogy of major aquifers to permit prediction of groundwater quality variations during and after *in situ* retorting operations.

Determination of groundwater quality and quantity changes associated with mine dewatering operations.

Development of monitoring systems to provide early detection of changes in surface or groundwater quality.

Solid Waste Control

Development and demonstration of technology to control leachate generation from surface spent shale disposal by minimizing generation of leachates and collecting, treating, and recycling leachates that are produced.

Assessment and development of technology to control leachate generation and movement from abandoned *in situ* and modified *in situ* retorts.

Laboratory and field study on the dispersion of spent shale leachate in groundwater systems.

Development and demonstratation of technology to construct impermeable barriers out of spent oil shale.

Demonstration of revegetation of spent oil shale disposal sites and assessment of the uptake of trace elements and other toxic substances by vegetation in comparison to vegetation on native soils.

Determination of the physiological requirements and tolerances of plant species likely to be used for revegetation of spent oil shale.

Investigation of the permeability of various types of spent shale under various compactive efforts and establishment of the relationship between time or quantity of water leached through spent shale and the change in water quality of the leachate, with special attention to organic compounds.

Development of technology for control of erosion on large spent shale piles.

Research to determine the nature of leachates from surface stored raw mined shale and potential impacts on surface and groundwaters.

Demonstration of overburden handling procedures to minimize environmental impact.

Definition of the nature and leachability of solids other than raw and spent shale that will be disposed of in surface piles.

Assessment and development of technology for control of subsidence impact resulting from underground mining and retorting.

Development of technology to monitor the groundwater impacts of true or modified *in situ* retorted shale.

Assessment and development of technology for disposal of solid wastes generated during the refining of crude shale oil (e.g., bottom sludges from shale oil storage tanks; spent guard bed catalysts).

Sampling and Analysis Technology

Standardization of methodology for analysis of water, air, solids, and leachates.
Interlaboratory validation studies of different types of environmental samples to validate methods best suited for oil shale pollutant analyses.
Standardization of sampling techniques and equipment for collection of leachates from solid wastes.

Validation of sample preservation techniques for shipping environmental samples.

Standardization of tests for leachate parameters.

Validation of methods for biological testing of oil shale waters and other environmental samples from oil shale retorting operations.

Development and application of rigorous quality assurance and standardization techniques to analytical methods.

Development of sampling and analysis methods for ambient BaP, PAH, POM and other trace organics.

Development of methodology to characterize stream sediments in oil shale areas.

General Research Needs

Health effects testing of oil shale residuals.

Economic assessment of control technology.

Optimization of control technology recognizing intermedia (air, water, and land) tradeoffs.

Determination of probable social and economic effects associated with development of an oil shale industry.

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SECTION 3
ENVIRONMENTAL IMPACTS

This section reviews the potential impacts of shale processing activities on the atmosphere, surface water and groundwater, and the health and welfare of workers in the industry and the general population.

Process emissions resulting from mining, processing, retorting, and disposal operations are projected for a 50,000-bbl/day plant. The impacts on the atmosphere of residual emissions from processing are also estimated. Fugitive dusts from mining, blasting, transportation, and disposal and trace metals in raw shale, process gas, process water, spent shale, and shale oil are discussed separately in some detail.

The source and nature of waters from oil shale processing are reviewed, followed by an evaluation of the effects of wastewater disposal on surface and groundwaters. The potential long-term effects of wastewaters on regional water supplies are reviewed.

A commercial oil shale industry will produce tremendous quantities of spent shale and smaller quantities of other solid wastes that will have to be disposed. An inventory of solid wastes indicates the magnitude of handling and disposal of raw and spent shale. In addition to fugitive emissions during handling and disposal, solid wastes present the problems of wind erosion, runoff and leaching, revegetation, and instability after disposal. In some cases, these problems may be partially alleviated by disposal of spent shale underground, though the potential for producing groundwater pollution must be carefully assessed.

The health effects problems posed by a commercial shale oil industry are little known, but some information is drawn from foreign experience in use of shale oil. This information indicates that careful attention will have to be given to industrial hygiene practices.

This section also reviews additional impacts such as those resulting from the use of shale oil, possible release of radiation and noise, and social and economic impacts on communities in the shale oil region.

ATMOSPHERIC IMPACTS

Robert Thurnau

Process Emissions: Mining, Processing, Retorting and Disposal

Mining—

The mining activities associated with oil shale operations are going to be among the largest in the world. To sustain an oil production level of 200,000 barrels per day (bbl/day), a mining effort of about 136,360 tonnes/day (150,000 tons/day) will be required. The potential for atmospheric air pollution exists in all phases of mining and includes: excavation, blasting, crushing, transport, and equipment operation phases.

Surface mining—The magnitude of air pollution emissions from mining is directly related to the type of mining practices. Open pit mining has been suggested as a surface mining technique applicable to oil shale extraction. Table 3-1 shows the estimate of four general open pit mining operations and one from an oil shale

development plan. With the exception of sulfur oxides, it looks as if particulates, oxides of nitrogen, hydrocarbons and carbon monoxide could be problem areas. The estimates of the emissions vary considerably, due to the nature of the problem and the fact that two of the sites claimed 80 percent control of the fugitive dusts. The information was taken from a detailed development plan and is now out of date.

Underground mining, particulates—Underground mining is the method selected by many developers because the particulate emissions are lower and easier to control with this method. Table 3-2 summarizes data reported for particulate emissions resulting from underground mining, blasting, and ground vehicles. Information is included on both modified *in situ* underground mining operations and conventional underground mining operations. At first the assumption was made that the reduced mining activity associated with the modified *in situ* retort would result in a lower rate of particulate emissions; however, the data for the particulate emissions from both operations were similar. The literature supports this conclusion (1).

The mining operations of true *in situ* retorts have received very little attention to date but particulate emissions from this source have been estimated by one investigator at 0.01 tonnes/day (.011 tons/day) (1). The bulk of the particulates included in this figure is derived from surface activities rather than from actual mining.

The usual method of breaking up the oil shale rock formations for use in the retorts is by blasting with explosives. Table 3-2 indicates that fraction of the total particulate emission that is attributable to the explosives. As shown, a wide range of values is presented, making this subject area a candidate for additional study.

Table 3-2 also indicates the percentage of total particulate loading associated with the movement of ground vehicles, which are a third source of fugitive dust emissions related to oil shale mining. The values are consistently low and do not seem to be a problem.

Underground mining, other emissions—The particulates generated from mining operations are not the only mining-related emissions that must be considered by developers. The explosives used to loosen the shale rock can produce CO, NO_x, and hydrocarbons, and can possibly release some hazardous pollutants such as trace metals, radon, and silica. The consumption of fuel by the mining equipment will also liberate sizable amounts of CO, NO_x, SO_2, and hydrocarbons.

Estimates of the gaseous emissions for underground mining are presented in Tables 3-3 and 3-4. Sizable amounts of NO_x are estimated, with most of the pollution coming from the ground vehicles. The carbon monoxide data appear to have more scatter and could represent an area requiring additional investigation. The emissions of sulfur dioxide and total hydrocarbons have been reported at low levels and do not presently seem to play a very important role in the gaseous emissions from the underground mining of oil shale.

As was the case for particulate emissions, the gaseous pollutants from underground mining seem to have a smaller emission rate than those from surface mining, and if any treatment is necessary, underground emissions would be easier to collect.

Processing—

Another important source of particulate is the fugitive dust from the processing of raw shale before retorting. All oil shale retorting operations will require a size reduction of some kind, and probably all surface retorts will rely on grinding to some degree. This processing step will result in particulate emissions to the atmosphere.

The transportation and disposal of the processed shale makes another contribution to the particulate loading in the ambient air.

Table 3-5 summarizes the particulate emissions resulting from the processing steps of crushing, transportation, and disposal. Limited data exist on surface-

TABLE 3-1. ESTIMATED ATMOSPHERIC EMISSIONS FROM 50,000-BBL/DAY OIL SHALE SURFACE MINING OPERATIONS (6,750 tonnes/day)

Mining operation	Particulates					SO_X					NO_X					HC					CO				
	Ref 2[a]	Ref 3[b]	Ref 4[c]	Ref 1[d]	Ref 5[e]	Ref 2[a]	Ref 3[b]	Ref 4[c]	Ref 1[d]	Ref 5[e]	Ref 2[a]	Ref 3[b]	Ref 4[c]	Ref 1[d]	Ref 5[e]	Ref 2[a]	Ref 3[b]	Ref 4[c]	Ref 1[d]	Ref 5[e]	Ref 2[a]	Ref 3[b]	Ref 4[c]	Ref 1[d]	Ref 5[e]
Excavation and blasting crushing	2.8	22	31.7	0.8	42.3	NR	NR	2.6	NR	Nil	NR	NR	36.0	NR	1.6	NR	NR	4.2	NR	NR	NR	NR	21.6	NR	1.5
Transportation and mining equipment	5.4	6.7	NR[f]	Nil	0.9	0.1	2.4	NR	NR	Nil	1.1	33.3	NR	NR	8.2	0.1	3.9	NR	NR	0.50	0.7	20.0	NR	NR	1.6
Sum	8.2	28.7	31.7	0.8	43.20	0.1	2.4	2.6	NR	Nil	1.1	33.3	36.0	NR	9.8	0.1	3.9	4.2	NR	0.50	0.7	20.0	21.6	NR	3.1

[a] Generalized Mining Conditions—does not refer to specific mining operation—Allows for 80 percent control of fugitive dust.
[b] Generalized Mining Conditions—does not refer to specific mining operation—No fugitive dust control given.
[c] Generalized Mining Conditions—does not refer to specific mining operation—No fugitive dust control given.
[d] Generalized Mining Conditions—does not refer to specific mining operation—Allow for 80 percent control of fugitive dust.
[e] Emissions based on mining operations presented in Tract CA DDP utilizing Tosco/Paraho Technology
[f] Not reported.

TABLE 3-2. ESTIMATED PARTICULATE EMISSIONS FROM 50,000-BBL/DAY UNDERGROUND MINING OPERATIONS (6,750 tonnes/day)

Mining operation	Ref 5[a]	Ref 5[b]	Ref 6[c]	Ref 7[d]	Ref 7[e]	Ref 8[f]	Ref 9[g]	Ref 3[h]	Ref 2[i]	Ref 4[j]	Ref 5[k]	Ref 5[l]	Ref 5[m]
Excavation (mining)	0.07	0.01	0.08	0.01	0.43	0.16	0.02	0.70	0.10	0.67	0.73	0.43	0.92
Blasting	NR[n]	0.03	NR	1.32	1.32	NR	NR	0.12	0.16	NR	15.26	8.98	19.15
Ground vehicles	0.01	0.14	NR	0.14	0.07	NR	0.06	0.01	Nil	NR	0.12	0.08	0.15
Sum	0.08	0.18	0.08	1.47	1.82	0.16	0.08	0.83	0.26	0.67	16.11	9.49	20.22

[a] Potential Fugitive Dust Emissions (p 75) General Room and Pillar Mining
[b] Ua, Ub estimates—Adapted from DDP
[c] Fugitive dust study—scale done by EPA
[d] Paraho Process—Adopted from White River Shale Project DDP
[e] Controlled emissions from Ocy MIS (p 3-5)
[f] Oxy Construction Permit
[g] Rio Blanco Construction Permit
[h] General Room & Pilar Mining (Table 2.1-5)
[i] 0.10 Tonees/day is the fugitive dust estimation from mining, General
[j] General Room & Pilar Mining, p 230
[k] TOSCO II mining estimation, p 12, Colony EIA
[l] Does not include estimate for rubbling retort, p 12
[m] Paraho mining estimation, p 12
[n] Not reported

TABLE 3-3. SUMMARY OF SULFUR DIOXIDE AND OXIDES OF NITROGEN EMISSIONS REPORTED FROM 50,000-BBL/DAY UNDERGROUND MINING OPERATIONS (6,750 tonnes/day)

	Sulfur dioxide								Oxides of nitrogen						
Mining operation	Ref 1[a]	Ref 3[b]	Ref 2[c]	Ref 8[d]	Ref 4[e]	Ref 5[f]	Ref 5[g]	Ref 5[h]	Ref 1[a]	Ref 3[b]	Ref 2[c]	Ref 4[e]	Ref 5[f]	Ref 5[g]	Ref 5[h]
Mining	NR[i]	NR	NR	0.08	NR	NR	NR	NR	NR	NR	NR	2.95	NR	NR	NR
Blasting	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.61	0.36	0.77
Ground vehicles	0.004	NR	0.005	NR	NR	NR	NR	NR	0.018	0.55	0.007	NR	2.39	1.70	2.99
Sum	0.004	NR	0.005	0.08	NR	NR	NR	NR	0.018	0.55	0.007	2.95	3.00	2.06	3.76

[a] Ua-Ub White River Oil Shale Project DDP
[b] General Room & Pillar Mining Technique given by Radian Corp.
[c] General Room & Pillar Mining Technique (p 130)
[d] Oxy—Construction Permit
[e] General Room & Pillar Mining (p 2-30)
[f] TOSCO estimate based on Colony EIA
[g] Oxy estimate based on Cb revised DDP
[h] Paraho estimate based on design for commercial plant
[i] Not reported

TABLE 3-4. SUMMARY OF HYDROCARBON AND CARBON MONOXIDE EMISSIONS FROM 50,000-BBL/DAY UNDERGROUND MINING OPERATIONS (6,750 tonnes/day)

Mining operation	Hydrocarbons								Carbon monoxide					
	Ref 1[a]	Ref 3[b]	Ref 2[c]	Ref 4[e]	Ref 5[f]	Ref 5[g]	Ref 5[h]	Ref 1[a]	Ref 3[b]	Ref 2[c]	Ref 4[e]	Ref 5[f]	Ref 5[g]	Ref 5[h]
Mining	NR[i]	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Blasting	NR	NR	NR	NR	NR	NR	NR	0.727	NR	NR	NR	0.608	0.359	0.768
Ground vehicles	0.018	0.55	0.007	0.59	0.16	0.01	0.19	0.055	4.79	0.039	5.18	0.459	0.03	0.579
Sum	0.018	0.55	0.007	0.59	0.16	0.01	0.19	0.782	4.79	0.039	5.18	1.067	0.389	1.347

[a] Ua-Ub White River Oil Shale Project DDP
[b] General Room & Pillar Mining estimate given by Radian Corp.
[c] General Room & Pillar Mining estimate given by TRW, p 130
[e] General Room & Pillar Mining estimate given by Cameron Eng., p 2-30
[f] TOSCO estimate based on Colony EIA
[g] Oxy estimate based on Cb revised DDP
[h] Paraho estimate based on design for commercial plant
[i] Not reported

TABLE 3-5. CONTROLLED PARTICULATE EMISSIONS FROM SURFACE AND UNDERGROUND MINING RESULTING FROM CRUSHING, TRANSPORTATION, AND STORAGE OF RAW SHALE (tonnes/day)

	Surface	Underground								
Mining operation	Ref 2[a]	Ref 1[b]	Ref 1[c]	Ref 11[d]	Ref 12[e]	Ref 13[f]	Ref 8[g]	Ref 9[h]	Ref 4[i]	Ref 14[j]
Primary and secondary crushing	2.07	0.292	0.777	1.03	0.485	0.687	NR	NR	0.731	0.44
Storage and transportation	5.42	0.043	0.125	0.145	0.192	NR[k]	0.099	0.420	NR	0.17
Sum	7.49	0.335	0.902	1.175	0.677	0.687	0.099	0.420	0.731	0.61

[a] Open pit mine—crushing onsite, p 133
[b] Ua-Ub estimated adapted from DDP, p 71
[c] CA—Detailed Development Plan
[d] SRJ estimate of TOSCO Process, p 93
[e] Oil Shale Leasing Program
[f] Project Independence
[g] Oxy Construction Permit
[h] Rio Blanco Construction Permit
[i] General Crushing
[j] Colony Permit
[k] Not reported

generated particulate emissions, but the underground processing data clearly show lower emission rates.

Retorting—

A third major source of air pollution from oil shale production is the actual retorting process of the shale. Various amounts of sulfur dioxide, particulates, oxides of nitrogen, hydrocarbons, carbon monoxide, and trace metals are emitted to the atmosphere as a result of the retorting. The data contained in this section show a wide range of emission estimates for most pollutants. These estimates evolved as the industry began to develop their estimates and generally reflected a more accurate level as more was known about the different processes. The data displayed in the latter entries on Tables 3-6 to 3-10 are indicative of the latest estimates. This can also be seen in Figure 3-1 in which the latest estimate of sulfur emissions converge below 5 tonnes/day (5.5 tons/day). The information viewed in Table 3-6 to 3-10 should also be viewed in this manner.

TABLE 3-6. PROJECTED CONTROLLED SULFUR DIOXIDE EMISSIONS FROM THE RETORTING OF OIL SHALE (50,000 bbl/day)

Process or location	Reference number	Projected emission rate (tonnes/day)
TOSCO II estimation*	2	57.9 (29.0)
TOSCO II, Colony	1	18.9
TOSCO II, Stanford Research Institute estimation	11	17.0
TOSCO II, Engineering Science, Inc. estimation	13	14.3
Union Oil retort	3	5.73
C-a, TOSCO II for 2/3 and Paraho (GCR) for 1/3	1	3.43
Colony PSD	14	3.43
C-b, TOSCO II, Colony	1	3.07
Paraho oil shale module	3	2.73
Union Oil B	1	2.08
Rio Blanco oil shale project PSD	8	2.00
U-a, U-b, Paraho technology	1	1.60
TOSCO II retorting	4	1.59
Union Oil retorting	4	1.53
Paraho Oil retorting	4	1.49
Union B PSD	15	1.11
C-b Occidental, modified *in situ* PSD	9	0.20

* Data given for retorting and upgrading emissions for retorting estimated by dividing in half.

The release of sulfur to the atmosphere by the retorting of oil shale can occur in several ways. Raw shale contains sulfur concentrations that range up to 3 percent. A more typical shale in the Green River Formation will contain about 0.7 percent sulfur. The sulfur is distributed between the organic and inorganic fraction in a ratio of one-third and two-thirds, respectively (10). During pyrolysis and/or partial oxidation, the organic fraction is the only sulfur-containing part that undergoes reaction, and about 40 percent is released in the form of hydrogen sulfide. The remaining 60 percent of the organic sulfur resides in the shale oil product as heavier sulfur-containing compounds. The amount of sulfur available for reaction is about 1 kg/tonne (2 lbs/ton), and assuming a Fischer assay of 104 l/tonne (25 gal/ton) and a 50,000-bbl/day operation, if uncontrolled, about 70 tonnes/day (77 tons/-day) could be emitted. The sulfur can be converted to gaseous sulfur compounds such as sulfur dioxide, hydrogen sulfide, carbon disulfide, carbonyl sulfide, and possibly even some thiocyanates. These compounds are of interest because of the health effects associated with them.

One of the sulfur compounds of particular interest to oil shale developers, State and Federal regulatory agencies, and environmentalists is sulfur dioxide. Sulfur dioxide is regulated by State and Federal emission standards as well as by the ambient air regulations. Table 3-6 summarizes the projected sulfur dioxide emissions from several retorting operations by several different investigators.

TABLE 3-7. PROJECTED CONTROLLED PARTICULATE EMISSIONS FROM THE RETORTING OF OIL SHALE (50,000 bbl/day)[a]

Process or location	Reference number	Emission rate (tonnes/day)
C-b, Colony, TOSCO II	2	7.81
TOSCO II, retorting	4	7.65
TOSCO II, Engineering Science, Inc. estimation	13	7.34
TOSCO II, Colony	1	7.14
TOSCO II, Ca-2/3 and Paraho (GCR) for 1/3	1	6.32
TOSCO II estimation	2	4.94
TOSCO II, Stanford Research Institute estimation	11	3.36
Colony	14	2.78
U-a, U-b Paraho technology	1	2.11
Union Oil retorting	3	1.95
Paraho oil shale module	3	1.16
Paraho retorting	4	0.99
Union Oil retorting	4	0.68
C-a Rio Blanco, modified *in situ*	10	0.13
C-b Occidental modified *in situ*	9	0.26

[a] Source: Reference 15

The retorting of oil shale offers another opportunity for particulate emissions to escape into the atmosphere. Table 3-7 illustrates the estimated particulate emissions from several oil shale retorting operations. The estimates vary for surface retorting units from 0.68 to 7.81 tonnes/day (.75 to 8.59 tons/day), and 0.13 to 0.26 (.14 to .29) for modified *in situ* operations.

Oxides of nitrogen can result from burning or pyrolyzing a fuel containing nitrogen and can also form from the elemental nitrogen present in the oxidizing medium (usually air). The rate of formation is a function of flame temperature, residence time, and the fuel-to-air ratio. Without upgrading, the raw shale oil is rich in nitrogen, and if used as a heat source in retorting, it could be a significant source of additional oxides of nitrogen. Table 3-8 summarizes the oxides of nitrogen emission rates that have been reported from several sources.

Hydrocarbons are present in the gas stream of any incomplete combustion process. The retorting of oil shale is such a process in that the pyrolyzing atmosphere is inherently low in oxygen. Significant concentrations of hydrocarbons are expected from retorting, and estimates of their projected emission rates are summarized in Table 3-9.

Like the hydrocarbons, carbon monoxide emissions are generated from the incomplete combustion of the oil shale. A summary of the emissions for carbon monoxide is shown in Table 3-10.

Another potential problem area associated with the retorting of oil shale, and which as yet is not covered by any regulations, is that of trace metal emissions.

TABLE 3-8. PROJECTED CONTROLLED OXIDE OF NITROGEN EMISSIONS FROM THE RETORTING OF OIL SHALE (50,000 bbl/day)

Process or location	Reference number	Emission rate (tonnes/day)
TOSCO II, Colony	1	64.16
TOSCO II, Stanford Research Institute estimation	11	22.23
TOSCO II estimation	2	21.45
Union Oil retorting	3	21.42
TOSCO II, Colony C-b	2	16.87
Colony	14	16.72
TOSCO II, Engineering Science, Inc. estimation	13	15.98
TOSCO II retorting	4	15.56
Paraho retorting module	3	13.79
Paraho retorting	4	12.40
TOSCO II for 2/3 and Paraho (GCR) for 1/3 C-a	1	10.83
U-a, U-b, Paraho technology	1	9.76
Union Oil retorting	4	6.79
Union Oil B	1	6.20

TABLE 3-9. PROJECTED CONTROLLED HYDROCARBON EMISSIONS FROM THE RETORTING OF OIL SHALE (50,000 bbl/day)

Process or location	Reference number	Emission rate (tonnes/day)
TOSCO II Estimation	2	28.25
Union Oil retorting	3	8.28
Paraho retorting module	3	7.94
TOSCO II for 2/3 and Paraho GCR for 1/3 C-a	1	3.79
TOSCO II, Colony	1	3.72
TOSCO II, Engineering Science, Inc. estimation	13	3.45
TOSCO II, Stanford Research Institute estimation	11	3.27
TOSCO II, Colony C-b	1	3.08
Colony	14	2.97
TOSCO II retorting	4	2.95
U-a, U-b Paraho technology	1	0.49
Union Oil retorting	4	0.33
Paraho retorting	4	0.27

TABLE 3-10. PROJECTED CONTROLLED CARBON MONOXIDE EMISSIONS FROM THE RETORTING OF OIL SHALE (50,000 bbl/day)

Process or location	Reference number	Emission rate (tonnes/day)
TOSCO II estimation	2	1.91
TOSCO II, Colony	1	1.60
U-a, U-b Paraho technology	1	0.90
TOSCO II, Colony C-b	1	0.74
Union Oil retorting	3	0.72
Colony	14	0.68
Paraho retorting module	3	0.59
Union Oil retorting	4	0.58
TOSCO II retorting	4	0.51
Paraho retorting	4	0.43

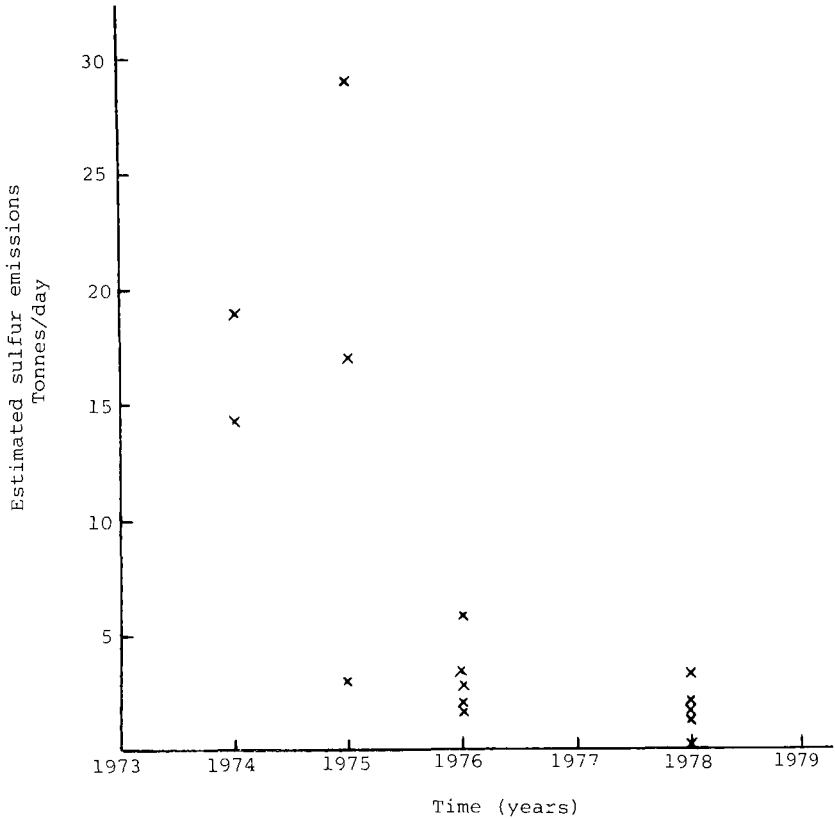

Figure 3-1. Estimated sulfur emissions as function of time.

Direct volatilization and carry-over on particulates are the two ways that trace metals can be released into the environment by retorting oil shale. Work done at the 9 tonne (10-ton) retort at the DOE Laramie Energy Technology Center identified arsenic, mercury, iron, chromium and zinc as being present in both fractions of the off-gas (the gaseous fraction and the particulate fraction) (15). Another investigator reports that up to 70 percent of the mercury present in raw oil shale is released in the off-gas (16). The Environmental Protection Agency sponsored a series of tests at the Paraho oil shale retort and found that small quantities of arsenic were present in the stack gas (17). There seems to be enough evidence to indicate that the trace metal emissions from oil shale retorting operations could be a problem and may need to be controlled.

Disposal—

Except for the operators of the true *in situ* retorts (see Inventory of Solid Wastes later in this section), the problems of disposing of large quantities of spent shale are being confronted by the oil shale industry. Several approaches are being considered, with backfilling in the mine and landfills being popular options.

Regardless of the method chosen, the transfer, handling, and disposal of the spent shale could cause some problems of particulate entrainment and/or hydrocarbon vaporization from the hot shale. The amount of information on the impact of these pollutants on the environment is quite small. One source lists 0.50 tonnes/day (.55 tons/day) as the contribution of dust that is due to disposal of the spent shale (1). Another investigator showed that the concentration of particulate matter in the ambient air was increased by about 500 mg/m^3 (2.18x10^{-4} grains/ft^3) near the spent shale transfer zone relative to another sampler stationed 305 m (1,000 ft) away (18). Table 3-11 shows some of the data collected at the retorted shale transfer station during the operation of the Paraho retort. The highest concentration of dust was found near the transfer site and seemed to level off at a distance of 20 and 35 m (65 and 115 ft). If the emission rate at 5 m (16 ft) is representative of the emission rate for spent shale disposal, and if a volume of 50 x 50 x 10 m (164 x 164 x 33 ft) is selected as equal to the point source, and if the process is scaled up to full size (50,000 bbl/day), an emission rate of about 1.5 tonnes/day (1.65 tons/day) would result.

Very little work has been done on identifying the hydrocarbon emissions derived from spent shale disposal sites. The hydrocarbons emitted would depend on the retorting conditions. One study by Schmidt-Collerus (19) identified some polynuclear aromatic hydrocarbons in the air at a shale disposal site, but they were associated with the airborne particulate emitted from the disposal operation. This, however, is not unusual because polynuclear aromatic hydrocarbons have been found on other rural and urban particulate samples.

Residual Atmospheric Emissions of Sulfur Dioxide, Particulate Matter, Oxides of Nitrogen, Hydrocarbons, and Carbon Monoxide

The concern for summarizing the emissions from oil shale operations (Section 3, Process Emissions) is important because of their impact on the surrounding area. The modeling of those emissions is the next logical step in studying environmental impacts. However, the application of any diffusion model in oil shale country must be done with care because of the complex geographical terrain. A regional dispersion model for rough terrain is not available at this time. Therefore, the individual sites were modeled separately using the EPA Valley Model to predict the ambient air concentrations resulting from the data that were summarized in Tables 3-6 to 3-10. Each site was treated as a point source, and the boundaries of the site were assumed to be representative of ambient air. Again in Section 3 the emissions have a historical flavor and latest estimates are the lowest.

Sulfur Dioxide—

The projected ambient concentrations of sulfur dioxide are summarized in Table 3-12. Assuming the later estimates are more accurate than the earlier estimates and that the air dispersion model is accurate, it appears that sulfur dioxide concentrations will be below the ambient levels specified by legislation. As stated earlier a regional model is not available to study the cumulative effects of sulfur dioxide emissions. However, if the concentrations are additive, the point would come quickly where additional development of oil shale reserves could be hindered by violations in the ambient air regulations for sulfur dioxide.

Particulates—

Under the same conditions as described for sulfur dioxide emissions, the projected ambient concentrations of particulates are shown in Table 3-13. Except for two surface mining estimates, significant emissions are associated with the retorting operations.

TABLE 3-11. FUGITIVE EMISSIONS AT THE PARAHO SHALE TRANSFER AREA[a]
(mg/m³ per hour)

Date	5 m (16 ft) north of station			20 m (65 ft) north of station			35 m (112 ft) north of station		
	Emission rate	background	net	Emission rate	background	net	Emission rate	background	net
9/03	7.01	—	7.01	—	—	—	—	—	—
9/04	8.44	0.25	8.19	3.75	0.25	3.50	—	—	—
9/05	—	—	—	7.04	0.33	6.71	7.35	0.33	7.02
				5.16	0.32	4.84	6.85	0.33	6.52
9/06	—	—	—	5.77	0.45	5.32	8.11	0.45	7.66
				6.23	0.45	5.78	1.22	0.45	0.77
				7.05	0.45	6.60			
9/08	—	—	—				1.80	0.45	1.35
				1.45	0.45	1.00	7.42	0.45	6.97
				3.75	0.45	3.30	4.33	0.45	3.88
							3.95	0.45	3.50
Average	—	—	7.60	—	—	4.63	—	—	4.71

[a] Source: Reference 6.
[b] Not reported.

TABLE 3-12. DISPERSION OF SULFUR DIOXIDE AND ITS RESIDUAL TIME-AVERAGED ANNUAL CONCENTRATIONS[a] FOR 50,000 BBL/DAY OPERATIONS,[b] EPA VALLEY MODEL

Oil shale operation	Emission rate tonnes/day	Ambient air concentration $\mu g/m^3$
Surface mining	2.64	10
	2.44	9
	0.10	< 1
	0.08	< 1
Underground mining	0.08	< 1
	0.005	< 1
	0.004	< 1
Retorting	29.	111
	18.9	72
	17.0	65
	14.3	55
	5.73	22
	3.43	13
	3.07	12
	2.73	10
	2.08	8
	2.00	8
	1.60	6
	1.59	6
	1.53	6
	1.49	6
	0.8	3
	0.20	1

[a] Standards for time-averaged concentrations are as follows: Federal-80 $\mu g/m^3$; Colorado—20 $\mu g/m^3$; Utah—60 $\mu g/m^3$; Wyoming—71 $\mu g/m^3$ (the Wyoming standard is H_2S for one-half hour maximum).

[b] Reference Table 3-6.

Oxides of Nitrogen—

Table 3-14 summarizes emission rates for oxides of nitrogen that have been reported and indicate their possible impact on the ambient air. Again,the same model conditions were used for NO_x as were used for sulfur dioxide and particulates. The latest estimates of NO_x emissions are in the bottom half of the table and seem to be well within the ambient air regulations. Again, however, these estimations are for individual sources and the combination of numerous oil shale operations could violate the statutes.

Hydrocarbons and Carbon Monoxide—

Table 3-15 summarizes the possible impact on the environment that could be due to hydrocarbons. As seen in the table, the impact seems quite high. The information available in the literature was for a three-hour averaged sample and not for an annual sample, and it is usually the case that the three-hour sample is an order of magnitude higher than the annual sample. Therefore, the hydrocarbon ambient concentrations fall within the same limits as the other pollutants and will not violate the ambient air regulations. The carbon monoxide results are summarized in Table 3-16 and do not appear to represent a problem.

TABLE 3-13. DISPERSION OF PARTICULATES AND THEIR RESIDUAL TIME-AVERAGED ANNUAL CONCENTRATIONS[a] FOR 50,000-BBL/DAY OPERATIONS[b]

Oil shale operation	Emission rate tonnes/day	Valley concentration ($\mu g/m^3$)
Surface mining	43.20	152
	31.01	109
	28.66	101
	6.08	21
	3.55	13
Underground mining	20.22	71
	16.11	57
	9.49	33
	1.82	6
	1.47	5
	0.83	3
	0.18	1
	0.17	< 1
	0.08	< 1
	0.08	< 1
	0.08	< 1
	0.08	< 1
Surface processing	2.07	7
Underground processing	1.18	4
	0.90	3
	0.73	3
	0.69	2
	0.68	2
	0.42	< 1
	0.34	< 1
	0.10	< 1
Retorting	7.81	28
	7.65	27
	7.34	26
	7.14	25
	6.32	22
	4.94	17
	3.36	12
	2.11	7
	1.95	7
	1.16	4
	0.99	3
	0.68	2
	0.26	1
	0.13	< 1

[a] Standards for time-averaged annual concentrations are as follows: Federal—75 $\mu g/m^3$ (19 $\mu g/m^3$ for Class II), Colorado—45 $\mu g/m^3$, Utah—90 $\mu g/m^3$; Wyoming—75 $\mu g/m^3$.

[b] Reference Table 3-7.

TABLE 3-14. DISPERSION OF OXIDES OF NITROGEN[a] AND THEIR RESIDUAL TIME-AVERAGED ANNUAL CONCENTRATIONS[b] FOR 50,000-BBL/DAY OPERATIONS[c]

Oil shale operation	Emission rate tonnes/day	Valley concentration ($\mu g/m^3$)
	35.99	33
Surface mining	33.26	31
	1.60	1
	1.11	1
	3.76	3
	3.00	3
Underground mining	2.95	3
	2.06	2
	0.55	< 1
	0.018	< 1
	0.007	< 1
Retorting	64.16	59
	22.23	21
	21.45	20
	21.42	20
	16.87	16
	15.98	15
	15.56	14
	13.79	13
	12.40	11
	10.83	10
	9.76	9
	6.79	6
	6.20	6

[a] Assumed complete conversion of NO_x to NO_2
[b] Federal standard for time-averaged annual concentration is 100 μ g/m^3.
[c] Reference Table 3-8.

Two important points effect the impact of the emissions modeled in Tables 3-12 to 3-17. The first factor is the size of the oil shale operations. The discussed emissions are relative to only 8,000-m^3/day or 26,246-ft^3/day (50,000 bbls/day) shale oil production. As production capacity is increased the emissions are increased and so is the impact on the atmosphere. It is conceivable that the dispersion characterizations of the Piceance Valley could be the limiting factor in the development of a commercial sized oil shale industry. Second, the air pollution standards against which the emission rates were compared were the most lenient, and this probably will not be the case for a commercial-sized facility. Stricter ambient air standards, if imposed, would probably affect the sulfur dioxide and oxides of nitrogen control strategies and could well cause a change in the process or require tighter control.

Fugitive dusts consist of any dust that escapes to the atmosphere from a source other than a stack or duct. Fugitive emissions are expected from mining, blasting, crushing, transportation, and disposal of the shale. Most of the emissions discussed as particulate air pollution in an earlier section were, in fact, fugitive dusts. They are summarized in Table 3-17. Using the same regional air pollution dispersion model as before, it appears that fugitive dusts may not be a serious regional prob-

lem for most oil shale operations, although they may present serious localized problems.

Trace Element Emissions

Another area of concern in the development of the oil shale industry is the release of trace elements. It has been suggested that trace elements will be found in all fractions of oil shale effluents and could have substantial impact on the environment. Presently, the only air pollution standards that might be applied to oil shale processing are the National Emission Standards for Hazardous Air Pollutants (NESHAP) for beryllium and mercury. There is some evidence in the literature that indicates mercury may be released from oil shale retorts in sufficiently high concentration to merit some control, but more information is necessary before a decision on potential hazards can be made (16). The trace metals that get into water discharges could be governed by either the drinking water regulations or the effluent guidelines. The trace element problem in the oil shale industry is at a stage where additional work must be done to determine the extent of the problem and to evaluate accurately its impact on the environment.

TABLE 3-15. DISPERSION OF HYDROCARBONS AND THEIR RESIDUAL TIME-AVERAGED 3-HOUR CONCENTRATIONS[a] FOR 50,000-BBL/DAY OPERATIONS[b]

Oil shale operation	Emission rate tonnes/day	Valley concentration ($\mu g/m^3$)
	4.17	267
Surface mining	3.86	247
	0.50	32
	0.13	8
	0.59	38
	0.55	35
Underground mining	0.19	12
	0.16	10
	0.018	1
	0.01	< 1
	0.007	< 1
Retorting	28.85	1,846
	8.28	530
	7.94	508
	3.79	243
	3.72	238
	3.45	221
	3.27	209
	3.08	197
	2.95	189
	0.49	31
	0.33	21
	0.27	17

[a] Federal guideline for time-averaged 3-hour concentration is 160 $\mu g/m^3$.
[b] Reference Table 3-9.

TABLE 3-16. DISPERSION OF CARBON MONOXIDE AND ITS RESIDUAL TIME-AVERAGED ANNUAL CONCENTRATIONS[a] FOR 50,000-BBL/DAY OPERATIONS[b]

Oil shale operation	Emission rate tonnes/day	Valley concentration ($\mu g/m^3$)
Surface mining	21.59	1,108
	19.96	1,024
	3.10	159
	0.67	34
Underground mining	5.18	266
	4.79	246
	1.35	69
	1.07	55
	0.78	40
	0.39	20
	0.04	2
Retorting	1.91	98
	1.60	82
	0.90	46
	0.74	38
	0.72	37
	0.59	30
	0.58	30
	0.51	26
	0.43	22

[a] Federal standard for time-averaged 8-hour concentration is 10,000 μ g/m^3.
[b] Reference Table 3-10.

Raw Shale—

The trace element composition of raw shale is quite variable. Differences have been attributed to natural geologic and geographic variations as well as to differences in sampling and analysis techniques. The nonuniformity of the trace elements in oil shale was illustrated by the Thompson-Raymo-Woolridge Corporation (TRW) in a report to EPA (18) (Table 3-18).

Process Gas—

Retorting of oil shale in surface modules is usually accomplished by heating the rock to 430° to 540°C (806° to 1004°F). It is generally accepted that most of the trace elements are not volatilized at these temperatures, with the possible exception of antimony, arsenic, boron, cadmium, fluoride, lead, mercury, selenium, and zinc. Trace element studies conducted by TOSCO Corporation confirmed the fact that the low retorting temperatures prevented the volatilization of the low vapor pressure elements and insured their remaining in the spent shale. The higher vapor pressure elements found their way into the shale oil retort water and off-gas (20). The TRW Corporation suggests that minor elements in oil shale such as mercury and arsenic constitute potential emission problems (18).

In situ retorting of oil shale has the disadvantage of poorer control over the retort temperature, and excursions beyond the 540°C (1004°F) level can be quite common. Under these conditions, the possibility of volatilizing some of the trace elements into the gaseous phase increases. It has been reported that arsenic and mercury concentrations for both volatilized and particulate-associated trace metals from a simulated *in situ* retort were 3,900x10^{-9}g/m^3 and 1,900x10^{-9} g/m^3

TABLE 3-17. FUGITIVE DUSTS AND THEIR RESIDUAL TIME-AVERAGED ANNUAL DUST CONCENTRATIONS[a] FOR 50,000-BBL/DAY OPERATIONS[b]

Oil shale operation	Emission rate tonnes/day	Valley concentration ($\mu g/m^3$)
Surface mining	43.20	152
	31.01	109
	28.66	101
	6.08	21
	3.55	13
Underground mining	20.22	71
	16.11	57
	9.49	33
	1.82	6
	1.47	5
	0.83	3
	0.18	1
	0.17	1
	0.08	< 1
	0.08	< 1
	0.08	< 1
	0.08	< 1
Surface processing	2.07	7
Underground processing	1.18	4
	0.90	3
	0.73	3
	0.69	2
	0.68	2
	0.42	< 1
	0.34	< 1
	0.10	< 1
Disposal	1.5	5

[a] Standards for time-averaged annual concentrations are as follows: Federal—75 $\mu g/m^3$, Colorado—45 $\mu g/m^3$, Utah—90 $\mu g/m^3$; Wyoming—75 $\mu g/m^3$.

[b] Reference Tables 3-1, 3-2, and 3-5.

(2.44×10^{-10} lb/ft^3 and 1.19×10^{-10} lb/ft^3), respectively (15). Preliminary investigation of pilot-scale, *in situ* oil shale processing plants indicates that approximately 88 percent of the mercury present in the raw shale is released in off-gas (16,21).

Fugitive Dust—

Trace elements emitted to the atmosphere via fugitive dusts as a result of raw shale handling and spent shale disposal could be significant. Fugitive dust data were taken at Paraho, and one of the areas of emission was the spent shale transfer area (6). The collected dusts were examined for trace metals, and the results are summarized in Table 3-19. In about half of the cases, the concentration of trace element on dust remained about the same as the background concentration. However, the other elements fluctuated, with Pb, As, Hg, Ni, Cr, S, V, and Se changing significantly. The meaning of the data is not yet clear. Additional testing is required before any conclusions about trace elements and their relationship with fugitive dust can be drawn.

TABLE 3-18. MEAN LEVELS OF SELECTED TRACE ELEMENTS IN RAW OIL SHALE—COMPARISON OF REPORTED DATA FOR CLASS 1 ELEMENTS[a,b] (ppm)

Element	USGS	LETC Mahogany Zone	LETC Saline Zone	Tract C-a	Tract C-b	Battelle	Berkeley	TRW	Representative mean value
BE	—	2.0	1.0	—	—	—	—	—	1.3
Hg	0.4	0.5	—	0.6	0.22	0.2	0.13	—	0.4
Cd	1.0	0.1	0.4	2.4	0.5	—	1.0	—	1.0
Sb	1.0	0.4	3.0	0.5	1.2	0.35	1.5	1	1.0
Se	1.5	3.0	1.5	0.32	2.2	5.0	—	—	1.5
Mo	10.0	15.0	30.0	—	—	—	14.0	—	10.0
Co	10.0	9.0	4.0	—	—	11.0	9.0	—	10.0
Ni	25.0	300.0	85.0	—	—	30.0	16.0	20	25.0
Pb	20.0	3.0	15.0	—	—	40.0	30.0	—	20.0
As	35.0	30.0	20.0	6.5	38.0	80.0	88.0	44	35.0
Cr	34.0	400.0	100.0	—	—	25.0	—	—	34.0
Cu	37.0	45.0	30.0	—	—	64.0	37.0	—	37.0
Zr	44.0	30.0	50.0	—	—	—	—	—	40.0
B	65.0	80.0	50.0	129.0	41.0	—	—	—	65.0
Zn	70.0	15.0	30.0	—	—	115.0	—	—	70.0
V	100.0	100.0	80.0	—	—	—	—	—	100.0
Mn	250.0	250.0	250.0	—	—	—	—	—	250.0
F	1,000.0	2,000.0	1,000.0	550.0	1,300.0	—	—	—	1,000.0

[a] Class I Elements are those that potentially pose environmental hazards and/or tend to be relatively abundant in fossil fuels.
[b] Source: Reference 18.

TABLE 3-19. TRACE METAL ANALYSES OF RAW AND SPENT SHALE FUGITIVE DUSTS FROM ANVIL POINTS, COLORADO[a] (ppm)

Element	Background[b] (upwind)	Crusher[c]	Mine adits	Haul road	Screening room baghouse	Retorted[d] shale transfer
Al	3.1×10^4	1.3×10^4	1.3×10^4	2.7×10^4	4.2×10^4	1.6×10^4
As	4.5	3.8	7.8	16	17	15
Ca	10×10^4	2.9×10^4	2.9×10^4	8.2×10^4	6.3×10^4	11×10^4
Cd		No Data	2	2	6	5
Cr	72	15	13	29	54	31
Cu	231	40	145	133	53	71
F	6.9×10^3	7.4×10^2	1.9×10^3	11×10^3	9.8×10^2	1.3×10^3
Fe	2.0×10^4	1.9×10^4	1.3×10^4	2.3×10^4	2.3×10^4	1.8×10^4
Hg	No Data	1.2×10^1	0.1	0.9	0.3	0.2
Mg	3.4×10^4	2.0×10^4	5.1×10^4	3.9×10^4	3.9×10^4	2.9×10^4
Mn	2.7×10^2	1.4×10^2	3.2×10^2	5.0×10^2	No Data	3.0×10^2
Na	1.6×10^4	1.3×10^4	3.2×10^4	2.0×10^4	2.9×10	2.3×10^4
Ni	3.2×10^2	12	19	43	39	30
Pb	1.9×10^2	17	68	96	64	55
S	4.5×10^3	2.4×10^2	1.3×10^4	3.0×10^3	6.4×10^3	5.3×10^3
Se	15	11	4.4	3.5×10^1	35	12
Si	1.0×10^5	1.2×10^5	8.3×10^4	3.0×10^5	5.0×10^4	4.1×10^4
V	38	24	43	57	2.3×10^2	1.3×10^2
Zn	4.2×10^2	1.6×10^2	1.5×10^2	2×10^2	1.6×10^2	1.8×10^2

[a] Source: Reference 6.
[b] Haul road was upwind of sampler.
[c] Crusher is not considered typical of those that might be used by industry.
[d] Paraho retort was operated in direct mode.

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Sources and Nature of Waters from Oil Shale Processing

Any commercial facility designed to produce liquid and gaseous fuels from oil shale will both produce and consume water. Under current planning, most of the oil shale developers envision zero discharge of wastewater from their commercial facility. To achieve zero discharge of wastewater, the water effluent streams from each unit operation must be treated to render them usable by other consumptive use operations. One concept for a water management plan is shown in Figure 3-2.

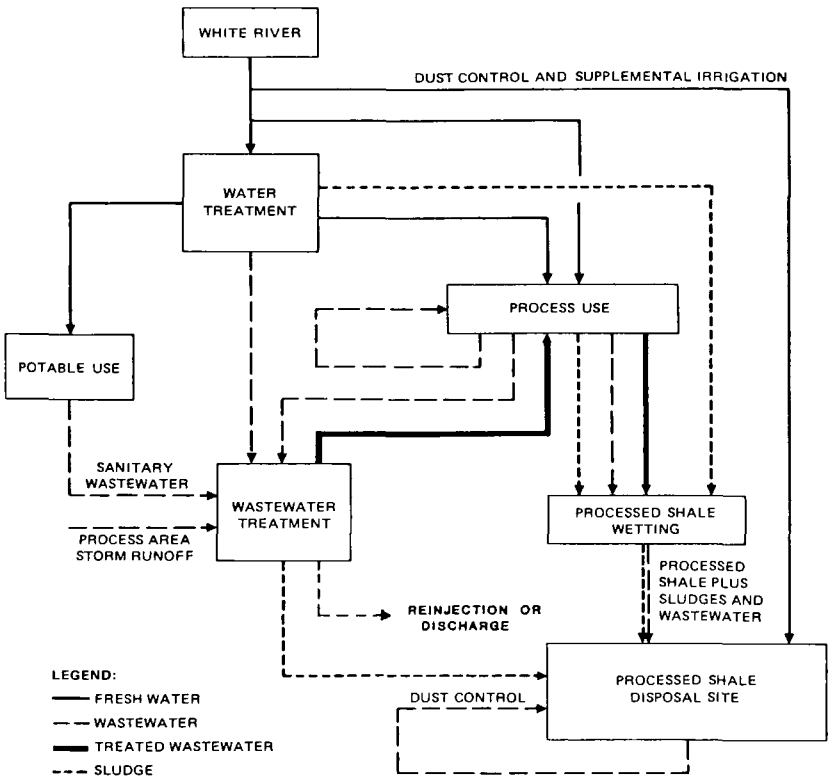

Figure 3-2. Overview of a possible water management plan.

Water supplies will probably be available from a number of sources, and the quantity and quality of water from each source will vary widely. Sources of relatively good quality water may include:

Stream flow (water rights)

Purchased water from existing U.S. Bureau of Reclamation or Colorado River Water Conservation District storage facilities

Groundwater

Runoff from undisturbed areas

Water from these relatively good quality raw water sources will generally be stored in an impoundment located onsite in quantities designed to assure adequate supplies during periods of low streamflow or drought. Before use in applications that require high quality water, these stored waters will require specific treatment, which may include sedimentation, filtration, and, if potable water is required, chlorination.

Sources of relatively poor quality water may include:

Wastewater from retorting operation

Wastewater from shale oil upgrading

Mine drainage and wastewater from mine dewatering and dust scrubbing operations

Raw water treatment plant effluent

Sanitary and sewerage system effluents

Leachate from spent shale or raw shale piles

Runoff from disturbed areas

Wastewater streams from power plant cooling and boiler facilities

Characteristics of water derived from the first six sources listed are described in the following paragraphs.

Wastewater from Retort Operations—

Sources of the wastewater released by retorting operations include moisture contained in the shale fed to the retort, water released as a product of pyrolysis of the kerogen, and, in some retorting processes, water obtained as a product of the combustion of organic matter. Water leaves the retort with the off-gas stream and appears as condensate when the gas stream is cooled. Some water accompanies the liquid shale oil, and some accompanies the uncondensed gas streams. Water may separate from shale oil during storage or may be recovered during subsequent shale oil upgrading operations. Water may be condensed from the retort gas product during subsequent gas cleaning operations, or it may exit with the flue gas product when the gas is burned as fuel. Section 7 contains more detailed data concerning water effluent streams from specific retorting processes.

Water separated from shale oil usually contains ammonia, carbonate, bicarbonate, sodium, sulfate and chloride ions, and certain dissolved or suspended organic compounds such as amines, phenolics, and mercaptans. Water condensed from retort gases contains ammonia and carbonates as the principal impurities.

Wastewater from Shale Oil Upgrading—

The characteristics of effluent water from shale oil upgrading depend on the extent of refining conducted at the site. Generally, these streams include cooling water, wash water, and sometimes, oil-contaminated wash water resulting from vessel cleaning and spills. A blending of all water effluent streams from oil refining would provide a water product displaying high biochemical oxygen demand and chemical oxygen demand (COD). This blended product would contain ammonia, carbonates and bicarbonates, sulfides, phenols, numerous trace elements, probably

some grease and oils, and potentially toxic materials. It would probably require treatment procedures similar to those currently employed in the petroleum refining industry.

Effluent from Mine Drainage, Mine Dewatering, and Dust Scrubbing Operations—

Mine waters range in quality from 300 to 900 ppm (above the Mahogany Ledge) to well over 5,000 ppm dissolved solids for deeper zone sources. Hydrogen sulfide and methane have been encountered emanating from coreholes and from shafts in the Piceance Creek Basin. Dust scrubbers will produce particulate-laden wastewaters from both the mining and rock crushing operations.

Raw Water Treatment Plant Effluent—

Raw water must be treated before use as potable water or for other uses requiring high quality water, such as steam generation. Water treatment system effluents contain lime sludge, sediment, blowdown of zeolite or other water softening compounds, and miscellaneous dissolved salts.

Sanitary and Sewerage System Effluent—

These streams include domestic sewage and kitchen, washroom, laundry, toilet, and equipment wash products. Such effluents would likely be kept separate for conventional treatment to destroy unstable organic matter and enteric microorganisms.

Leachate from Spent Shale or Raw Shale Piles—

Should water percolate through and emanate from spent oil shale piles, the several soluble salts present in the spent shale will be present in the leachate product. Ions expected in leachate in significant quantity include sulfate, sodium, bicarbonate and calcium. Present in smaller concentrations will be ions of magnesium, nitrate, chloride, and potassium. A more comprehensive discussion of the leachate problem appears later in this section under Leaching of Solid Wastes.

Considerable amounts of water may be added to spent shale during compacting operations, and additional quantities will be added by rainfall, snowmelt, and sprinkling during establishment of plant growth, leading to the possibility of leachate from spent shale piles. Some leachate is expected, but high evaporation rates and the chemical, physical, and cementitious properties of spent shale may tend to inhibit the percolation of water through the piles.

Effects of Wastewater Disposal on Surface Waters—Leonard Mueller

Present oil shale processing technologies are varied, as are the water resources associated with each. Oil shale retorting can generate chemically complex aqueous waste effluents containing many common organic and inorganic components. Potential release of such waste effluents to the aquatic environment may create harmful effects. To ascertain the degree to which these effects exist, the chemical characteristics of the compounds—solubility, degradability, toxicity, and bioaccumulation—must be reviewed.

At present, all major oil shale developers plan a zero discharge of wastewaters to surface waters. All process waters will be contained in holding ponds, and any discharge will be accidental. Wastewater treatment technologies can be employed to meet effluent guidelines listed in NPDES permits which are based on aquatic life criteria. Because of the complex nature of organic and inorganic components in process water, the effects of an accidental discharge need to be determined. It is essential that an assessment of the potential effects on the aquatic environment be included as a fundamental part of the receiving water quality criteria. Effects of wastewater on the aquatic ecosystem in surface waters can be determined in exposure tests with aquatic organisms. Methods for the measurement of the acute toxicity of effluents to macroinvertebrates and fish are described by several groups

(22,23,24). Chronic effects from prolonged exposure to sublethal effects can be observed by life cycle tests, embryo-larvae studies, or bioaccumulation studies.

A 96-hr (acute) flow-through bioassay with fish or invertebrates with an aqueous effluent will provide toxicity data. These data can then be used to evaluate the immediate effects of wastewater on receiving surface waters, but they do not identify the specific compound responsible for the toxicity. Most toxicity data available in the literature deal with single compounds in water; a compilation is given in Reference 25. Wastewater from oil shale processing includes many compounds, as shown in Table 3-20 and later in this section and in Section 4.

Bergman (26) reported flow-through acute bioassays conducted with Omega-9 and Geokinetics oil shale process waters according to standard toxicity testing procedures (23). Test organisms were exposed to seven concentrations of the test solution plus well water controls. Fish were tested for 96 hrs, while *Daphnia pulex* were exposed for 48 hr. The results of acute flow-through bioassays are presented in Table 3-21. The 96-hr (fathead minnow and rainbow trout) and 48-hr *(Daphnia pulex)* TL_{50} dilutions for both process waters tested were at dilutions of less than 1 percent process water for all test animals. The Omega-9 retort water TL_{50} ranged from 0.42 to 0.57 percent, and the Geokinetics retort water TL_{50} ranged from 0.46 to 0.88 percent for the three species tested. Acute toxicities of Omega-9 and Geokinetics oil shale retort waters were remarkably similar for the three aquatic species tested. Bergman recommended an estimated safe concentration for this particular Geokinetics oil shale retort water to be 0.09 percent based on flow-through, 96-hr bioassays and application factors estimated from similar process waters.

The chemical characteristics of Omega-9 retort water (28) suggest that inorganic constituents may contribute substantially to its acute toxicity. Bergman (26) found that an artificial mixture of inorganic constituents in Omega-9 retort water was only slightly less toxic in acute tests than Omega-9 retort water alone. His studies indicate that inorganics, primarily ammonia, are responsible for the toxicity of Omega-9 retort water.

Bergman (26) conducted a 69-day embryo-larval test following procedures published by McKim (29). Rainbow trout eggs were exposed to five concentrations of Omega-9 oil shale retort water through hatching and an initial period of fry growth. Egg survival, hatchability, fry survival, and growth were monitored. The lowest dilution or concentration which had any significant effect on egg hatchability, or fry survival or growth was 0.16 percent, and the highest concentration which had no effect on fry survival or growth was 0.08 percent.

The 96-hr TL_{50} values for rainbow trout and fathead minnows exposed to Paraho oil shale retort water (1977-78 composite) in flow-through bioassays were 0.068 and 0.071 percent, respectively, whereas the 48-hr TL_{50} for *Daphnia pulex* was 0.15 percent (26). To protect aquatic species in the event of an accidental release of untreated Paraho Tank-500 process water to natural waters, a dilution factor of 10,000:1 would be required.

TABLE 3-20. WATER QUALITY CHARACTERISTICS OF GEOKINETICS OIL SHALE RETORT WATER[a,b]

Water quality parameter	mg/l[c]
Alkalinity, Total ($CaCO_3$)	9,500
Biological Chemical Demand (5 day)	—d
Carbon:	
Bicarbonate (HCO_3^-)	8,000
Carbonate (CO_3^{--})	1,800
Dissolved Organic Carbon	—d
Total Organic Carbon	—d

Water quality parameter	mg/l[c]
Chemical Oxygen Demand	6,200
Chloride	e
Conductance (mmno/cm)	13,800
Cyanide	2.6
Fluoride	1.2
Hardness ($CaCO_3$)	280
Metals:	
Arsenic	0.47
Aluminum	< 0.1
Barium	0.5
Boron	78
Cadmium	0.05
Calcium	4.9
Chromium	< 0.1
Copper	< 0.1
Lead	0.6
Iron	1.3
Manganese	0.08
Magnesium	64
Mercury	< 0.001
Nickel	0.2
Potassium	9.0
Selenium	3.1
Silver	< 0.05
Zinc	0.51
Nitrogen:	
Ammonia (NH_3)	1,900
Ammonium (NH_4^+)	2,000
Nitrate (NO_3^+)	e
Nitrite (NO_2)	0.0
Total Kjeldahl (N)	1,800
pH (units)	8.8
Phenols	6,800
Phosphorus	
Total Orthophosphate ($PO_4^{\equiv}$)	d
Silica	310
Solids:	
Suspended	20.0
Total	15,900
Total Dissolved	15,900
Volatile	2.0
Sulfur:	
Sulfate	1,600
Sulfide	< 0.5

[a] Source: Reference 27.
[b] Analyses performed by Wyoming Department of Agriculture, Division of Laboratories, Laramie.
[c] Unless otherwise noted.,
[d] Analyses not completed.
[e] Analysis not done because of interfering compounds.

TABLE 3-21. SUMMARY OF ACUTE, FLOW-THROUGH BIOASSAY RESULTS FOR RAINBOW TROUT *(Salmo gairdneri)*, FATHEAD MINNOWS *(Pimephales Promelas)*, AND *Daphnia pulex* EXPOSED TO PROCESS WATERS[a,b]

Process water	Species[c]	Number of organisms per concentration	Highest test concentration	TL_{50}	Observations
Omega-9 oil shale retort water	Fathead minnows	20	0.8%	0.57%	Lethargic at 0.4%
	Rainbow trout	20	0.8%	0.42%	Lethargic and loss of equilibrium at 0.4%
	Rainbow trout[d]	—	—	0.51%	[c]Dechlorinated tap water for dilution
	Daphnia pulex	10	0.8%	0.54%	Test duration was 48 hr
Geokinetics oil shale retort water	Fathead minnows	20	1.25%	0.88%	Hyperactive and sensitive to disturbance at 0.625%
	Rainbow trout	20	1.25%	0.46%	Sensitive to disturbance at 0.31%
	Daphnia pulex	10	1.25%	0.56%	Test duration was 48 hr

[a] Source: Reference 26.

[b] *All acute tests were conducted at 14°C for 96 hr and well water dilution, unless otherwise specified.*

[c] Rainbow trout mean weight was 15.6 g and mean length was 105.4 mm; fathead minnow mean weight was 0.93 g and mean length was 41.2 mm.

[d] Omega-9 TL_{50} dilution of 0.51% was obtained using dechlorinated tap water as dilution water in a separate test; a value of 0.38% to 0.39% was reported earlier (1977 Annual Report) for the TL_{50} dilution in this test, but the TL_{50} dilution was recalculated at 0.51% after all tests with low dissolved oxygen levels were discounted.

The research reported here is limited to three specific retort process waters. More extensive and longer studies are needed to evaluate the biological and ecological effects of an oil shale industry on surface water. Monitoring devices are available to detect leaks from holding ponds and waste treatment facilities and they can be used as an early warning of faulty containment systems. Section 2 lists pollutants which should be part of a monitoring program. Other tests may be developed as early indicators of toxicity. Lebsack (30) developed a rapid aquatic toxicity screening technique using luminescent bacteria. (Algae are also quite sensitive to toxic materials.) Aquatic organisms serve as continuous monitors of their environment and are sometimes quite sensitive to very low (ppb) concentrations of organic pollutants. Disappearance or relocation of aquatic organisms may be an effect of a change in water quality parameters.

Possibly no acute or chronic effects will result from a wastewater discharge because of the low concentrations of compounds. However, compounds of low water solubility may be bioaccumulated by aquatic organisms and become toxic to the consumer, other fishes, birds, or man. Oil shale process water contains single-ring aromatics and polynuclear aromatics that contain suspected carcinogens. If there is a discharge of process water into the aquatic environment, sediments may accumulate these compounds and later release them slowly. Research is needed on the degradation of these compounds and their potential for bioaccumulation in the aquatic environment.

Effects of Wastewater Disposal on Groundwaters—Backflood Waters—Bob Newport

Although the following discussion focuses on modified *in situ* retort operations of the Piceance Basin, general information contained here will be applicable to other oil shale regions and surface retorting.

Numerous hydrological investigations by government agencies and mining interests have attempted to define local and regional groundwater systems and their relationship to oil recovery from vast oil shale deposits of the Piceance Basin. These efforts have contributed significantly to the understanding of this quantity relationship, but they have failed to define groundwater quality variations likely to occur during oil recovery. In the Piceance Basin, the groundwater system is complex. Predictive movements of groundwater and multiple aquifer relationships have defied quantification. Using available hydrogeological information and the current state of knowledge about oil shale operations, this section addresses potential problems and operational and treatment scenarios as they relate to groundwater quality. In this effort, it will be necessary to summarize regional hydrology, wastewater types, and waste disposal options.

Hydrology of the Piceance Basin

In addition to a significant alluvial aquifer, the Piceance Basin has two major aquifers separated by the Mahogany Zone, which acts as an aquitard. The Mahogany Zone also is the richest oil shale formation scheduled for exploration. This zone, varying in permeability because of ill-defined fractures, restricts full communication between the two major water systems. These two aquifers are fed by percolating surface water that generally passes from the upper aquifer through the Mahogany Zone to the lower aquifer. In the northern part of the basin, heads of the aquifers are reversed, resulting in reverse flow—from the lower to the upper aquifer.

Base flows of area springs and streams are fed by the alluvial and both major aquifers. Attempts to determine what percent of stream flow could be attributed to each aquifer have been unsuccessful.

Included in both major aquifers are less defined minor aquifers separated by aquitards considerably thinner and exhibiting higher transmissibilities than the

Mahogany Zone. Communications between minor aquifers result in uniform water quality throughout the major zone. In the lower major aquifer, water quality decreases with depth.

Detailed quality of surface and groundwaters will be considered in other sections of this report. For the purpose of this section, total dissolved solids concentration (averaged from various sources) will be used as an indication of water quality throughout the system.

The following figures represent the gross differences between various water types of the Piceance Basin:

Water Type	TDS
Springs	925
Alluvial aquifer	1,000
Piceance Creek	800
Upper aquifer	1,100
Lower aquifer	6,200

As indicated by the foregoing discussion, surface water, shallow alluvial aquifers, and the upper and lower major aquifers are intimately related. Physical or chemical changes in part of the system will ultimately affect the rest of the system. Without intensive research investigations, effects of these changes on area water resources will await several years of commercial oil shale operations. The purpose of this section is to indicate probable areas of primary concern and suggest control and disposal options.

Wastewater Types

Water from mine dewatering operations, process water, boiler blow down, domestic waste and cooling tower water are major wastewater types considered as potential contaminants to groundwater. Wastewater from various other sources will possibly be combined with major wastewater volumes, simplifying treatment and disposal options. Because of their quality and volume, process water and water from mine dewatering are of prime concern.

Mine Dewatering—

At the various sites under serious consideration for surface retorting, mine dewatering will be insignificant. Locations of these operations are in areas where major groundwater aquifers are not intercepted by shale removal activities.

Active *in situ* operations in the Piceance Basin are currently conducting or anticipating extensive dewatering programs that will permit shaft sinking, mining, and eventual retorting. Two approaches to this major problem are being considered by mining operators. One is to drill peripheral wells around the area to be mined and to conduct the recovery activities in the cone of depression formed by continuous groundwater evacuation. The second approach is to dewater the mine directly as mining operations progress and water enters the mine. Regardless of the method used, mine dewatering will significantly affect groundwater quantity. In addition, adverse groundwater quality variations may result.

Estimated quantities of groundwater production resulting from dewatering one mine range from 1,893 lpm (500 gpm) at the initiation of the mining operation to more than 37,850 lpm (10,000 gpm) when full scale production is reached. Annual groundwater demands during full-scale production amount to 246 ha m/year (2000 acre ft/year) and will eventually create a radius of influence 9.6 to 16 km (6 to 10 mi) from the mine.

Following formation fracturing and mining, but before retorting, groundwater evacuated may decrease in quality because of new mineral surface exposure. This quality change, if anticipated, could be controlled by one of various treatment options discussed later. Increased water consumption during operational expansion should reduce the volume of evacuated water requiring treatment.

Process Water—Process water (water produced with the oil) is estimated to approximate oil production volumes. Thus, in the case of full-scale production of one mine at 100,000 bbl/day, large volumes of low quality water will require extensive treatment before disposal.

During full-scale retorting operations, both process water and water from dewatering operations will be produced. Treatment and disposal options and their potential effect on groundwater must be a consideration throughout the operational phase.

Wastewater treatment is covered at length in Section 4 of this document. Specific treatment options likely to be used during commercial operations will be mentioned here as they relate to groundwater quality. Each treatment or disposal method will be discussed in terms of its short-term, long-term, or intermittent application and potential impact on area groundwater resources.

The nature of developing oil shale operation dictates that water supplies and demands will be extremely variable. In the initial stages of mining development, disposal of essentially all water evacuated from the mine will be necessary. When commercial retorting begins and water demands increase, it is conceivable that supplemental off-site supplies will be required. Even during full-scale operations, variations of production-consumption ratios will occur, necessitating standby treatment, disposal, or supply systems. Considering extremely variable production and consumption estimates, one or more of the following treatment or disposal systems will be utilized.

Waste Disposal Options

Reinjection—From the beginning of shaft construction until commercial-scale retorting begins, essentially all water from dewatering operations will require disposal. Selective reinjection of this water is one method currently in use and appears to be an acceptable disposal method. Groundwater quality variations associated with this practice are unknown. The general assumption is that groundwater extracted could be reinjected into the same groundwater system causing negligible changes. While in fact this may be true, consideration must be given to possible water quality changes caused by mining, dewatering, and reinjection that will necessitate operational adjustments in treatment and disposal systems.

During injection, increased mineralization of groundwater may occur as a result of increased groundwater flow, exposure of new mineral surfaces following fracturing, changes in microbial populations as a result of environmental alterations, and increased mineral availability resulting from varying water types moving through foreign mineral strata. The effect of these complex and interrelated factors on groundwater has not been determined. Research addressing groundwater quality variations associated with oil shale development has begun, but accelerated efforts are necessary to assess the magnitude of the problem. If significant groundwater quality changes do occur, existing technology and hydrogeological information cannot be expected to foretell its long-term effects on regional water resources.

Many of the potential problems associated with wastewater injection can be effectively controlled by pretreatment. For this reason, injection of wastewater should be considered as a viable disposal method.

It should be mentioned that well integrity is basic to development of an acceptable injection system. Injection wells should be constructed and maintained to insure that wastewater flows are confined to preselected formations.

Spray Irrigation/Soil Treatment—Soil treatment of industrial and municipal wastewater is well documented and is recognized as an environmentally acceptable treatment method. Considering anticipated oil shale waste quality, this treatment method, with slight variation, could be extended to include oil shale wastewater. Application of wastewater to semiarid areas of oil shale country appears feasible and possibly beneficial. This system could be used full- or part-time or in series with other treatment methods.

Successful adaptation of a soil treatment system to industrial waste in Wyoming indicates that regional climatic restraints of the Piceance Basin would not adversely affect waste treatment.

Groundwaters associated with soil treatment systems have been and continue to be investigated. Current indications are that groundwater is not adversely affected by this method of treatment.

Ponds or Lagoons—Collection of large volumes of water in holding ponds or lagoons for the sole purpose of treatment by evaporation or percolation is not recommended. However, ponds constructed for the purpose of temporary containment of wastewater awaiting treatment before disposal seem necessary. These ponds would be available as emergency storage reservoirs in the event of treatment system failures or modifications, and they would serve as surge tanks if operational variations resulted in wastewater volumes exceeding design limitations of treatment systems.

Ponds should be constructed to eliminate percolation effectively; otherwise, adverse effects on groundwater will result. The active life of an *in situ* oil shale operation is estimated to be 30 years. Small percolation volumes of wastewater over several years could be significant. If wastewaters are to be confined in ponds, liners or other acceptable materials are recommended. Groundwater quality monitoring (addressed in a later section of this document) is recommended.

Spoil Stabilization and Revegetation—Various figures, depending on the investigator, have been used to indicate the amount of wastewater that can or must be used for stabilization and revegetation of spoil piles. The two basic recovery methods, *in situ* and surface retorting, add additional variables. Surface retorting spoils are composed of spent shale residues, whereas *in situ* spoils consist of raw shale. Water requirements for stabilization, revegetation, or saturation will vary considerably, depending on spoil type. Groundwater is the ultimate recipient of leachate from either spoil type.

Leachate quantities are a function of porosity and application rates. Leachate quality is a product of spoil mineralogy, organic residues, and quality of water used for stabilization and revegetation. Minor changes in wastewater quality used for stabilization may result in major changes in leachate quality. It is anticipated that wastewater will be used for spoil stabilization. If wastewater is to be applied to spoil piles, the nature and quality of leachate should be carefully considered. Groundwater monitoring associated with spoils wastewater disposal is covered in a later section.

Backflood Waters—Following the retorting operations, groundwater will be allowed to fill the rubblized retorts. Groundwater chemical changes associated with backflood waters during advance oil recovery operation and following eventual mine abandonment are unknown. Estimates of potential problems associated with this post operational phase vary considerably. One theory is that abandoned retorts will act as carbon filters, improving groundwater quality. Another theory indicates that numerous organic and inorganic contaminants will be placed in solution and released to groundwater.

Current oil shale operators seem prepared to continue dewatering operations associated with abandoned retorts until backflood water quality stabilizes at an acceptable level. Time required for stabilization will depend on absorption capacity or deabsorption persistence of retorted mineral surfaces. Conceivably, this could require years of dewatering, treatment, and subsequent disposal.

It is recommended that backflood waters of low quality be confined to local groundwater systems, regardless of time or funding demands.

Long-term Effects of the Oil Shale Industry on Surface Water Resources of the Colorado River Basin—Wesley Kinney

The total impact of a mature oil shale industry on surface water resources cannot be quantitatively assessed until long after production on a commercial scale has begun. Accurate prediction requires a thorough knowledge of the hydrological regimes of the area and an understanding of the nature, transport routes, and fates of pollutants subject to release to surface waters. Recent investigations have greatly advanced the knowledge of subsurface and surface water regimes throughout the oil shale area, to the point where water resources are fairly well described with respect to both quality and quantity. But knowledge about the pollutants themselves is still lacking, i.e., their mobilization potential, chemical nature, transport pathways, fates, and consequences of exposure to receptors. This is particularly true of the numerous complex trace organic constituents associated with raw and retorted shale and wastewaters. A great number of constituents have been identified as potential pollutants with carcinogenic, mutagenic, teratogenic or other toxic properties based on laboratory studies. However, little information is available on the potential hazards of these constituents at levels likely to be encountered in surface waters.

In the following section, potential water-related problems are addressed in the context of the probable cumulative regional impact of a maturing, commercial oil shale industry, assuming utilization of a mix of extraction and processing technologies. The possible effects of potential pollutants on surface water quality and quantity and the resulting impact on aquatic life, public water supplies, livestock, irrigation agriculture, and selected industries are evaluated. Where sufficient data are available, attempts are made to relate historical, current, and projected water quality data to water quality criteria for the various water use categories.

Salinity—

A mature oil shale industry and related industrial and urban development could, over the long term, increase the salinity at Hoover Dam through both salt-concentrating and salt-loading processes. Salt-concentrating effects would occur as relatively high quality surface waters are withdrawn for consumptive uses and as a result of evaporation and transpiration. Assuming that substantial amounts of groundwater and process water are available for use, it is not anticipated that salt concentrating effects will add to the salinity detriment of the Colorado River until many years after development is instituted (12). Salt loading could result from leaching of spent shale disposal piles or byproduct storage piles, release of saline mine or process waters, groundwater disturbances caused by reinjection of excess waters, and municipal and industrial waste discharges. Construction of roadways and utility corridors, removal of overburden, and the actual mining operations would enhance weathering and erosion of exposed materials, thereby increasing the potential for mineral release to surface waters directly and via subsurface waters.

With the practice of surface retorting, leachates from spent shale constitute a potential source of salt loading to surface water owing to the proposed disposal methods and the physical and chemical characteristics of spent shale (12). The mineral composition of spent shale varies somewhat, depending on the retorting process used and the differences in peak temperatures reached in the various retorts. But regardless of the process used, spent shale materials are represented primarily as oxides of the various minerals present in raw shales, many of which are highly water soluble (12). Ward *et al.* (31) investigated the water pollution potential of spent shale residues from various retorts. Analyses of water after intimate contact with spent shale from the TOSCO and Union Oil Company retorts revealed high concentrations of sodium, calcium, magnesium and sulfates. Leaching tests demonstrated that soluble salts are readily leached from spent shale columns; con-

sequently, a definite potential exists for high concentration of the major ions (Na^+, Ca^{++}, Mg^{++}, and $SO_4^=$) in the runoff from spent oil shale residues (31).

Weathering and leaching of spent shale piles will occur over long periods of time. Even though attempts will be made to stabilize the piles through compaction and with natural soil and vegetative cover, erosion and leaching of dissolved solids will undoubtedly occur, particularly during the periods of active disposal and shale-pile buildup.

Raw wastewater produced by retorting oil shale contains a variety of constituents, thus presenting a wastewater disposal or treatment problem. If the untreated water is used to moisten shale piles, the mineral components may be physically or chemically trapped within the shale pile temporarily, but the potential for leachates eventually moving through the pile would seemingly be increased.

In the Piceance Basin, disposal of excess mine waters poses a potential problem that may be intensifed as the oil shale industry matures. During the early stages of development, relatively high quality excess water will be released directly to local drainages; but through time, the excess water will increase in salinity, and discharge of untreated water to local streams may not be permitted. It may be necessary during initial development to store excess or poor quality groundwater in impoundments, and during later stages of development to reinject the excess water into aquifers (12). Both methods of disposal could potentially result in release of saline waters into streams. The first would be through failure of a dike impounding saline waters, and the second through upward movement of poor quality groundwater and eventual discharge to surface waterways (12).

Municipal and industrial developments could cause additional salinity problems. As the population of the area expands, increased amounts of salts may enter surface waters by means of municipal and industrial discharges, thereby increasing the total mineral burden in localized areas. Since the nature and extent of urban and associated industrial growth cannot be predicted with certainty, the extent to which such growth will compound the salinity problem is unknown.

As water becomes highly mineralized, its utility for industrial and agricultural purposes, public water supply, and as a medium for freshwater organisms is impaired. Present salinity concentrations in the lower Colorado River have reached the level at which some impairment for industrial purposes, irrigated agricultural uses, and municipal uses is occurring (32). As TDS levels increase above 500 mg/l (4.17×10^{-3} lbs/gal), treatment costs soar for industrial and municipal water users, and irrigated agricultural crops characteristically undergo reductions in yield (33). Highly mineralized water causes scaling and corroding of water pipes, boilers, and heaters, adding to increased maintenance and treatment costs for industrial and household users. As salt concentrations in irrigation waters increase, soils become more saline, thereby restricting the variety of crops that can be grown successfully (33).

Levels of TDS, hardness, and specific constituents that normally represent maximum acceptable limits for particular industrial purposes were summarized by the National Academy of Sciences (NAS) (33). Alhough ambient surface water quality throughout the Colorado River system is acceptable for a wide range of industrial uses, concentrations of specific constituents that exceed the recommended limits for cooling purposes and certain industrial process uses have been reported.

In terms of EPA guidelines, the surface waters of the Colorado River system are acceptable for livestock watering purposes, but most of the mainstem waters have for years exceeded the guideline level for sensitive irrigated crops (33). Conductivity and TDS values for these waters typically fall into the 750- to 1,500-mmhos/cm (295- to 590-mmhos/in.) and 500- to 1,000-mg/l (4.17×10^{-3}- to 8.24×10^{-3}-lbs/gal) ranges, respectively, the levels of possible detrimental effects for sensitive crops.

Although drinking water criteria before 1973 recommended against using waters with a TDS limit exceeding 500 mg/l (4.17×10^{-3} lbs/gal) (34), this recommendation was not adopted by EPA (33,35). Many public drinking water supplies with TDS

levels exceeding 500 mg/l are in current use with no ill effects to the consumers. The EPA does, however, recommend limits of 250 mg/l (2.09×10^{-3} lbs/gal) for both chlorides and sulfates in public drinking water supplies (33,35).

The effects of highly mineralized or saline water on aquatic life vary tremendously with the concentrations of specific ionic constituents. Salinity in fresh water is defined as the total concentration of the ionic components (36,37). The most conspicuous anionic substances that contribute to salinity in the Colorado River system are bicarbonates, sulfates, and chlorides. These substances combine with the metallic cations calcium, magnesium, sodium, and potassium to form ionizable salts. Silica, which contributes to the total mineral burden, may be present in several forms, including complex ions such as colloidal silica or as sestonic mineral particles; but most silicates in inland waters are probably present as undissociated silicic acid (36). The absolute and relative abundances of these materials are important factors regulating productivity of waters and influencing the structure of communities.

Water hardness is governed chiefly by the presence of calcium and magnesium cations in waters. In general, the biological productivity of a water body is directly correlated with its hardness. However, hardness per se has no biological significance because biological effects are functions of specific ions and combinations of elements (33). Many minor dissolved substances contribute to the total hardness and salinity of waters, but since they are usually present only in trace quantities, their total contribution from the standpoint of hardness is rather insignificant.

It is estimated that the salt concentrating effects alone of a 1-million-bbl/day industry would increase the salinity at Hoover Dam by 10 to 27 mg/l (8.34×10^{-5} to 2.25×10^{4} lbs/gal), depending on the sources and quantities of water required (12). The impact on the river would not be immediate, but as high quality groundwater supplies decreased and the rate of surface water withdrawal increased, the effects would become more pronounced (12).

Toxic Substances

Many activities associated with the development and operation of an oil shale industry that could potentially increase the total salt burden of surface waters could similarly increase the potential for contamination with a variety of toxic substances, including trace elements and numerous organic substances.

Raw and retorted shale contain a number of potentially toxic substances in varying concentrations, as discussed in Section 3 (Solid Waste Impacts). Leaching studies by Culbertson *et al.* (38) and Ward *et al.* (31) have shown that soluble salts are readily leached from spent shale piles; but the mobilization potential of many inorganic and organic trace constituents is virtually unknown (38,39). Consequently, knowledge of elements and compounds associated with oil shale and subject to release to surface water as a result of industrial development is incomplete. The extreme difficulty in conducting organic analyses has discouraged most researchers and has largely limited monitoring efforts to the measurement of organic carbon, phenols, oils and grease, and a few similar analyses. Thomas (40) summarized the results of a study by Pellizzari (41), which reported organic substances found in process water from oil shale based on analyses of six samples. Thomas listed maximum levels of those compounds that occurred at an arbitrary level of 100 ppb or greater (Table 3-22).

Other possible sources of trace elements and other toxic substances include stack emissions from processing operations, catalysts and chemicals used in oil upgrading and gas processing, contact of high quality water with highly mineralized groundwater, municipal and industrial wastes from expanding communities, and development of ancillary extractive industries.

TABLE 3-22. VOLATILE AND SEMIVOLATILE ORGANIC COMPOUNDS PRESENT AT CONCENTRATIONS OF 100 ppb OR GREATER IN AQUEOUS SAMPLES FROM 136-TONNE LETC OIL SHALE RETORT.

Volatile compounds	ppb[b]	Semivolatile compounds	ppb
Acetone[c]	200	Benzylamine	377
Benzene[c]	134	Benzoic acid	493
Cyanobenzene	235	$C_8H_{11}N$ isomer	621
t-butanol	130	$C_9H_{13}N$ isomer	422
2-heptanone	244	$C_9H_{14}O$ isomer	175
Methyl ethyl ketone	152	Cresole isomers[c]	779
2-octanone	126	n-heptanol	165
Methylcyclopentane	680	Dimethylnaphthalene isomers	199
2-pentanone	123	n-octanoic acid	155
n-methylpyrazole	177	Phenol[c]	461
Pyridine	185	C_2-alkyl phenol isomer	337
C_2-alkylpyridine isomer	240	Ethylphenol isomer	321
Toluene[c]	300	Dimethylphenol isomer[c]	1011
		Alkylpyridine isomer	176
		Trimethylpyridine isomer	762

[a] Source: Modified from Thomas (40) after Pellizzari (41).
[b] Values represent maximum concentrations reported based on analyses of six samples.
[c] Listed as suspected carcinogens by Christensen and Fairchild (42).

A total population increase of 66,000 to 115,000 is estimated to be required to support a mature oil shale industry—representing nearly a twofold increase over the 1970 population of the area (12). Potential toxicants that may be introduced to waters as a result of industrial and urban growth include chlorine, cyanide, detergent builders, phenolic compounds, phthalate esters, polychlorinated biphenyls (PCB), and toxic forms of nitrogen, including ammonia, nitrites, and nitrates.

Increased levels of pesticides and their residues in waterways can be expected as pesticide usage increases. The creation of new lawns, parks, and recreational facilities will likely result in greater domestic use of pesticides by homeowners and communities. Expanded industrial growth also characteristically results in increased usage of various pesticides, as does maintenance of utility corridors and roadside rights-of-way.

The types and extent of ancillary industrial growth that may be stimulated by oil shale development cannot be predicted with any certainty. The extensive deposits of nahcolite and dawsonite found in association with oil shale may lead to the recovery of soda ash, aluminum, or compounds thereof. Technology for the recovery of sodium materials from these deposits has been demonstrated on a pilot scale, but commercial extraction has not been attempted. Aluminum and aluminum compounds contained in dawsonite have been recovered from retorted shale on a small scale. Trona and halite occur to some extent in the Green River Basin in Wyoming, and sodium materials, petroleum, natural gas, asphalt, tar sands, and coal are scattered throughout the Green River Formation of the oil shale area. It is not presently known if all of these materials are present in commercially significant quantities.

Concentrations of trace elements and other toxic substances vary widely throughout the Colorado River system with time and location. Trace element data presented by Kopp and Kroner (43) reveal few conclusive trends with respect to

trace metal concentrations relative to location, but a few observations are noteworthy. Arsenic, beryllium, and cadmium were not detected at all and cobalt and vanadium were each reported at only one site—the former in the upper Green River, and the latter in the upper Colorado. Barium, boron, copper, iron, manganese, strontium, and zinc were reported at all locations, but only boron exhibited conspicuously increasing concentrations in a downstream progression. Silver and molybdenum were detected at all but the lower Colorado mainstem stations. The distribution of lead, nickel, and aluminum was sporadic, each being detected in only one or two samples at various locations.

Data on concentrations of trace metals in the mainstream of the Colorado at Yuma, Arizona, during 1958-59, as compiled by A. D. Little (44), revealed maximum concentrations of aluminum, barium, chromium, copper, iron, and manganese in the range of those reported by Kopp and Kroner (43) at the same location, but the latter reported much higher concentrations of boron and strontium. Conversely, nickel concentrations were reported to be an order of magnitude higher during the 1958-59 study than were reported by Kopp and Kroner (43). Rubidium and titanium were present at Yuma in concentrations of less than 0.01 mg/l (8.34×10^{-8} lbs/gal) during 1958-59 (44).

Maximum concentrations of boron, fluoride, and iron at selected sites on the Colorado, Green, and White Rivers during 1964-65 and 1968-70 were summarized from USGS documents (45,46) by Kinney *et al* (47). The boron data for the upper watershed are in line with those reported by Kopp and Kroner (43), but the USGS data do not show the increase in concentrations in the lower watershed that was so apparent in the Kopp and Kroner data.

Iron concentrations reported by USGS were typically lower than those reported by Kopp and Kroner and A. D. Little for the same general area of watershed. Fluoride concentrations were not reported by Kopp and Kroner or A. D. Little, but USGS data show relatively uniform concentrations ranging from 0.30 to 1.0 mg/l (2.50×10^{-6} to 8.34×10^{-6} lbs/gal) throughout the watershed.

Data on ambient levels of such toxic substances such as chlorine, detergent builders, phenolic compounds, phthalate esters, and PCB in the Colorado River system are scarce or nonexistent. A single analysis for methylene blue active substances (MBAS) on the White River near Watson, Utah, yielded concentrations of 0.02 mg/l or 1.67×10^{-7} lbs/gal (USGS data from EPA's water quality computerized storage and retrieval system (STORET)). Water analysis for PCB on filtered, unfiltered, and suspended samples yielded no positive results, but a single mud analysis revealed a concentration of 2.0 mg/kg (2×10^{-6} lbs/ton) on the Colorado River near Cisco, Utah (USGS data from STORET).

Cyanide and phenol data were collected by Voorheis-Trindle-Nelson (48) on the White River stations adjacent to Tracts U-a and U-b and on Evacuation Creek, which transects the sites. Eighty-six analyses of White River water for phenols and 50 analyses for cyanide revealed maximum concentrations of 0.014 and 0.01 mg/l (1.17×10^{-7} and 8.34×10^{-8} lbs/gal), respectively. Maximum concentrations in Evacuation Creek were 0.024 mg/l or 2.00×10^{-7} lbs/gal for phenols (30 analyses) and 0.02 mg/l or 1.67×10^{-7} lbs/gal for cyanide (18 analyses).

Low levels of chlorinated hydrocarbon pesticide residues have been detected in the Colorado River system by a number of investigators. A. D. Little (49) summarized levels of organochlorine pesticides that have been reported at various locations in the Colorado River system during 1964-68. Sufficient data are not available to discern trends with respect to time or location.

Toxic substances in surface waters are primarily of concern because of their potential impact on the aquatic biota, agriculture, and man. Since the impacts of toxic materials on freshwater biota, livestock, irrigation crops, and man are discussed in great detail by McKee and Wolf (50), the National Technical Advisory Committee (50), and NAS (33), they are only superficially addressed in this report.

Many naturally occurring dissolved substances in water, although vital to life functions in trace amounts, can prove harmful or fatal to plants and animals, including man, when present in high concentrations. The toxic properties of trace metals such as arsenic, copper, and zinc, all essential to human nutrition, are well known, and various compounds of these metals have been used for years in the manufacture of pesticides.

The toxicity of metals in water varies considerably with the chemical and physical characteristics of the waters. For example, the pH of water influences the solubility and therefore the toxicity of many metals, including aluminum, copper, and zinc. The presence of certain metals in water can enhance the toxicity of other metals by synergistic reactions. For example, the toxicity of zinc, cadmium, and mercury is increased by the synergistic action of copper. On the other hand, the toxic effects of many metals, including zinc, copper, lead, cadmium, chromium, and nickel, are much less pronounced in highly mineralized (hard) waters than in soft waters owing to the antagonistic action of calcium, carbonates, and other common hard water constituents.

Cadmium, lead, chromium, and mercury are examples of nonessential, nonbeneficial elements in the diet that are highly toxic to aquatic life, humans, and livestock in low concentrations. Boron, cobalt, and molybdenum are known to be essential to higher plants in trace quantities, but may be deleterious to crops if highly concentrated in irrigation waters.

Ambient surface water data for waters within the Colorado River system reveal that maximum concentrations of boron, molybdenum, and nickel exceeded the acceptable limits for continuous irrigation at several locations. Maximum concentrations of iron and lead at some stations in the lower Colorado exceeded the recommended limits for drinking water. Lead concentrations in one sample in the lower Colorado near Boulder City, Nevada, also exceeded the maximum acceptable limit for aquatic life.

These comparisons of water quality criteria with ambient water quality data clearly illustrate that concentrations of certain trace minerals in Colorado River Basin surface waters at times exceed the maximum acceptable limits for specified water uses. The utility of these waters can only be further impaired by activities that disturb large areas of the landscape, create large volumes of waste material for disposal, alter surface water and groundwater regimens, and lead to increased usage of chemicals in the area—unless such developmental activities are carefully planned and closely regulated.

Although concentrations of trace minerals in the surface of the Colorado River Basin are not exceptionally high when compared with river basins in heavily industrialized areas of the country, the extent to which the surface water characteristics will be altered by industrialization and urbanization of the area is unknown. For example, arsenic and cadmium, both highly toxic metals, are common constituents of rocks and could be released to the aquatic ecosystem through weathering of the exposed bedrock. In addition, cadmium could be released as a leachate from spent shale, and arsenic, which is expected to volatilize during retorting, may become an air emission. Numerous additional heavy metals could be released to waterways in quantities sufficient to impair seriously the utility of these waterways for specific beneficial uses.

In the Colorado River Basin, pesticides may constitute the greatest potential hazard of all toxic substances of nonpoint source origin. Pesticides include a myriad of natural and synthetic chemicals used to control or destroy plant and animal species under a variety of situations. Depending on the intended use or target organisms, pesticides are frequently categorized as insecticides, herbicides, fungicides, rodenticides, nematocides, etc.

The major threat of pesticide contamination of waterways arises from insecticides and herbicides because they are the most widely used categories of pesticides

and many are resistant to degradation, persisting in the environment in forms that are toxic to aquatic and terrestrial life, including humans. The entry of pesticides into waterways in large doses, as frequently occurs with spills or accidental discharges, may have an immediate and dramatic impact resulting in annihilation of the biota and poisoning of public water supplies. More frequently, however, pesticide pollution of waterways has a more subtle effect as residue levels slowly build up over time.

Most pesticides undergo rapid degradation in the environment and, though they are highly toxic for a short while, they soon are degraded, metabolically or otherwise, to relatively innocuous materials. On the other hand, some pesticides, particularly the organochlorine insecticides are extremely resistant to degradation and are subject to biological accumulation directly from the water and through the food web. This results in insecticide concentrations in higher trophic-level organisms several thousand times higher than ambient water levels.

Ambient water quality data for the Colorado River System reveals that concentrations of aldrin, DDT, dieldrin, and endrin approached or exceeded the recommended maximum levels for the protection of aquatic life, humans, and livestock at various locations. In recent years fish and bird mortalities attributable to organochlorine pesticides have occurred in and downstream from irrigation ditches in the Lower Colorado Basin. Few ambient data on levels of other categories of pesticides in the Colorado River system are available. Consequently, it is not known whether they constitute a potential hazard.

Of the organic compounds identified in process waters, phenols, dimethyl phenol isomer, cresole isomers, acetone, benzene, and toluene are of specific concern. All are suspected carcinogens that have been identified as high priority EPA effluent pollutants. The cresoles and phenols are of particular concern since they have toxic as well as carcinogenic properties and may occur in high concentrations. Concentrations of phenols in the White River and Evacuation Creek, as reported by Voorheis-Trindle-Nelson (48) exceed the EPA guideline levels for drinking water (33).

Certain toxic substances (e.g., phthalate esters, polychlorinated biphenyls, cyanide, and chlorine) generally occur in water at hazardous levels only in heavily industrialized metropolitan areas. Consequently, it is unlikely that they pose a serious hazard in the Colorado River Basin at the present time. Accelerated industrial and urban expansion, however, could significantly increase ambient levels of these substances in the aquatic ecosystem.

Microorganisms

Possibilities exist for the microbial contamination of surface waters as a consequence of rapid population increases. This can result in overloaded sewage treatment facilities and the subsequent discharge of improperly treated sewage. Bacteria, viruses, protozoa, and fungi are all potential waterborne transmitters or causative agents of diseases. The extent to which public health might be affected by expanded population cannot be projected at this time (48). The common and well documented precautionary sanitation measures and construction or expansion of sewage treatment facilities would minimize risks of microbial contamination of waterways and subsequent potential public health hazards.

Oil and Grease

The possibilities for oil losses exist wherever oil is produced, processed, or transported. A mature 1-million-bbl/day industry is estimated to require about 280 km (150 mi) of new pipeline to transport shale oil to major existing pipelines (12). Predicted loss through spillage resulting from pipeline transport ranges from 1 to 100 bbl/year (12). The potential for much larger volume spills exists, however.

In the event that a large-volume spill reaches a waterway and the oil cannot be contained or removed, very severe damage to the aquatic biota and waterfowl would result. Smaller volume spills such as those resulting from smaller pipeline leaks could cause local damage to the biota, and if undetected for a long period of time, the damage could be substantial.

Oil and grease in public water supplies can also cause objectionable taste, odor, and appearance problems, and it can be hazardous to human health (33). To avoid such problems, the NAS recommends that public water supply sources be essentially free from oil and grease.

Hydrographic Modification

Hydrographic modification refers to procedures that change the movement, flow, or circulation of any navigable waters or groundwaters.

Anticipated disturbances can be categorized by the manner in which they alter water systems as follows: (1) creation of new impoundments, (2) drainage of existing impoundments, (3) diversion of natural drainage, (4) flow depletions, and (5) disturbances to streambeds.

Historically, mining operations have been equated with landscape destruction and water quality degradation. Typically, mining operations involve the movement and relocation of large volumes of extracted material, resulting in drastic changes in the topography and drainage characteristics of exploited areas. The oil shale industry will be similar to most other extractive mining and processing industries in that large expanses of the landscape are disturbed by the development and operation of a commercial industry, resulting in permanent alteration of the water storage and drainage system.

Development of the oil shale industry will differ from that of most mining industries in that it occurs under rigid governmental controls and regulations instituted to minimize environmental impacts. However, in spite of strict adherence to environmental guidelines, deleterious consequences unavoidably and inevitably result. Many disturbances are localized and temporary and ultimately reparable and do not permanently alter the regional hydrological regimes.

Other disturbances which potentially alter the water budget of entire river systems could, however, seal the fate of the industry during the early developmental stages.

Activities such as road building, pipeline installation, shale disposal, mine dewatering, etc. could permanently alter the hydraulics of streams in the area. Groundwater withdrawals probably have the greatest impact, as continuous pumping over a period of years could dry up a number of springs in the Piceance Basin and eliminate much of the seepage to surface waters. Mine dewatering at the rate of 0.85 m^3/s (30 ft^3/s) for a 30-year period in the C-a tract would lower the entire water table within a 13.5 km (8-mile) radius of the site (12). Estimates show that as many as 37 springs within this area may experience adverse effects, ranging from reduction of flow to complete cessation of flow (28). Reduction in total flows from springs will ultimately reduce the amount of water reaching Yellow Creek. If excess groundwater of suitable quality is available to replenish flows, changes in stream hydraulics will be minimal. In the event that high quality groundwater is not available to replenish surface flow, however, groundwater withdrawal could have a substantial impact on the hydrological regimes of the area.

pH

The pH of water receiving industrial wastes and mine drainage may be drastically altered by the addition of acids or alkalies. Such additions, particularly in poorly buffered systems, not only result in acidic or alkaline conditions, but may increase the toxicity of various components in the water (33). In well buffered systems, the addition of small quantities of acids has little effect on the pH of the system. Since

the Colorado River system waters contain sufficient CO_2 to maintain equilibrium in the bicarbonate system, it is doubtful that oil shale developmental activities will substantially alter the buffering capacity of the system unless considerable quantities of acids are discharged to waterways. Significant changes in pH or alkalinity (bicarbonate) levels would serve as an immediate alarm that the buffering system was disturbed and the equilibrium upset, thereby signaling the need for intensive investigation to determine the cause of the disturbance.

Nutrients

The term "nutrient" can legitimately be applied to any element, vitamin, hormone or other substance that is utilized metabolically for growth or maintenance by living organisms. From the standpoint of water quality, the nutrients of major concern are nitrogen and phosphorus, owing to their contributions to the eutrophication problems. It is these macronutrients that are addressed in this section.

Both nitrogen and phosphorus enter surface waters by natural and man-induced processes. Nitrogen enters waters naturally through fixation from the atmosphere and through geologic and biogenic processes. Leaching of phosphorus from calcium-phosphate rocks and soils and importation of allochthonous organic materials are among the most important natural sources of phosphorus in waters.

Potential sources of nitrogen and phosphorus loading to surface waters as a result of the development of an oil shale industry include municipal wastes, groundwater discharge, stack emissions, runoff from raw and spent shales, and commercial fertilizers.

The primary effect of urban growth on water quality would result from increased nutrient loading via domestic sewage. An influx of people to the oil shale area will place an added burden on existing sewage treatment plants, requiring expansion of existing plants or construction of new facilities if the State's water quality standards are to be met. Increasing the capacity of municipal treatment plants should partially alleviate the problems of additional nutrient release to surface waters as a result of population growth, but additional loading over the present level is to be expected. Municipal wastes receiving secondary treatment are very high in plant available nutrients; consequently, the increased volume of treated wastes will result in increased nutrient loading to waterways.

Groundwaters in the oil shale area are rich in nitrogen, with concentrations of nitrates as high as 55 mg/l (4.59×10^{-4} lbs/gal) reported from a spring in the Piceance Basin (51). Data available on phosphorus concentrations in groundwater indicate levels are not unacceptably high. Release of groundwater to surface waters, regardless of the mechanism, represents a potential source of nitrogen loading but probably does not represent a significant source of phosphorus.

Stack emissions from industrial operations are a potential source of nitrogen entry to waterways via atmospheric rainout. Nitrogen oxides will be emitted from retorting operations and power generation, but the quantity of nitrogen that will reach waterways via this route is unknown.

Nutrients in various forms as well as the excessive productivity they induce in aquatic systems can interfere with beneficial water uses. The Environmental Protection Agency has no numerical water quality nutrient criteria for purposes of limiting productivity of aquatic life. It is necessary to know the productivity responses of various water types to ambient nutrient concentrations of loading rates. Such relationships are presently being developed and tested at the EPA Environmental Monitoring and Support Laboratory in Las Vegas, utilizing data obtained from lakes sampled in the National Eutrophication Survey. This study may provide a basis for the development of numerical criteria.

The NAS has recommended criteria for particular nutrient forms for beneficial water uses (33). Included are criteria for waters used for industrial purposes, public

water supplies, and livestock watering. In addition, criteria were established for the protection of aquatic life from toxic ammonia.

Available water quality data suggest that Colorado River waters are acceptable for most beneficial uses as regards nutrient levels. Additional nutrient loading in the Colorado River system resulting from an oil shale industry and associated urban development would undoubtedly adversely affect localized reaches of streams, but the cumulative impact on the Colorado River system cannot be predicted with certainty. The rate of loading will depend in part on the distribution and the density of the human population, as well as the degree of treatment that the wastes receive.

Temperature

Temperature differences between the upper and lower reaches of the Colorado River system are pronounced during all seasons, primarily because of climatic, geographic, and topographic factors. Natural temperature regimes of the river system are disrupted by large reservoirs such as Flaming Gorge Reservoir on the Green River and Lakes Powell and Mead on the Colorado River. The effects of the reservoirs are to lower summer temperatures and, in some ,cases to increase winter temperatures for considerable distances downstream from the discharge.

Thermal springs, wastes discharges, and irrigation return flows may increase temperatures of receiving waters locally, but heat added from such sources is usually quickly dissipated.

As the oil shale industry matures, stream temperatures may be altered somewhat by municipal and industrial waste discharges, consumptive uses of surface waters, lowering of the groundwater table, landscape modifications, and construction of new reservoirs. A potential source of temperature increases is the discharge of heated water (used in cooling processes) from power generating plants, although none of the major developers has indicated any intention of discharging directly to surface waters.

Considering the vastness of the Colorado River system and the inherently wide natural variability in temperatures, thermal effects resulting from oil shale development are expected to be of little significance in terms of the natural temperature regime of the river system (12).

Temperature is not a critical factor for water used for industrial, agricultural, or public water supply purposes, but aquatic biota could be adversely affected by localized thermal effects since aquatic invertebrates and fish are very sensitive to temperature changes. Temperature extremes and variations, (and particularly sudden changes in temperature) affect all components of the aquatic ecosystem. Not only are the biota affected directly, but their susceptibility to disease and toxic compounds is also influenced. Temperature extremes and changes also affect solubility of oxygen and other gases, decomposition rates of organic materials, and the community structure and stability of aquatic ecosystems.

Dissolved Oxygen

Since waters of the Colorado River system differ dramatically in the types of fisheries they support, seasonal temperature maxima, and major uses, it would be beyond the scope of this report to review ambient dissolved oxygen levels in terms of EPA water quality criteria. Anaerobic conditions have been reported in the Green River (USGS data through STORET), and minimum values below the 4.0 mg/l (3.34×10^{-5} lbs/gal) recommended minimum have been recorded at two of the White River stations near the leased tracts (USGS data through water data storage and retrieval system [WATSTORE]). Therefore, it is obvious that stress conditions for a balanced fishery presently exist at times in the lower reaches of both streams. Further depression of oxygen levels could be induced by oil shale developmental activities and related industrial and urban development, thereby further jeopardizing the aquatic biota in these areas.

Any introduction of oxidizable materials, whether organic or inorganic, creates an additional oxygen demand through increased biological or chemical activity, or both. The primary potential sources of such materials would undoubtedly be municipal wastewater discharges, but industrial discharges and diffuse sources including groundwater seepage also constitute potential threats. Increased oxygen consumption through respiration and decomposition of aquatic biota may follow a general enrichment of localized stream reaches resulting from increased nutrient impact.

Sediments

Erosion, transport, and deposition of particulate matter are natural geologic sedimentation processes that have been in continuous operation for millions of years. Much of the oil shale area is highly susceptible to both wind- and water-induced natural sedimentation processes, owing to the semiarid climatic condition and the rugged topography characterizing much of the area. The rather scant vegetation affords little protection against solids loss in an area that receives much of its precipitation as snowfall and torrential thunderstorms and is frequently exposed to high velocity, turbulent winds.

Development of an oil shale industry and associated activities will exacerbate sedimentation problems by disturbing large expanses of the landscape and thereby increasing the susceptibility of the area to erosion. Three basic processes are known to be the most significant in affecting erosion: (1) the scouring and transport of sediment by intermittent and ephemeral streams, (2) slope erosion (sheet erosion, channel erosion, and gullying of slopes), and (3) downslope mass movement of consolidated materials (52). However, the potential contribution of each process to the total sediment load of perennial streams in the area has not been quantified. These problems will have to be solved, at least in part, before sedimentation sources can be identified and the relative contribution of each to the stream sediment loads determined.

The composition and concentration of suspended sediments in surface waters are important because of their effects on light penetration, temperature, solubility products, and aquatic life. Sediments in industrial waters also erode power turbines and pumping equipment.

Suspended sediment levels have been measured by the USGS at several sites throughout the Colorado River Basin since the early 1930's. Suspended sediment data for the 1964-65 and 1968-69 water years were examined for three stations on the Colorado River and on the Green River. Based on these data, maximum daily values exceeded the least restrictive NAS criteria for the protection of aquatic life (400 mg/l or 3.34×10^{-3} lbs/gal) and criteria for many industrial uses (1000 mg/l or 8.34×10^{-3} lbs/gal) during nearly every month (33).

A 1-million-bbl/day industry is estimated to affect an aggregate area of approximately 32,376 ha (80,000 acres) over a 30-year period, of which 20,235 ha (50,000 acres) would be required for actual production (disposal, etc.), while the remainder would be required for utility corridors, roads, and urban expansion (12). Accelerated sedimentation would necessarily result from such industrial disturbances to the landscape as removal and deposition of overburden from open pit mining, the construction of roads and pipelines, and the disposal of spent shales in high canyons, etc. The questions that emerge, however, are: To what degree will erosion and sedimentation be increased? What material will be most susceptible to movement? And what will be the impact on waterways? At present, these questions cannot be answered given the current state of knowledge of the sedimentation potential and processes in the area.

SOLID WASTE IMPACTS

Inventory of Solid Wastes

One of the major environmental problems to be solved before development of a commercial oil shale industry is that of providing environmentally safe handling and disposal procedures for the vast amounts of solid waste that would be produced. Wastes would include raw mined oil shale, spent oil shale, overburden in the case of stripping, raw and spent shale fines from dust control devices and other process wastes such as spent catalysts, water treatment sludges, oil sludges and shale coke. Disposal would require dealing with handling, stabilization, and revegetation operations. The potential environmental impact on air and water quality that may be caused by fugitive dusts and leachates from these solid wastes must be addressed. Further, locating suitable disposal sites for the large quantity of solid waste may be difficult in some areas.

A feel for the magnitude of the solid waste handling and disposal problem can be obtained from Table 3-23, which provides an estimate of spent shale quantities and size of disposal areas for several levels of shale oil production. As shown in the table, a commercial oil shale industry producing 159,000 m^3/day (5,615,033 ft^3/day) of shale oil (1 million bbl/day) would process 490 to 540 million tonnes (540 to 600 million tons) of raw oil shale each year, requiring disposal of 250 to 300 million m^3 (9 to 10 billion ft^3) of compacted spent shale each year. If continued at this level for 30 years, the spent shale would cover an area of 170 to 190 km^2 (65-75 mi^2) to a depth of 45.7 m (150 ft). True or modified *in situ* retorting could substantially reduce the quantity of spent shale for surface disposal but would increase the total quantity of spent shale (surface and underground) produced for a given level of oil production since the recovery rate is lower, and leaner shales would be included in the retorting. The huge quantity of spent shale produced could create a serious potential for air pollution from fugitive dusts as well as for surface and groundwater pollution from spent shale leachates unless appropriate control technology were developed and applied.

Also, the huge quantity of raw shale that must be mined (Table 3-23) would create a risk of fugitive dust from the mining, crushing, and transport operations (Reference, "Atmospheric Impacts") as well as a potential risk of surface water and groundwater impacts from raw shale storage piles and disposal of collected fugitive dusts. Other process solid wastes such as spent catalysts from hydrotreating, sulfur recovery and arsenic removal, water treatment sludges, oil sludges, and shale coke are produced in retorting and upgrading operations. These wastes, though far smaller in quantity, may contain toxic substances that could affect surface water and groundwater quality. Estimates of quantities of these wastes have been made by some developers.

Overburden removal, storage, disposal, and revegetation operations would reach large dimensions only for a surface mining operation. The quantity of overburden handled would vary greatly, depending on location. However, a feel for the magnitude of the effort can be obtained from the DDP submitted for Federal lease Tract C-a (53). (This DDP was later revised to provide for modified *in situ* development rather than open pit mining.) The mine production schedule in the original DDP estimated that production of sub ore, overburden, and waste would be approximately equal to the quantity of ore to be mined and returned (53). Environmental impacts associated with such overburden removal and restoration include impacts on the land surface, resulting impacts on vegetation and wildlife, air pollution from fugitive dusts, disruption of the water table, and possible impacts on surface and groundwater quality as a result of leachates from overburden storage and disposal areas.

TABLE 3-23. ESTIMATED SPENT SHALE QUANTITIES AND DISPOSAL AREAS REQUIRED

Item	Production level				
	50,000 bbl/day 7,949 m^3/day	50,000 bbl/day 7,949 m^3day[a]	100,000 bbl/day 15,898 m^3/day	250,000 bbl/day 39,745 m^3/day	1,000,000 bbl/day 158,980 m^3/day
Raw shale processed:[b]					
10^6 tons/year	26.9 - 29.9	26.9 - 29.9	53.8 - 59.8	134.5 - 149.5	538-598
10^6 tonnes/year	24.4 - 27.2	24.4 - 27.2	48.9 - 54.4	122.3 - 135.9	489-544
Compacted spent shale:					
10^9 ft^3/year[c]	0.45 - 0.52	0.45 - 0.52	0.90 - 1.04	2.25 - 2.60	9.00 - 10.4
$10^6 m^3$/year	12.7 - 14.7	12.7 - 14.7	25.5 - 29.4	63.7 - 73.6	255-294
10^6tonnes/year[d]	20.4 - 23.6	20.4 - 23.6	40.8 - 47.2	102-118	408-472
Required annual disposal area:[e]					
Acres	69.8 - 79.6	27.9 - 31.8	138-159	344-398	1378-1592
Hectares	28.2 - 32.2	11.3 - 12.9	55.8 - 64.3	139-161	558-644
Disposal area required for 30 years:[e]					
mi^2	3.27 - 3.73	1.31 - 1.49	6.47 - 7.45	16.1 - 18.7	64.6 - 74.6
km^2	8.47 - 9.66	3.39 - 3.86	16.7 - 19.3	41.7 - 48.4	167-193

a Assumes 60 percent disposal in underground mine workings.
b Source: Reference 53, Section 1. Based on 103 l/tonne (30 gal/ton) shale, yield 86 to 95 percent by volume.
c Source: Reference 53, Section 1. Based on 1,441 to 1,602 kg/m^3 (90 to 100 lb/ft^3).
d Assumes 1,602 kg/m^3 (100 lb/ft^3).
e Assumes disposal pile 45.7 m (150 ft) deep.

Raw Shale Handling and Disposal

A commercial oil shale operation must mine, temporarily store, or dispose of huge quantities of raw mined oil shale. A modified *in situ* operation would bring substantially less mined shale to the surface but would still produce large volumes. As indicated in Table 3-23, a surface retorting oil shale industry producing 15,900 m^3/day (100,000 bbl/day) would mine approximately 49 to 54 million tonnes (54 to 60 million tons) of oil shale per year. The mining, crushing, transporting, transfer and temporary storage of this raw shale would impact both air and water quality.

Temporary or permanent surface storage of raw mined oil shale presents an unknown potential for surface water and groundwater pollution. The greatest concern is that precipitation and possibly water sprays applied to control dust may produce surface runoff or leachates with trace elements and organic compounds that could affect surface water or groundwater quality. The potential impact from surface storage of raw mined oil shale must be addressed before a commercial oil shale industry is developed. One position states that raw shale fines disposed of on process shale piles or surface storage of raw mined oil shale will present no more risk of environmental impact than shale eroding along natural outcrops. This opinion needs to be evaluated by field tests. Leachates of raw oil shale are discussed in more depth later in this section under Leaching of Solid Wastes.

As discussed earlier in this section, fugitive dusts from the substantial quantities of raw shale dust will be produced by mining, crushing, and transfer operations may be expected to affect air quality unless carefully controlled. Raw shale fines collected during dust control operations must be carefully disposed of to prevent erosion by wind and water and to assure that they do not generate leachates that affect surface water or groundwater quality. Disposal of these raw shale fines along with retorted shale waste may be desirable if proper precautions are taken to prevent fine particles from contaminating air or water resources and if leachates are controlled to prevent impacts on surface water and groundwater quality. Underground disposal in conventional mines or modified *in situ* retorts would likewise present some risk of affecting groundwater and perhaps surface water quality.

Spent Shale Handling and Disposal

Spent oil shale weighs about 80 to 85 percent the weight of raw mined oil shale. Even with maximum compaction, it occupies a volume approximately 12 percent greater than the volume of the original in-place shale (52). As discussed under Inventory of Solid Wastes, spent shale handling and disposal presents one of the major environmental problems to be solved before proceeding with commercial oil shale development. As shown in Table 3-23, a commercial oil shale industry producing 159,000 m^3/day (5,615,033 ft^3/day) shale oil by surface retorting would produce 250 to 300 million m^3 (9 to 10 billion ft^3) of compacted spent shale each year. *In situ* or modified *in situ* retorting would leave the spent shale underground, but the volume of spent shale would likely be even greater, and it would be of a different chemical nature. The environmentally safe handling and permanent disposal of such a huge quantity of solid waste poses a challenge for both industry and government.

Surface retorting processes and the chemical nature of the spent shale produced from each are discussed in Section 7. Table 3-24 summarizes the major components of spent shale from the leading retorting processes, and Table 3-25 summarizes the trace elements in selected spent shales. Volatile and semivolatile organic compounds reported in oil shale wastes were previously listed in Table 3-22. Potential environmental impacts and problems which should be considered in surface disposal of spent shale include:

Location of disposal sites large enough to accommodate the large amounts of spent shale and yet permit the disposal site to blend into the natural topography.

The generation of fugitive dust until the disposal site has been revegetated. Table 3-19 included an analysis of dust from the Paraho direct mode process. In a commercial process, spent shale dust is likely to be incorporated into the spent shale disposal pile, requiring careful control to prevent a significant impact on air quality.

Residual heat of freshly retorted shale. Unless cooled properly the temperature of retorted shale could be a serious impediment to revegetation.

Deterioration of surface water and possibly groundwater quality by runoff from the disposal piles. Table 3-26 presents surface runoff water quality for several types of spent shales. Runoff is considered to pose a salinity hazard for irrigation use. In addition, the concentrations of some metals and ions are substantially higher in runoff from spent shale than in runoff from native soils.

Deterioration of groundwater and possibly surface water quality by leachates permeating through the disposal pile. This problem is discussed at greater length in this section under Leaching of Solid Wastes.

Difficulty in revegetating some spent shale piles without soil cover, since some spent shales are highly alkaline and contain few nutrients.

Instability of spent shale piles, resulting from improper pile design, which may produce erosion, soil creep, and possibly land slides. Fine-textured spent shales may be more prone to slippage. Some proposed disposal sites are located in gulches susceptible to flash flooding.

Change in type of vegetative cover. Existing soil and vegetation would be removed and replaced by a different mix of vegetation.

Possible reduced ability of the land to support wildlife or domestic stock, depending on the type of vegetation planted, success in revegetating spent shale, and the presence or absence of significantly greater quantities of bioaccumulative toxic elements and organics concentrated in plants grown on spent shale as compared to plants grown on native soil.

Because of the very large areas required for surface disposal of spent oil shale (Table 3-23), the quality of surface runoff water is of great concern. The following observations can be made from the data in Table 3-26, which presents analyses of runoff water quality for spent oil shale test plots:

At least initially, runoff from spent shale is of lower quality than runoff from native soil.

Storm runoff from spent shale is generally of lower quality than snowmelt runoff. This relationship also applies to native soil test plots. Because snowmelt runoff is usually much greater in quantity, it is very possible that its apparent better quality is due to dilution.

Storm runoff may present a high salinity hazard for irrigation.

Quantity of runoff and sediment eroded was much higher for the fine-textured TOSCO II shale plots than for the course-textured USBM or native soil plots. Union B shale also exhibited higher erosion rates than native soil.

Quantity of snowmelt runoff was greater for the high elevation (Piceance Basin) sites than for the low ones.

Use of underground disposal of spent oil shales in conventional underground oil shale mines could avoid many of the potential environmental impacts of surface disposal. However, since the volume of spent shale exceeds the in-place volume of the original mined shale, not all spent shale can be disposed of underground. Underground disposal could possibly increase the potential for groundwater contamination unless great care is taken to prevent contact with groundwater.

TABLE 3-24. CHARACTERISTICS OF SPENT OIL SHALES FROM THE LEADING RETORTING PROCESSES

Shale characteristic	Retorting process					
	Paraho Indirect[a]	Paraho direct[a]	TOSCO II[b]	Union A[c]	Union B[c]	Union SGR[c]
Component (wt. %)						
SiO_2	23.1	28.0	33.0	35.3	31.5	39.2
CaO	15.3	18.3	15.8	27.2	19.6	27.3
MgO	6.5	6.5	5.31	9	5.7	8.2
Al_2O_3	8.0	6.9	6.80	8.5	6.9	8.9
Fe_2O_3	2.7	2.7	2.52	7.3	2.8	3.8
Na_2O	2.3	2.6	8.68	5.5	2.2	3.7
K_2O	2.4	6.6	3.28	2.8	1.6	2.7
SO_3	0.7[d]	0.2[d]	—	0.1	1.9	1.4
P_2O_5	—	—	—	2.2	0.4	0.5
Mineral CO_2	18.1[d]	13.3[d]	5.71	1.6	22.9	3.1
Organic C	1.84	2.18	4.49	0.5	4.3	0.3
Inorganic C	4.95	4.15	5.71	—	—	—
Texture	silty gravel	silty gravel	silt	graded gravel to silty gravel	silty gravel	silty gravel
pH	10.9	11.1	7.5-9.0	12.5-13.0	8.7	12.5

[a] Source: Reference 55.
[b] Source: Reference 56.
[c] Source: Reference 57.
[d] Paraho data are for SO_4 and CO_3.

TABLE 3-25. MEAN LEVELS OF TRACE ELEMENTS IN PROCESSED OIL SHALE[a,b]

Element	Ash, Mahogany Zone		Retorted shale					
			Paraho					
	Utah	Colorado	Direct mode	Indirect mode	Fischer assay	TOSCO II	Gas combustion	
Be	—	35.0	2.0	0.7	—	—	—	—
Hg	—	0.1	0.07	0.03	0.38	—	0.002	0.04
Cd	—	0.14	—	—	2.1	—	—	0.56
Sb	—	0.39	0.7	0.8	0.3	—	2.7	—
Se	—	0.08	0.3	0.2	0.4	4.9	2.9	—
Mo	—	4.9	12.0	10.0	—	38.0	—	7.0
Co	—	39.0	13.0	16.0	—	—	17.0	8.0
Ni	70	11.0	38.0	14.0	—	38.0	56.0	19.0
Pb	100	10.0	18.0	11.0	—	42.0	80.0	34.0
As	—	7.2	21.0	18.0	4.1	105.0	73.0	58.0
Cr	170	49.0	136.0	66.0	—	—	42.0	244.0
Cu	—	15.0	44.0	26.0	—	62.0	—	—
Zr	33	9.3	43.0	62.0	—	—	106.0	—
B	136	140.0	52.0	18.0	87.0	—	—	—
Zn	35	13.0	16.0	21.0	—	108.0	100.0	—
V	78	29.0	116.0	88.0	—	—	—	—
Mn	420	34.0	600.0	272.0	—	—	—	270.0
F	—	1,700.0	1,000.0	450.0	380.0	—	—	—

[a] Source: Reference 5.
[b] Calculated as ppm of raw shale. Where ash equivalent of raw shale is not known, a value of 0.8 is assumed for calculations in this table.

TABLE 3-26. SURFACE RUNOFF WATER QUALITY FOR SPENT OIL SHALE TEST PLOTS

Test plot[a]	Elevation m	Event	Sediment (Kg/ha)	Runoff (m^3/ha)	pH	EC (μmhos/cm)	Component (ppm) Na	Ca	Mg	K	CO_3	HCO_3	NO_3	SO_4	Cl	SAR
Soil Control	1,700	Storm[b]	52.8	0.78	7.7	1,106	70	75	16	69	0	451	4	115	40	0.8
Soil Control	1,700	Storm[c]	172	5.51	7.9	1,000	13.8	135.3	26.1	23.5	0	241	3.1	374.6	12.4	0.37
Soil Control	1,700	Snowmelt[d]	11.8	10.5	7.3	255	4.9	21.0	5.2	23.4	0	88.5	5.6	25.8	9.8	0.23
Soil Control	2,200	Storm[e]	10.1	0.68	7.6	730	22	67	17	3	0	238	1.0	77	12	0.6
Soil Control	2,200	Snowmelt[f]	16.9	83.3+	7.2	185	5.5	17.1	5.8	5.4	0	91.1	1.2	8.2	4.6	0.30
TOSCO II	1,700	Storm[b]	281	10.1	7.1	1,294	75.5	118.8	52.8	28.2	0	145.8	3	611.5	26.2	0.78
TOSCO II	1,700	Storm[c]	379	13.2	8.2	2,900	122.7	261.9	156.5	129	240	760.6	10.7	824.5	164.3	1.3
TOSCO II	1,700	Snowmelt[d]	137	107+	7.0	635	5.5	105.6	15	10	0	57.2	1.0	298.9	4.0	0.15
TOSCO II	2,200	Storm[e]	136.1	10.2	7.4	2,416	88.2	317.9	126.8	11	0	96.7	0.37	1352	11.7	1.03
TOSCO II	2,200	Snowmelt[f]	29.8	120+	7.1	772	10.4	120.8	24.3	8.4	0	73.1	1.01	354.7	4.0	0.21
USBM	1,700	Storm[b]	63.4	0.55	7.6	1,563	95	122.7	29.3	65.7	0	459.3	4.3	188.7	138	1.97
USBM	1,700	Storm[c]	73.3	0.92	8.3	2,300	103.5	184.4	48.6	164.2	0	1134.8	2.5	76.8	159.6	1.75
USBM	1,700	Snowmelt[d]	10.2	28.4+	7.3	299	5.2	22.5	11.7	22.5	0	109.8	1.4	49.8	22.2	0.21
USBM	2,200	Storm[e]	7.1	1.04	7.7	1,676	96.4	139.3	59.8	17K4	0	215.7	3.2	588	30	1.93
USBM	2,200	Snowmelt[f]	20.3	117+	7.1	457	14.3	28.0	19.3	13.2	0	111.7	1.51	93.8	4.6	0.49
Paraho	1,700	Snowmelt[g]	—	16	7.3	280	14	12	21	7	0	99	4	64	17	0.6
Union SGR	1,770	h	—	—	7.8	460	—	—	—	—	—	—	—	—	—	0.38
Union B	1,770	Snowmelt[i]	439[p]	903.2	7.6	767	3.5	135	12.2	4.3	0	56.5	< .01	311	8.7	.07
Union B	1,770	Snowmelt[j]	192[p]	760.1	6.6	227	3.15	23.4	4.1	5.2	0	63.81	.23	36.7	5	.15

[a] 25 percent slopes, except Paraho, which has 2 percent slope. Averaged values for several plots.
[b] Reference 59, Appendix Tables 47, 48; 19.05 mm precipitation in 30 minutes, 8-14-74.
[c] Reference 59, Appendix Tables 51 and 52; 10.6 mm precipitation in 30 minutes, 7-16-75.
[d] Reference 59, Appendix Tables 49, 50, 53, 54; averaged values, 1975 and 1976.
[e] Reference 59, Appendix Tables 86, 87; 12.7 mm precipitation, 8-14-74.
[f] Reference 59, Appendix Tables 88-95; averaged values, 1975-1976.
[g] 1979 Data, personal communication with Ms. Kathleen Kilkelly, Colorado State University.
[h] Reference 57, average values of snowmelt and storm runoff.
[i] Reference 60, Appendix Table 7, 3-18-76.
[j] Reference 60, Appendix Table 10, 4-5-78.

TABLE 3-26. (continued)

Test plot[a]	Elevation m	Event	Sediment (Kg/ha)	Runoff (m^3/ha)	pH	EC (μmhos/cm)	Component (ppm) Na	Ca	Mg	K	CO_3	HCO_3	NO_3	SO_4	Cl	SAR
Union B	1,770	Storm[k]	253[p]	11.3	7.1	1,280	84.4	134.0	101.6	33.9	0	168	.59	881	19.3	1.35
Union B	1,770	Snowmelt[l]	319[q]	710.6	6.9	1,493	23.2	130.1	42.9	7.1	0	65.5	3.65	843	10	.40
Union B	1,770	Snowmelt[m]	533[q]	599.7	6.9	323	2.87	42.93	8.1	6.4	0	89	1.6	82.3	7	.11
Union B	1,770	Storm[n]	935[q]	35.8	7.1	735	9.5	142	26.5	10.3	0	142	.93	349	11.3	.19
Soil Control	1,770	Snowmelt[l]	27[p]	—	7.9	310	8.9	27.4	8.7	15.3	0	134	< .01	30.7	12.5	.37
Soil Control	1,770	Snowmelt[l]	37[p]	225.2	6.5	110	1.88	8.50	3.15	6.23	0	49.37	.80	2.5	6.5	.14
Soil Control	1,770	Snowmelt[l]	175[q]	459.2	7.4	274	4.8	19.7	7.9	19.1	0	113.1	< .01	17.5	11.3	.23
Soil Control	1,770	Snowmelt[m]	175[q]	393.6	6.9	189	1.45	21.7	2.93	14.5	0	95.1	.65	2.3	10	.07
Soil Control	1,770	Storm[n]	233[q]	11.5	7.3	630	17.4	25.7	12.7	58	0	331	.41	43.7	24.3	.71
East Fork of Parachute Creek		Stream[r]	—	—	8.2	1,400	53	56	—	—	1.8	329	—	90	9.3	—
Union SGR	2,300	Snowmelt[s]	29	164.5	7.8	290	10.5	15	17.6	3.9	0	77.5	4.2	52.5	12.5	.41
Union SGR	2,300	Snowmelt[s]	35	164.5	6.8	530	15.6	38.7	47.3	13.6	0	96.1	13.1	242	10	.44
Union SGR	2,300	Snowmelt[s]	10	119.8	8.0	230	6.4	19.3	15	19	3	73.4	.78	69.2	18.2	0.30
Union SGR	2,300	Storm[s]	33	4.2	7.2	260	.21	1.79	.87	3.3	0	109	3.2	25.6	7.5	.18
Union SGR	2,300	Storm[s]	24	5.4	7.0	215	4.8	16.4	6.21	6.0	0	98.4	1.3	10.9	5.0	.87
Soil Control	2,300	Snowmelt[s]	—	259.1	7.2	106	4.4	13.3	1.4	1.2	0	44.8	2.9	8.7	2.3	.26
Soil Control	2,300	Snowmelt[s]	56	208.5	6.1	134	9.4	12.9	3.2	11.2	0	66.4	.99	10	11.2	.62
Soil Control	2,300	Snowmelt[s]	50	174.8	7.8	230	16.4	22.2	4.3	5.2	4.8	116.4	1.1	17.8	3.2	.76
Soil Control	2,300	Storm[s]	127	20.2	7.1	148	0.2	1.16	0	3.5	0	56.5	1.9	16.1	7.5	.26
Soil Control	2,300	Storm[s]	226	40.1	7.0	215	17.7	14.4	3.4	8.4	0	89.2	.80	7.1	4.9	1.06

[k] Reference 60, Appendix Table 9, 8-30-77.
[l] Reference 60, Appendix Table 26, 3-18-76, 50% slope
[m] Reference 60, Appendix Table 28, 4-5-78, 50% slope.
[n] Reference 60, Appendix Table 27, 8-30-77, 50% slope.
[p] Reference 60, Table 8.
[q] Reference 60, Table 15.
[r] Average of data taken during Union's baseline sampling, 9-24-74 to 9-13-77, Personal communication from Allen C. Randle, Union Oil Co.
[s] Reference 61, Table 15.

Underground disposal may also affect future recovery of the remaining oil shale resource. Underground disposal of at least part of the produced spent shale has been proposed by some developers, but more study on possible environmental impacts needs to be done.

In situ or modified *in situ* retorting of oil shale leaves all or most of the spent shale underground, avoiding some problems of surface disposal. However, the underground retorts invariably intersect aquifers or zones of groundwater movement, which creates a possibility for serious groundwater impact. The retorting temperatures of these retorts are reportedly much higher (approximately 1,000 °C or 1,832 °F) than surface retorts. These higher temperatures permit recrystallization of the minerals present, significantly altering their chemical nature. Research to date has been insufficient to establish whether this recrystallization reduces the potential for groundwater pollution. There is some concern that high retorting temperatures may increase the risk of producing carcinogenic materials. Because of the great technical difficulty in treating a groundwater problem, should one develop from true or modified *in situ* retorting, this aspect of shale handling deserves thorough investigation. It has been proposed by some that surface-retorted shale could be injected as a slurry into burned-out modified *in situ* retorts, where it would undergo a cementing action to block groundwater flow through the retorts (61,62). This technology is yet to be proven as applicable for modified *in situ* retorts, and the injection of surface-retorted shale may itself pose a risk of groundwater pollution.

Other Solid Process Wastes

In addition to the spent shale, oil sludges, shale coke, and spent catalysts are process solid wastes that also contain numerous pollutants that must be controlled to protect the environment. The oil shale processing techniques used in a commercial oil shale industry would determine the quantities and chemical-physical characteristics of the spent materials to be disposed of.

On-site upgrading of shale oil crude planned for the first generation of commercial operations consists of: (1) filtration for solids removal, (2) distillation and coking, and/or (3) catalytic hydrogenation of whole shale oil or its fractions. Filtration of shale oil generally removes insoluble inorganic materials and the trace element components. These heavy metals contained in the sludge extracted from the shale crude should be contained so as to preclude their transport into surface and groundwater streams.

In the distillation of shale oil, most minor elements tend to concentrate in the higher boiling fractions and in shale coke. In a commercial operation, elements such as Ni, V, and Fe would tend to concentrate along with the shale fines in the shale coke. The shale coke could be disposed of with the other solid wastes (i.e., with the spent shale).

The hydrotreating of shale oil for sulfur and nitrogen removal is typically performed over nickel or cobalt-molybdate catalyst supported on alumina. The relatively high arsenic levels in shale oils have necessitated treatment steps for arsenic removal to maintain bulk catalytic activity during hydrotreating operations. The steps of treatment generally employ a selective absorbent for arsenic and other trace elements, or a portion of the catalyst bed itself acts as the removal media. The contaminated media or catalyst bed should be periodically removed for ultimate solid waste disposal, or it will be reprocessed for material resource conservation and recovery.

Considering the nickel or cobalt-molybdate, a value of 7 percent by weight of arsenic in the catalyst would be the approximate cutoff point for replacement of the catalyst. At greater than 7 percent by weight, arsenic begins to appear in the hydrotreated product. The spent catalyst would also contain about 10 percent carbon, 8 percent sulfur, and small quantities of other shale-derived elements (Sb, Se,

and transition metals). The chemical forms of arsenic in the spent catalyst are not known, although As_2S_3 or elemental arsenic are likely candidates.

Spent catalysts would generally be stored with other solid wastes in a commercial oil shale operation until sufficient quantities of such materials could justify shipping to a processor. In recent years, prices for metals such as Ni, Co, and Mo have increased to the point where reclamation firms can offer attractive terms to refiners for spent catalysts. However, contaminants such as arsenic in spent catalysts from shale operations may present technical, economic, or waste disposal problems for reclaimers. Storage or direct disposal with other wastes may be the likely fate of these materials, at least during the early stages of oil shale commercialization. The quantities requiring disposal are very small relative to the quantities of retorted shale. An option for disposal of the catalyst materials may be to place them in suitable nondeteriorating containers for landfill disposal, as is a common practice with spent petroleum catalysts. The alternative of mixing spent catalysts with retorted shale as a disposal option should be fully researched. At this time, there is little information to indicate the chemical stability or potential for mobility of catalyst metals (Ni, Co, Mo) and trace element contaminants (As, Se, Hg) disposed of in either concentrated or dispersed form with retorted shale. (An example for As: at 14 percent total arsenic in guard catalyst, the *water soluble* As is 0.003 percent - before "dilution" by mixing with spent shale in 1:33,000 ratio. Personal Correspondence, ARCO Coal Company, August 29, 1979.)

Leaching of Solid Wastes—Edward Bates

As discussed earlier, a surface-retorting oil shale operation will produce spent shale waste of greater volume than the original in-place oil shale. Even a modified *in situ* operation will bring to the surface solid waste equal to approximately 25 percent of the retort volume. In the interest of maximizing resource recovery and providing economic advantages as well, it is expected that raw shale brought to the surface in modified *in situ* operations will be surface retorted. In addition, some developers have also proposed disposing of other solid wastes within the spent shale disposal area. Some or all of these wastes will be disposed of on the ground surface in the form of disposal piles or various forms of valley fills. These wastes will then be subject to leaching by water from several sources, including normal precipitation, water applied to cool the spent shale, water applied for dust control, water needed to achieve compaction of the spent shale pile, water applied to leach the spent shale before revegetation, and irrigation water needed to establish vegetative cover. In addition, spent shale piles have appealed to some as possible disposal sites for wastewater not recycled in the process. The condition of large quantities of solid waste exposed to water from varied sources may create a risk of generating leachate that could affect surface and groundwater quality.

Many factors interact in determining how much leachate will be produced from a given disposal site. Factors which would tend to increase the quantity of leachate include:

Spent shale must be cooled before placement in the disposal site—Otherwise, elevated temperatures will persist in the disposal pile for several months, inhibiting revegetation (63);

Spent shale may require leaching to lower its pH and move soluble salts to a sufficient depth to prevent resalination of the surface, or revegetation may not be successful (64). Indirectly retorted spent shale may require less or no leaching;

Spent shale may require irrigation to initially establish a satisfactory vegetative growth; the use of a soil or other cover could substantially reduce or eliminate the need for irrigation;

To maximize compaction and lower permeability, some water must be added to the spent shale;

Even after placing, compacting, and revegetating the shale, rainfall and snowmelt will continue to contribute water that may leach through the spent shale;

EPA studies show that it may not be possible to make all spent shale impermeable (63,65).

On the other hand factors which would tend to decrease the quantity of leachate include:

The high evapotranspiration rates and low precipitation rates at some locations will reduce infiltration;

Surface runoff will decrease the amount of water available for infiltration;

The moisture retention capacity of the spent oil shale will retain significant amounts of infiltration water.

A discussion of surface water balance relationships including precipitation, water holding capacity of soils, and evapotranspiration in the Piceance Basin is presented by Wymore (66). Water requirements for stabilization of spent oil shale are discussed in reports by Harbert, Berg, and McWhorter (63) and Wymore (67).

The extent of environmental impact to surface and groundwater from spent shale leachates depends on the chemical nature and quantity of leachate produced and the extent to which the leachate is contained and treated before its contact with the water supply. Extensive studies on the nature of leachate produced from spent shales of each retorting process are not available. Studies to date indicate that leachate quality will vary with each specific retorting process and may vary for any one process as specific retorting conditions vary. Table 3-27 provides a summary of leachate analyses for several types of spent shale, including simulated *in situ* retorts. Table 3-27 should not be used to compare leachates from one spent shale type with those of another, since various methods were used to obtain the data presented. This table does show that in general, spent shale leachate may be expected to contain organic carbon and such cations, anions, and trace metals as B, Ba, Be, Ca, Cl, F, Fe, HCO_3, K, Li, Mn, Mo, Mg, Na, Ni, Pb, Sn, SO_4, Sr, V, and Zn. The specific nature of potential organic compounds in spent shale leachate is not well-defined at present. It must be emphasized that each particular spent shale will likely produce a unique leachate that may include some or all of the above pollutants, plus others specific to itself. The important point is that surface disposal of spent shale may produce leachates that affect surface and groundwater quality unless the leachate is collected and treated. Spent shale in true and modified *in situ* retorts may likewise affect groundwater quality and surface water quality as well through recharge to surface streams.

Table 3-28 presents data on spent shale leachates in an alternate form. Rather than describing the water quality of leachate, this table describes the maximum quantity of major leachate constituents that may result from the leaching of a given quantity of spent oil shale. For example, from Table 3-23, a surface oil shale facility producing 15,900 m^3 (100,000 bbl) of oil per day would have to dispose of approximately 45 million tonnes (49.5 million tons) of spent shale each year. If retorted by the TOSCO II process, this spent shale has a potential for leaching approximately 51 tonnes (56 tons) of Ca. The data in Table 3-28 assume that adequate water is available and that permeability does not seriously restrict leaching. Since the oil shale areas of Colorado, Utah, and Wyoming are quite dry, and since spent shale should be disposed of in a manner that minimizes permeability, the data of Table 3-28 represent maximum potentials rather than actual quantities that would likely be leached. However, the table clearly indicates the potential for environmental impact if spent shale disposal is not properly handled.

The question of permeability of spent shale deserves special attention. Great variation in permeability values has been reported for various spent shales compacted under different conditions. Table 3-29 indicates the variation in permeabil-

TABLE 3-27. ANALYSIS OF SPENT SHALE LEACHATES[a]

Constituent	Soil Control[b]	Paraho (ppm) A[b]	Paraho (ppm) B[c]	TOSCO II (ppm) A[d]	TOSCO II (ppm) B[e]	USBM[f] (ppm)	Union A[f] (ppm)	Union SGR[g] (ppm)	Surface retorts[h] (mg/100g)	Simulated *in situ* retorts[h] (mg/100g)
pH	7.7	9.57	8.4	8-9	—	7.78	9.94	9.7	7.78-11.2	7-12.7
EC μmhos/cm	5,690.0	21,110.0	14,600	10,000	—		—	7,170	—	—
OC	64.8	127.0	—	402	—	—	—	—	—	1.0-38
IC	40.2	20.5	—	—	—	—	—	—	—	—
TDS	—	—	—	42,000	—	970-1,091	10,011	—	970-10,011	0-2,800—
Ag	0.001	0.001	—	—	—	—	—	—	—	—
Al	0.05	0.05	0.25	—	—		—		—	0.095-2.8
As	0.02	—	< 0.001	—	0.05	—	—	0.41	0.1	—
B	1.14	1.64	0.73	—	4.6	—	—	—	2-12	0.075-0.14
Ba	0.07	0.12	0.15	—	—	—	—	—	4	—
Be	< 0.005	0.01	< 0.025	—	—	—	—	—	—	—
Ca	166.4	421.4	200.0	—	—	42	327	11.2	42-114	3.6-210
Cd	—	—	< 0.025	—	—	—	—	—	—	—
Cl	428.0	526.0	111	—	—	13	33	24	5-33	5.5
$CO_3^=$	—	—	7.8	—	—	—	—	695	21	30-215
Cr	0.01	0.01	< 0.025	—	—	—	—	—	—	0.002-1.8
Cu	0.02	0.05	< 0.025	16.6	—	—	—	—	—	—
F	1.31	11.9	13.0	—	—	—	—	—	3.4-60	1.2-4.2
Fe	< 0.01	0.03	< 0.05	—	16.0	—	—	—	—	0.0004-0.042
HCO_3^-	—	—	516	—	—	38	28	1,716	20-38	22-40
Hg	—	—	< 0.001	77.2	—	—	—	—	—	—
K	0.02	834.0	580	—	—	72	625	358	10-625	0.76-18
Li	—	—	7.4	—	—	—	—	—	—	.020-0.42
Mn	0.05	0.05	< 0.05	—	—	—	—	—	—	—
Mo	0.44	3.92	4.3	—	3.0	—	—	—	7-8	trace
Mg	190.3	7.74	1,190.0	—	—	3.5	91	7.5	3.5-91	0.002-8.0
Na	712.0	5,591.0	2,500.0	10,700	—	225.0	225	1,110	2,100	8.8-235

(continued)

TABLE 3-27. (continued)

Constituent	Soil Control[b]	Paraho (ppm) A[b]	Paraho (ppm) B[c]	TOSCO II (ppm) A[d]	TOSCO II (ppm) B[e]	USBM[f] (ppm)	Union A[f] (ppm)	Union SGR[g] (ppm)	Surface retorts[h] (mg/100g)	Simulated *in situ* retorts[h] (mg/100g)
Ni	0.1	0.01	< 0.025	—	—	—	—	—	—	—
NO_3^-	31.6	0.09	96.0	—	—	—	—	12.4	5.1-5.6	0.2-2.6
Cll	—	—	—	—	—	—	—	—	—	22-40
Pb	< 0.005	0.01	0.31	—	—	—	—	—	—	0.014-0.017
Se	< 0.02	0.03	< 0.001	—	—	—	—		0.005-0.006	—
Si	—	—	5.6	—	—	—	—	—	—	25-88
SiO_2	9.02	8.31	—	—	—	—	—	—	—	—
Sn	—	—	0.83	—	—	—	—	—	—	—
$SO_4^=$	1,954.0	12,354.0	9,990.0	—	—	600	6,230	1,012	600-6,210	50-130
Sr	2.7	10.4	5.4	—	—	—	—	—	—	0.004-8.7
V	< 0.10	0.24	—	—	—	—	—	—	—	—
Zn	0.04	0.15	0.05	—	—	—	—	—	—	0.001-0.025

[a] Note: This table is not to be used for comparing leachates from different spent shales, since the methods of leaching and analysis varied.
[b] Reference 64, Tables 129, 131, and 133 (averaged values). Anvil Points, Colorado. Leached with Colorado River Water.
[c] Personal communication with Dr. David McWhorter, Colorado State University, Leached with snowmelt water, seven samples.
[d] Reference 69, Table 5-13 (averaged values).
[e] Reference 70, Page 1025, leached with distilled water, 12 days in pyrex.
[f] References 71 and 72.
[g] Reference 61, averaged values, Table 32-36.
[h] Reference 73. Summary of data from several sources and retorting processes reported as mg of constituent per 100 grams of spent shale leached.

TABLE 3-28. ESTIMATED QUANTITIES OF SOME MAJOR CONSTITUENTS LEACHABLE FROM OIL SHALE (ASSUMING PERMEABILITY AND WATER AVAILABILITY ARE NOT LIMITING FACTORS)

Characteristic	Raw shale[a]	TOSCO[a]	USBM[a]	Union A[a]	Simulated *in situ*[b]
Constituent (kg leached/tonne shale):					
Ca^{++}	0.1	1.14	0.42	3.27	0.04-2.1
Cl^{-}	0.02	0.08	0.42	0.33	0.06
HCO_3^{-}	0.75	0.20	0.38	0.28	0.22-0.40
K^{+}	0.24	0.32	0.72	6.25	0.000-0.18
Mg^{++}	0.01	0.27	0.04	0.91	0.00002-0.08
Na	0.48	1.65	2.25	21	0.09-2.35
$SO_4^{=}$	0.79	7.3	6.00	62	0.50-1.3
TDS (103°C)	2.77	12.6	10.9	100	—
pH	8.15	8.40	7.78	9.94	7.76-12.7
Conductance (μmhos at 25°C)	310	1750	1495	11,050	—

[a] References 71 and 72.
[b] Reference 73.

TABLE 3-29. PERMEABILITY OF PARAHO SPENT OIL SHALE FOR VARIOUS COMPACTIVE EFFORTS AND LOADINGS[a]

Compactive effort g-cm/cm³ (ft lb/ft³)	Dry Density g/cm³	lb/ft³	Gravel size after compaction (% passing No.4 screen)	Permeability, cm/yr (ft/yr) under loadings of 3,515 g/cm (50 psi)		7,030 gcm (100 psi)		14,061 g/cm (200 psi)		Remarks
Direct mode:										
3,027 (6,200)	1.41	(88.0)	43	457	(15)	168	(5.5)	52	(1.7)	
6,042 (12,375)	1.48	(92.5)	42	213	(7)	43	(1.4)	24	(0.8)	
27,464 (56,250)	1.58	(98.7)	33	34	(1.1)	18	(0.6)	3	(0.1)	
6,042 (12,375)	1.48	(92.5)	—	256	(8.4)	219	(7.2)	198	(6.5)	Cured 28 days at 52°C
3,027 (6,200)	1.41	(88.0)	43	1,280-67	(42-2.2)	—	—	—	—	Effluent recirculated.
6,042 (12,375)	1.48	(92.5)	42	1,036-110	(34-3.6)	—	—	—	—	Effluent recirculated.
Indirect mode:										
3,027 (6,200)	1.50	(93.9)	47	2,164	(71)	1524	(50)	914	(30)	
6,042 (12,375)	1.58	(98.9)	42	116	(3.8)	113	(3.7)	88	(2.9)	
27,464 (56,250)	1.69	(105.8)	38	61	(2.0)	76	(2.5)	73	(2.4)	

[a] Reference 55, page 127.

ity values for Paraho spent shale compacted by different pressures (54). As expected, greater compaction leads to lower permeability values. However, it would probably be very costly and difficult to achieve near maximum compaction throughout a spent shale disposal operation. Therefore, the medium and higher permeability values would likely apply to most of a spent shale disposal site.

Results of EPA-sponsored field studies indicate that permeability values of compacted, direct-mode Paraho spent shale are quite high. Table 3-30 indicates the variability in reported permeability of several spent oil shales. All that can be stated with certainty at present is that any proposed spent shale disposal providing for compaction to make the shale impervious should first prove that the particular spent shale and compactive effort can indeed make the spent shale impervious. Even though an impervious layer (30 cm/yr or 12 in./yr or less permeability) is installed below a disposal pile, there is still a risk of groundwater pollution if the groundwater flow rate below the pile is too low to provide substantial dilution for any leachate that eventually seeps through the impervious bottom of the disposal pile.

TABLE 3-30. RANGE OF REPORTED PERMEABILITY VALUES OF VARIOUS COMPACTED SPENT OIL SHALES

Type of shale	Permeability value (cm/yr)	Comment
Paraho, direct mode	2.2×10^3 to 4.7×10^3	EPA field study (66)
USBM	1.6×10^1 to 3.2×10^1	Lab-weathered shale (74)
Paraho pilot plant	3.4×10^1 to 6.4×10^4	Lab study, various particle sizings and compactive efforts (75)
Paraho	3×10^2 to 4.6×10^2	
Paraho, direct mode	3×10^1 to 4.6×10^2	Standard tests (76)
TOSCO II	8.8×10^2 to 1.3×10^3	Rainfall permeability (77)
TOSCO II	3.0×10^1	Colony study[a]

[a] Personal communication from M. W. Legatski, ARCO Colony Development Operations, 1979.

The period of time over which pollutants may continue to leach from disposal piles in concentrations and quantities sufficient to present pollution hazards is not known. Research is needed to establish such a relationship between time or quantity of water leached through shale and the resulting change in water quality of the leachate. However, it is possible that leachate of poor water quality could be produced for many years beyond the period of time that any particular oil shale facility would be in operation. Two additional types of solid waste deserve special attention—raw mined oil shale and process-generated wastes, such as spent catalysts, sludges, and shale oil coke. Overburden could be considered another type of solid waste, especially if the oil shale is strip mined; but its environmental impacts and control technologies should be essentially similar to those associated with other types of surface mining.

Raw mined oil shale would have to be temporarily stored in significant quantities on the surface to assure a steady supply of crushed raw shale for a continuous retort operation. In addition, the mining, crushing, and transfer operations themselves will produce some raw shale waste (especially in the form of dust) that will require disposal. No exhaustive studies have been made to determine the nature of leachates from raw shale that may be produced by precipitation or water sprays

applied to control dust. Presently, EPA is in the process of assessing the nature of these leachates, and preliminary results under saturated conditions are presented in Table 3-31. Leaching results from wet/dry cycles are being studied and may be quite different than results from saturated conditions.

In general, the data in Table 3-31 indicate that under saturated conditions leachates from freshly mined raw shale, weathered oil shale (talus) and soil presumably derived from oil shale all produce leachates that are similar. However, soils produced from different original material may be quite different. Also, shale from different hydrogeologic environments, such as the saline zone, may produce substantially different leachate. In general, Table 3-31 shows a significant improvement in leachate quality with passage of as few as three pore volumes of water under saturated conditions. Results under wet/dry cycles may vary significantly from those under saturated conditions and are presently being investigated. It should be noted that at least one study comparing leachates from raw oil shale with those from retorted oil shale reported that some pollutants, such as fluoride, may leach more readily from raw shale than from retorted shale (70).

Process-generated solid wastes such as spent catalysts, lime sludges, coke, and other solids from water and wastewater treatment systems may present a threat to surface and groundwater quality if not handled and disposed of carefully. Some of these wastes may contain highly toxic substances, as discussed in the preceding subsection. Disposal of these wastes by burying them in the spent shale piles may result in increased levels of toxic pollutants in the spent shale leachate and subsequent impacts on surface water and groundwater quality.

HEALTH EFFECTS OF REFINING AND USE OF SHALE OIL AND OIL SHALE

Dr. David Coffin

The development of the synthetic fuels industry poses health hazards which must be understood and solved in order to have hydrocarbon fluid fuel substitutes for petroleum in the near future. This goal appears possible since prior experience with the petroleum industry has demonstrated that potentially hazardous fuels may be refined and used without obvious undue danger to human health. The problems posed by shale oil appear more complex and will probably require extra steps in treatment prior to refining as well as careful attention to hygienic practices.

Human Health Effects

There is little actual experience with the toxicity of the American oil shale industry because of the limited amount of time of its existence and the relatively small number of persons exposed. A survey at the U.S. Bureau of Mines operations was reported by Birmingham (77) with data being completed for the years 1952 (197 workers), 1953 (170 workers), and 1954 (181 workers). A large number of benign skin lesions was observed in the workers, but when they were compared to a matched group according to age and their length of residence in the Colorado Plateau, no apparent increase was found from occupational contact with this particular shale oil technology.

Such an incidence of lesions would be likely from exposure to the intense solar irradiation characteristic of this region. No conclusions can be made from this first tentative epidemiological study because of insufficient time of exposure and the limited number of persons involved.

A more recent study is being conducted by Costello (78) in which cases have been selected from the 1,198 persons who have worked at the Anvil Point operations and from a control sample composed of 320 cases selected from 1,000 coal miners in eastern Utah and western Colorado. Methods used in this survey are described by the author.

TABLE 3-31. LEACHING CHARACTERISTICS UNDER SATURATED CONDITIONS OF RAW SURFACE STORED OIL SHALE—PRELIMINARY RESULTS[a]

		Colony soil[b]		C-b soil[c]		Colony raw shale[d]		Colony weathered[e]	
	UNITS	INITIAL	~3PV	INITIAL	~3PV	INITIAL	~3PV	INITIAL	~3PV
Al	Mg/1	< 0.05	0.07	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
As	"	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
B	"	0.70	0.53	0.65	0.87	0.75	0.43	0.365	0.170
Ba	"	0.40	0.12	0.169	0.038	0.34	0.16	0.495	0.088
Be	"	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Ca	"	960	200	330	6.5	1110	200	500	25
Cl	"	200	1.4	—	—	22	3.0	71	1.5
CO_3	"	0.17	1.04	—	—	0.18	1.2	0.12	0.63
Cr	"	< 0.025	< 0.025	0.069	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Cu	"	0.38	0.075	0.28	< 0.025	0.16	< 0.025	0.31	0.05
EC-μmhos/cm@25°C		9000	2000	3300	750	527	106	537	48
F	Mg/1	10	1.4	—	—	7.2	5.0	5.2	8.7
Fe	"	0.01	0.18	—	—	< 0.03	< 0.03	< 0.03	< 0.07
HCO_3	"	233	192	—	—	304	250	233	189
Hg	"	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
K	"	270	50	22	1.3	19	2.3	57	0.8
Li	"	0.47	0.09	—	—	0.085	0.10	0.012	< 0.004
Mg	"	1450	140	145	2.6	72	18	365	17
Mn	"	0.10	0.38	0.075	< 0.025	0.240	0.820	0.07	0.068
Mo	"	0.84	0.18	0.125	< 0.05	0.07	0.18	0.74	0.11
Na	"	340	6.2	2050	210	100	15	350	33
Ni	"	0.060	0.040	0.075	< 0.05	0.087	< 0.05	0.06	< 0.05
NO_3	"	1800	< 0.2	—	—	25	< 2.5	245	0.8
Pb	"	0.27	0.20	0.31	0.070	0.17	0.095	0.22	0.13
pH	—	7.1	8.0	8.3	8.8	7.8	7.9	8.1	8.3
Se	Mg/1	< 0.01	< 0.01	< 0.0005	< 0.0005	< 0.01	< 0.01	< 0.01	< 0.01
Si	"	7.3	8.0	11.0	11.7	7.61	4.54	14.7	6.78
Sn	"	1.37	0.25	—	—	0.24	0.17	0.67	0.047
SO_4	"	4200	1000	—	—	4250	400	2650	33
TDS	"	19800	1850	—	—	6000	770	4750	220
TOC	"	512	44	—	—	—	—	—	—
Zn	"	0.65	0.02	—	—	0.62	0.06	0.11	0.24

[a] Preliminary Results from EPA Grant R806278, initial leachate and leachate after 3 pore volumes. Personal communication from Dr. David McWhorter, Colorado State University, 10-21-79. Inquiries regarding availability of the final report f r Grant R806278 should be addressed to E. R. Bates, IERL, US EPA, Cincinnati, Ohio, 45268.

[b] Colony soil—Approx. 500 yards north of mine portal.

[c] C-b soil—Cottonwood Gulch SE of plant.

[d] Colony raw shale—Mine stockpile below surface.

[e] Colony weathered—400 yards SW of mine portal—tailus slope material.

TABLE 3-31 (continued)

		Horse draw saline[f]		Union Nat. retorted[g]		C-a composite[h]		C-a, R-5 & Mahogany[i]	
	UNITS	INITIAL	~3PV	INITIAL	~3PV	INITIAL	~3PV	INITIAL	~3PV
Al	Mg/1	1.85	0.80	< 0.05	< 0.05	< 0.05	< 0.05	< 0.70	< 0.30
As	"	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
B	"	29.5	0.95	0.370	0.210	1.45	0.40	0.59	< 0.025
Ba	"	0.17	0.10	0.120	0.037	0.093	0.051	0.11	0.088
Be	"	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Ca	"	520	220	45	13	425	100	1430	900
Cl	"	430	5	—	—	—	—	—	—
CO_3	"	0.10	0.15	—	—	—	—	—	—
Cr	"	0.55	< 0.025	0.400	0.031	< 0.025	< 0.025	< 0.025	< 0.025
Cu	"	0.22	< 0.025	0.160	< 0.025	0.060	< 0.025	0.16	< 0.025
EC-μmhos/cm@25°C		11000	1100	1100	385	6500	750	15000	2750
F	Mg/1	75	25	—	—	—	—	—	—
Fe	"	0.75	0.01	—	—	—	—	—	—
HCO_3	"	243	122	—	—	—	—	—	—
Hg	"	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
K	"	19	2	55	11	34	2.0	280	50
Li	"	2.4	0.11	—	—	—	—	—	—
Mg	"	1050	12.2	103	60	415	48	—	—
Mn	"	2.9	0.23	0.05	< 0.05	0.240	0.062	0.35	< 0.05
Mo	"	0.44	0.09	0.32	0.125	2.20	0.475	0.20	0.225
Na	"	1430	65	44	16	740	33	3600	310
Ni	"	0.48	0.04	< 0.05	< 0.05	0.090	< 0.05	0.085	< 0.05
NO_3	"	< 25	< 6.25	—	—	—	—	—	—
Pb	"	0.57	0.080	0.10	0.105	0.204	0.075	0.150	< 0.05
pH	—	6.8	7.3	8.6	8.3	8.2	8.3	11.4	12.0
Se	Mg/1	< 0.01	< 0.01	< 0.0005	< 0.0005	< 0.005	< 0.005	< 0.005	< 0.005
Si	"	7.5	3.4	11.0	12.0	10.0	10.9	5.94	1.65
Sn	"	1.1	0.38	—	—	—	—	—	—
SO_4	"	5600	425	—	—	—	—	—	—
TDS	"	12600	1300	—	—	—	—	—	—
TOC	"	228	11	—	—	—	—	—	—
Zn	"	5.2	0.39	—	—	—	—	—	—

[f] Horse draw—saline zone.
[g] Union naturally retorted—90 yards SW of mine portal.
[h] C-a composite—Composite of raised bore cuttings from the G-level in the R-5 zone to surface. Includes some overburden that is not shale.
[i] C-a, R-5 & Mahogany—Composite of materials from the R-5 and Mahogany zones.
Note: All data in this table were obtained by leaching columns 106 cm in length under saturated conditions with de-ionized water. All concentration data is in milligrams per liter.

An occupational health survey of the Paraho oil shale works has recently been reported by Rudnick and Voelz (79) who examined 87 persons employed in various categories of the industry. These were grouped as "highest exposed," "less exposed," and "minimally exposed." The authors concluded that no disease problems were shown to be attributable to the oil shale exposure in this study. They do point out, however, that seven lost work time episodes were attributable to accidental physical trauma in a twelve-month period.

In consideration of occupational health surveys of employees of the American oil shale industry, a number of limitations must be kept in mind. Since the effort thus far has been small and frequently intermittent, very few workers at risk for any appreciable time can be found. Futhermore, since miners "tend to work in mines" employees of the oil shale industry frequently have experience in coal, uranium or other mining opportunities in the Rocky Mountain region. Another factor in occupational surveys is the necessity of comparing the oil shale workers to matched controls in some other industry where physical exertion would be similar but with entirely different exposure possibilities. Such design is required because physical workers tend to have health profiles which differ from more sedentary workers or the general population. It would thus appear that occupational data must remain quite tentative until the industry has expanded to provide continuous employment to a larger number of persons.

Considerably more experience with human exposure is available for the Scottish Lothian oil shale industry which existed for a period in the latter half of the past century and for the Estonian shale industry which has been actively pursued for about 40 years. These data have been the subject of recent detailed reviews so will be only briefly mentioned here (80).

In brief, the Scottish industry which existed before and during the early years of this century shows data for skin cancer among workers in the oil industry and more particularly for scrotal cancers among workers in the British cotton spinning industry of the period. These latter, the "mule spinners cancer," have become notorious as examples of occupationally-induced cancer and were occasioned by heavy contaminations with rather highly carcinogenic material and very poor standards of personal cleanliness and occupational hygiene. The incidence of this disease markedly diminished in later years as shale oil was gradually replaced by petroleum products.

The Estonian shale differs strikingly from shale which is expected to be exploited in the United States. Because of its high organic content it is possible to extract energy by direct combustion of the pulverized rock for electric power generation and the like. This mode of combustion accounts for approximately 75 percent of current usage. Another difference is its high content of phenolics which are extracted for commercial purposes during the production of shale oil.

Data from Estonia suggests a small increase in pneumoconiosis in oil shale mine workers presumably from exposure to rock dust and some acute and chronic neurological disturbances among retort workers which they attribute to the exposure to phenols. There appears to be no measurable increase incidence in cancer among males occupationally exposed or in the general population of the region although they report a slight increase of cancers in women in the area (81).

Biological Experimentation

Considerable biological data have been accumulated over a number of years in the United States for the TOSCO II process by Coomes (82,83) who conducted skin bioassays comparing various petroleum products—coke oven tar and whole shale oil and whole shale oil upgraded by hydrotreating. Coomes (84) summarizes these studies and presents new data from the Kettering Laboratory.

Biological testing of oil shale effluents and products has recently intensified, largely due to the U.S. Navy-sponsored retorting by the Paraho technology and

subsequent refining at Sohio which has made materials for testing available. These testing programs consist of a comprehensive effort funded by the American Petroleum Institute (API), specific tests conducted by the U.S. Navy and an Interagency Matrix Approach sponsored by EPA and DOE. Preliminary data from the API-sponsored study were presented at the Ninth Conference on Environmental Toxicology on the 28th, 29th, and 30th of March 1979. Among these studies Slomka *et al.* (85) have reported acute experiments on the skin, conjunctiva, cornea and iris and oral LD_{50} rat studies to various shale oils and retorted shales as well as systemic effect on rabbits and sensitization studies on guinea pigs. As might be expected, toxicity was noted in other tests—the LD_{50} for rats being reported as 8 to 10 g/kg (8.00×10^{-3} to 1.00×10^{-2} lbs/lb) while dermal LD_{50} for rabbits was above 10 ml/kg (1.2×10^{-3} gals/lb). Systemic toxicity, noted after oral and percutaneous administrations, was decreased locomotor activity, pilo erection and ptosis. Shale oils showed moderate reversible irritation to the skin and eye. The liver appeared to be the target organ for systemic and the skin and mucous membranes for percutaneous applications. No sensitization was noted in guinea pigs.

Weaver and Gibson (86) have reported on acute and chronic studies of a crude shale oil and their upgraded counterparts by various routes (oral, dermal, and conjuctival). They also have described inhalation studies on unretorted and retorted shale dust. They describe no significant nonreversible lesions.

Toxicity studies of shale rock and retorted shale dust have been reported by McFarland (87) who conducted inhalation experiments in rats and cynomologous monkeys at concentrations of 10 and 30 mg/m^3 (4.37×10^{-3} and 1.31×10^{-2} grains/ft^3) for five days a week for two years. According to the author, results available from this study indicate no abnormalities attributable to the exposure regimen. Conoway (88) reports mutagenesis and teratogenesis studies by various methods on shale rock, retorted shale and shale oil. All shale oil samples studied were mutagenic by microbial tests, negative by mouse lymphoma tests and negative in rat bone marrow cytogenetics tests. Fetal toxicity was observed at high dose levels of shale oil. Cowan and Jenkins (89) report preliminary studies on the effect of shale derived fuels and their petroleum analogues by inhalation exposure of vaporized material in laboratory animals. The parameters of this study include physiological and biochemical, and behavioral tests and pathological examination. Data suggest an overall increase in tumors (gross evidence only) from petroleum products. No data are yet available for shale oil products.

Barkley *et al.* (90) have studied various oil shale materials for carcinogenicity. These consisted of nonretorted and retorted shale rock dust suspended in whole mineral oil and two crude shale oils—one extracted by heat transfer process and one by the retort combustion process. They also studied, comparatively, shale crude versus upgraded shale crude. Chemical determinations are also reported by these authors. In summary, this report is similar in the two shale crude studies—namely, eight malignancies out of 12 mice and 43 weeks as average time of appearance of papillomas. In their experiments to compare raw shale oil (direct retort product) and the same oil upgraded by hydrotreating, striking differences were noted. They noted 21 malignant and 18 benign tumors for the raw oil compared to three malignant and two benign tumors from the upgraded oil. The average time to the appearance of papillomas was 30 weeks and 49 weeks, respectively. Their experiments with unretorted and retorted shale rock dust were negative (Table 3-32).

These same investigators report chemical analytical data for shale oil from information supplied by the American Petroleum Institute. They identify the following hydrocarbons classified as follows: carcinogens—Benzo(a)pyrene and Benz(a)anthracene; borderline carcinogens—chrysene and nine additional polycyclic aromatic compounds and those which are noncarcinogenic. They conclude that the carcinogenicity of the shale oils tested does not correlate well with the carcinogenic

compounds which were isolated (see Table 3-32). They also report experiments designed to detect embryotoxicity and teratogenicity by oral dosing in rabbits. No dose dependent abnormalities were noted and no differences were observed from comparative dosing with inert carbon.

The program in the federal laboratories consists of an integrated coordinated evaluation of the potential toxicity of shale oil development and use under the EPA/DOE Matrix Approach as well as independent studies. In the Matrix Approach a central materials repository receives specimens from the respective technologies, processes them and distributes aliquots to participating investigators. More than 15 public and private laboratories are now participating in this effort. The plan for this study was addressed at a joint EPA/DOE meeting in March 1979 (91,92). Data from these efforts will be presented at a second conference scheduled for June 1980. The overall rationale and plan which is concentrating on the Paraho above ground retort process and the Sohio refining program as a model is portrayed in Tables 3-33 and 3-34.

Considerable data are now available from the federal program from an interplay of chemical analysis and short term mutagenesis testing. Guerin *et al.* (93) and Epler *et al.* (94,95) have noted that the highest specific activity is contained within the basic fraction of the crude shale oil. Subsequent analyses have shown that one half or more of the total mutagenicity is found in the basic fraction which constitutes only five percent of the mass. Further fractionation demonstrated that this activity can be again concentrated in 10 percent or less of the total basic fraction. This phenomenon probably explains some of the striking difference of shale crudes (and coal fluids) from petroleum crudes where the basic fraction content is insignificant. While the most conclusive results are from coal fluids, preliminary results show that the activity within the basic fraction for shale oil as well is due to its content of polycyclic aromatic amines. Experiments have shown that light hydrotreating easily destroys the specific mutagenic activity of these alkaline constituents of shale oil. Additionally, there appears to be general agreement between the Ames test for mutagenesis and skin bioassay for carcinogenesis in both crude shale oil and hydrotreated oil.

Pelroy *et al.* (96) have compared the mutagenicity of several different "crude" shale oils and various coal fluids by short term testing after fractionation by solvent extraction and by partition chromatography. They report the most activity in the basic fraction or the equivalent methanol fraction. The highest mutagenic activity was noted for coal with a much lower content for crude shale oil and very little activity for crude petroleum. They attribute the mutagenic activity for both coal fluids and shale oil in this fraction to the presence of aromatic amines. The data from biological studies of the American shale oil are currently preliminary and tentative. It is evident from information now available that the so called shale oil "crudes" are more carcinogenic than petroleum crudes but that this difference is ablated by hydrotreating. Mutagenesis studies with the Paraho shale "crude" suggest that there is agreement from the summation of various fractions of the whole oil with skin carcinogenic bioassay both from the presence of mutagenicity/carcinogenicity in the crude shale oil, and from its removal by hydrotreating. For mutagenicity, shale oil ranks above petroleum but far below coal fluids. The intensely mutagenic materials contained in the basic fraction (or equivalent methanol fraction from partition chromatography), presumably polycyclic aromatic amines, are readily altered by hydrotreating. Thus, when the shale retort fluids are hydrotreated, the resulting refinery feed stock has little or no significant mutagenic activity, being essentially similar to crude petroleum in this aspect. While shale oil crude appears much less active than coal fluids, it should be recognized as being potentially carcinogenic and handled accordingly. The differences reported in mutagenicity of various shale retort tars may reflect the organic compounds in the rock, but probably is a function of temperature and other variables during the retort process. There is an indicated need for coordinated chemical and

TABLE 3-32. CARCINOGENIC POTENCY OF RAW AND UPGRADED SHALE OIL[a]

Sample	Strain of mice	Dosage	Number of	Final[b] effective mice	BaP (%)	Number of mice developing tumors		Average time of appearance of papillomas (weeks)
						Malignant	Benign	
Raw shale oil	C3H	50 mg. twice weekly	50	45	<0.00005	21	18	30
Upgraded shale oil	C3H	50 mg. twice weekly	50	39	0.0006	3	2	49
Positive control (0.05 BaP in toluene)	C3H	50 mg. twice weekly	100	92	0.05	75	9	46
Negative control (toluene only)	C3H	50 mg. twice weekly	100	91	0	0	0	

[a] Source: Reference 91.

[b] The final effective number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

TABLE 3-33. REPOSITORY DISTRIBUTION OF PARAHO ABOVE GROUND RETORT MATERIALS

Shale material	Mineral-ogical	Infrared finger print	Chemical fraction-ation	P&H	Organic analysts	Trace element analysts	Particle sizing	Morpho-logical	Ames Assoc.	Droso-philia	Trachael trans-plant	Intra-tracheal	Oral toxicity	Organ culture
Raw shale	X													
Airborne raw shale particles	X	X			X	X	X	X						
Raw shale particles, baghouse		X			X	X	X	X			X	X		X
Retorted particles, baghouse		X			X	X	X	X			X	X		X
Product oil									X	X				
Product water									X					
Process water									X					
Thermo-oxidizer particles														
Leachate, retorted shale						X								
Composite shale oil			X	X									X	
Hydrotreated shale oil			X	X									X	

TABLE 3-34. REPOSITORY DISTRIBUTION OF SOHIO-REFINED PARAHO SHALE OIL MATERIALS AND PETROLEUM EQUIVALENTS

	Sample requirements study							
Shale oil material	Carcinogenesis	PAM anal.	Comprehen-sive anal.	Marine eco-sys. effect	Carcinogenesis	Diesel exhaust	Mutagenesis	Mutagenesis & chemical anal.
Crude shale oil	X	X	X		X		X	X
Hydrotreated shale oil	X	X	X		X		X	X
Weathered gas feedstock			X				X	
JP-5 precursor			X		X		X	
JP-6 precursor			X				X	
DFM precursor	X	X	X		X	X	X	
Hydrotreated residue	X	X	X		X		X	X
JP-5 product			X		X		X	X
JP-6 product			X		X		X	X
DFM product	X	X	X	X	X	X	X	X
Combustion effluent DFM							X	
Acid sludge							X	
Petroleum equivalents								
JP-5 product					X		X	X
JP-6 product					X		X	X
DFM product	X			X	X		X	X

(continued)

TABLE 3-34. (continued)

Shale oil material	Sample requirements study							
	Mutagenesis & short-term animal	Pond Eco-sys. effect	Gas chroma-tography	Acute oral mouse toxicity	Drosophilia mutagenesis	Cytocicity	Chemical class fractionation	Stability screening
Crude shale oil	X	X		X	X	X	X	X
Hydrotreated shale oil	X	X		X	X	X	X	X
Weathered gas feedstock					X		X	X
JP-5 precursor					X		X	X
JP-6 precursor					X		X	X
DFM precursor					X		X	X
Hydrotreated residue		X		X	X	X	X	X
JP-5 product		X	X		X		X	X
JP-6 product					X		X	X
DFM product		X			X		X	X
Combustion effluent DFM								
Acid sludge					X		X	X
Petroleum equivalents								
JP-5 product		X			X		X	X
JP-6 product					X		X	X
DFM product		X			X	X	X	X

mutagenic/carcinogenic studies of shale crudes and various refined products to determine the influence of retorting and refining techniques on these parameters. While preliminary American studies suggest that no significant chronic pulmonary changes after 2 years' exposure result from inhalation of shale rock dust or retort particulate emission products, such data should be viewed with caution since shale rock contains sufficient silica to render it suspect. The carcinogenicity of the raw shale crude should be noted and ways derived to reduce the activity or otherwise guard against it by control practices. Few data are available for emission products. It is of paramount importance to compare combustion emissions from shale fuels with their petroleum counterpart since the quantitative and qualitative differences (organic compounds) in fuels may contribute to variations in levels of mutagens or carcinogens in the exhaust emissions.

In summary, preliminary biological studies of the oil shale industry have not yet demonstrated unmanageable problems of toxicity. Additional studies are in process from which data will be available in the present year. These experiments will further delineate potential toxic profiles and possibly confirm provisional data now available. Continued research is needed for strengthening of data now in existence and developing data as required on various refinery cuts including residual oil, emission products from retorting and refining, and combustion of fuels for the production of power. Data are needed on the potential health hazards which might be associated with the contamination of stream estuaries or underground water by various leachates from shale oil technologies. While results thus far are encouraging, it would be prudent to reserve judgment on the potential toxicity of oil shale development and shale oil production and use until the data base is extended to other parameters and there are confirmatory results of other investigators. Such an approach can assure the rapid development of this resource in an acceptable manner from the standpoint of risk to human health.

OTHER ENVIRONMENTAL IMPACTS

Prepared for Dale Denny & Bruce Tichenor of RTP
By Radian Corporation

Shale Products Utilization

Refining—

To date, refining studies concerning shale oil have been limited in scope and size and have primarily been concerned with demonstrating technology rather than determining effluent concentrations and properties. Therefore, as stated in the previous topic, limited information exists on the health and environmental impacts from shale oil utilization.

In addition to the carcinogenic potential of crude shale oil, the health impact of other toxic chemicals in crude shale oil must also be considered. Arsenic is found in all fractions of crude shale oil at concentrations up to 1,000 times that of natural crude levels. Nitrogen, in the form of cyanides, pyroles, pyridines, and other compounds, is present in concentrations that are 6 to 10 times that of most crudes. Oxygen levels of shale oils are twice those of natural crudes, resulting in larger amounts of acids, phenols, and other oxygenated compounds (97,98,99).

As with carcinogenic potency, the toxic effects of these compounds decrease with upgrading, since further processing eliminates these contaminants from product streams. Therefore, any significant increase in health problems will occur during upgrading, when the physical and chemical properties of shale oils differ the most from those of natural crude oils. The upgrading steps to which crude shales will initially be exposed include dearsenation, coking, and hydrotreatment. These initial processing steps are sufficient to remove the high heteroatom and arsenic concentrations that are the refiners' major processing, environmental, and health and safety concern when dealing with raw shale oil. In addition, another important

source of potential health risk is exposure to fugitive emissions, especially when they originate from crude shale oil leaks and spills.

Caustic washing and guard beds have been proposed for arsenic removal from shale oils. However, in comparing economics, process operability, and environmental effects, the guard bed process has been found to be superior to caustic washing in all three respects (100). Chevron found that the guard beds removed essentially all the arsenic and 70 percent of the iron in raw Paraho shale oils, based on material balances in a recent refining study (101). The guard bed adsorbent catalyst was also effective in removing zinc and selenium from the shale oil. Since the catalyst involved is a relatively inexpensive commodity, disposal is the most likely fate of spent guard bed catalysts. Special handling and disposal precautions should be employed to avoid any health, environmental, or safety problems that may be associated with high arsenic and other trace metals.

The greatest concern for employee health in regard to coking processes is exposure to air emissions. These emissions include coke dust from decoking, combustion gases from coking process heaters, and fugitive emissions. Particulate emissions from delayed coking are associated with removing the coke from the coke drum, and subsequent handling and storage operations. Hydrocarbon emissions from cooling and venting the coke drum before coke removal are also present.

Particulate emissions and hydrocarbon emissions from delayed coking of synthetic liquids will not be greater than that for natural crude oil coking, but they are potentially more toxic because of chemical dissimilarities. Wetting down the coke during the decoking operation should alleviate any additional impact from the coking particulates of synthetic liquids. Also, hydrocarbon emissions from coke drums can be collected and routed to a refinery flare in order to reduce their impact. These practices are routine in modern refinery operations.

Fluid coking is a continuous process that uses the fluidized solids technique to convert residues to lighter products. This process entails high operating temperatures and short residence times, thus eliminating the need for coke drums and avoiding the environmental and health problems associated with decoking. However, flue gases from the burner beds are passed through cyclones and discharged to refinery stacks. If refinery schemes include fluid cokers for processing large quantities of synthetic liquids, the potential exists for higher nitrogen oxide levels in combustion gases.

Hydrotreating is a catalytic process that uses hydrogen to stabilize and/or to remove objectionable elements such as sulfur, nitrogen, oxygen and trace metals from feedstocks or products. The heteroatoms removed, primarily in the form of hydrogen sulfide, ammonia, and water, will be accompanied by traces of light hydrocarbons. This gas stream can be routed to ammonia recovery and acid-gas removal units because of the extremely high nitrogen content of shale oils. Additional ammonia recovery facilities may be necessary if substantial shale oil refining is undertaken. Hydrocarbons emitted from shale oil hydrotreating should be similar in quantity and composition to those resulting from natural crude oil hydrotreating and can be handled using existing refinery equipment.

Of the trace elements found in shale oils, only arsenic is found to be higher in concentration than in normal crude oils, and essentially all of it can be removed before treatment with adsorbent guard bed catalysts. Therefore, effluents from the regeneration of spent shale oil hydrotreating catalysts that have been contaminated with trace metals or nitrogen compounds should not cause any additional health or environmental problems.

Fugitive emission sources are the second largest source of hydrocarbon emissions in petroleum refineries (102). All chemical species present in shale oils may possibly be present in fugitive emissions; therefore, the exact composition and magnitude of fugitive emissions depend primarily on maintenance and housekeeping practices of the individual refinery.

Evaporation from open surfaces and leaks from valves and fittings associated with processing equipment such as cokers and hydrotreaters that operate under high temperatures may discharge significant levels of heteroatomic substances. Exposure to shale-oil-derived fugitive emissions might result in additional health hazards if major utilization of shale oil is undertaken.

Fugitive emission controls are primarily based on procedures rather than equipment. Design and maintenance techniques can be employed to reduce or eliminate fugitive emissions and are discussed in Section 4.

The limited data base on shale oil refining emissions will be expanded as a result of the November 1978 refining run of 16,000 m^3 (100,000 bbl) of Paraho shale oil at Sohio's Toledo, Ohio, refinery. The run included processing by hydrocracking (to reduce the nitrogen levels) to produce jet fuel, marine diesel fuel, and residual fuel oil (No. 5 or 6).

Radian Corporation conducted an assessment of fugitive emissions and an industrial hygiene survey for the U.S. Navy under an EPA contract. The data from this study are not yet published, but preliminary analyses indicate that no abnormal environmental emissions occurred when compared to refining of conventional crude oil. Unfortunately, the data used to draw the preliminary conclusion are very sparse. Only an extremely small number of fugitive emission sources were found and sampled.

In summary, the limited data available to date suggest that the refining of shale oil in petroleum refineries should produce emissions that are similar to those now produced when conventional crude oils are refined. These emissions include atmospheric discharges of particulates, sulfur and nitrogen oxides, heavy metals, and hydrocarbons (including potentially hazardous materials). Liquid effluents can be expected to contain biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, oil and grease, phenols, ammonia, sulfides, heavy metals, and hydrocarbons. Control techniques now being employed in the petroleum industry should be applicable to controlling emissions from shale oil refining. The environmental and health effects associated with shale oil refining should be similar to those occurring under conventional crude oil refining. Again, it is stressed that the data available are very limited. Further data must be collected and analyzed before the environmental impacts of refining shale oil are fully known.

Storage and Handling—The evaporation of volatile hydrocarbon components during storage and handling is the greatest source of atmospheric emissions in the refinery. It is recognized that many products handled and stored at a refinery are more volatile than crude shale oil. Nevertheless, the storage and handling of crude shale oils, which contain higher levels of arsenic, nitrogen compounds, and oxygen compounds, could pose potential health or environmental problems for the refiner.

Raw shale oils are expected to undergo a mild thermal treatment at the retort facility to crack the long paraffin chains that contribute to high pour points. This would make pipelining of the crude shale oil possible at ambient or slightly elevated temperatures. Despite this thermal treatment, shale oils can still be expected to contain fewer light ends than typical petroleum crudes. Lower emission rates, therefore, would be associated with ambient storage and handling of these naphthadeficient shale oils. (See Section 4 for a discussion of storage tank vapor controls.)

Initial upgrading steps at the refinery such as dearsenation, coking, and hydrotreatment of shale oils will result in a synthetic fuel remarkably similar to natural crude oil. The degree of processing will, of course, affect the ultimate carcinogenic activity of the refined shale oil. The storage and handling of upgraded shale oil products are therefore not expected to provide the refiner with additional health or environmental problems.

Refinery Sludges—Biological sludges, tank bottom sludges, and API separator

sludges that contain substantial amounts of crude shale oil contaminants might pose additional health or environmental problems for the refiner. These contaminants will include increased amounts of nitrogen oxygen compounds. Trace element concentrations will be similar to those of natural crude oils, except for arsenic, which might be present in storage tank sludge at significant levels. Source controls for refinery sludges are discussed in Section 4.

Combustion of Shale Oil Products

It is very likely that early utilization of shale oils will be as utility fuel or as a refinery fuel in boilers or process heaters. All criteria pollutants can be expected to be emitted from the combustion of shale oils, as with petroleum fuels. However, the quantities of these emissions will be a function of the degree of upgrading involved and the nature of contaminants in the synthetic fuel.

Although little information is available concerning the emissions from the combustion of shale oils, present data indicate that differences between shale-derived fuels and their petroleum counterparts in either performance or emissions are insignificant. [A 1977 Paraho refining study revealed that slightly higher nitrogen and ash contents of certain shale oil fractions account for the differences in emissions between shale and petroleum-derived fuels (103)] .Also, evidence to date suggests that particulate polycyclic organic matter emissions associated with combustion of refined shale oils are not inherently greater than those from combustion of similar boiling-range petroleum oils (98).

Thus, the only emission problem that might be associated with the combustion of shale-derived fuels, as compared with normal fuels, would be slightly higher NOx emissions when limited upgrading is applied. Four general techniques or modifications that can be employed for the control of NOx emissions are:

Combustion modification

Fuel modification

Alternate furnace design

Flue gas treatment

Radiation—Prepared by The Pace Company Consultants & Engineers, Inc., a Division of Jacobs Engineering Group Inc.

Among trace elements found in Green River Formation oil shale are thorium, uranium, and potassium. Thorium and uranium are the naturally occurring heavy radionuclides that decay into various products (daughters) that are also ubiquitous in nature. The decay products of thorium-232, uranium-235, and uranium-238 are all found in the earth's crust or atmosphere, and they account for much of the background radiation to which man is exposed. Of naturally occurring potassium, the light radionuclide, potassium-40, is only 0.012 percent abundant. Potassium-40 has a half-life of 4×10^8 years and decays by beta emission to stable calcium-40.

Trace element analysis of TOSCO II spent shale from the Colony Development Operation site revealed concentrations of 0.99 ppm uranium, 0.77 ppm thorium, and 2.72 percent potassium, or 3.26 ppm potassium-40 (104). Allowing for a mineral content of 82.6 percent for 120 l/tonne (35-gal/ton) raw oil shale, and assuming that all uranium, thorium, and potassium remain in the spent shale after pyrolysis, the uranium-238, thorium-232, and potassium-40 concentrations in the raw shale would be 0.82, 0.64, and 2.7 ppm, respectively (105). These data and assumptions are summarized in Table 3-35.

Table 3-36 is an extension of Table 3-35 and presents a summary of estimated total radionuclide release anticipated from a 13,600-tonne/day (100,000 bbl/day) oil shale facility. Such a facility would process approximately 119,724 tonnes (132,000 tons) of oil shale daily. In a radioactive disintegration series where the half-life of thorium-232 or uranium-238 (parent) is much longer than that of the

daughters, the daughters can be assumed to be in secular equilibrium with the parent. Thus, in natural deposits of heavy radionuclides, the daughter's radioactivity is assumed to be the same as the major parent. The calculations presented in Table 3-36 assume that all of the radon gas trapped in the oil shale will be released to the atmosphere during mining, crushing, and retorting; they should be regarded, therefore, as representing an upper limit.

TABLE 3-35. ESTIMATES OF RADIOACTIVE ELEMENT CONCENTRATIONS IN COLONY SHALE[a] (ppm)

Type of shale	Uranium-238[b]	Thorium-232	Potassium-40
Spent shale	0.99	0.77	3.26
Raw shale	0.82	0.64	2.7

[a] Source: References 105 and 106.

[b] The low relative natural abundance of uranium-235 (0.715 percent) results in activity of only 4.5 percent of uranium-238 and its daughters.

The concentration of radon-220, radon-222, and their daughters in an underground mine atmosphere depends not only on the uranium and thorium content of the oil shale, but also on the ventilation rate of the mine. In 1975, a survey was made of the presence of radon-222 and radon-220 daughters in 223 operating underground coal mines in 15 States (106). According to this survey, there appears to be no significant health hazard from inhalation of radon-222 and radon-220 daughters in underground coal mines. Coals generally contain more trace amounts of uranium and thorium than does Green River Formation oil shale.

Radon emanates naturally from soils at the average crustal rate of 1.4 pCi/m^2-s ($4x10^{-2}pCi/ft^2$-s). Approximately 400 MCi of radon-222 per year are emitted naturally from the conterminous United States. In performing an initial assessment, this natural emission would have to be compared with anthropogenic emissions. Anthropogenic emissions would involve the emanation of terrestrially entrained radon-222 from ores during mining, crushing, and retorting, and the residual emanation of radon-222 from spent shale disposal areas.

Secular equilibrium will be reestablished in spent shale disposal areas. Because of the similarity of spent shale to the composition of the rock and soil of the surrounding area, it is probable that little or no additional radon emanation above that of the natural background of the area will be induced by spent shale disposal operations (106). This will depend to a certain extent on the methods of shale crushing, retorting, and stabilization of spoil.

No population exposure or worker dose calculations have been made for the purpose of projecting health effects of oil shale development. Estimates have been made (106), however, that indicate that population exposure doses derived from the extraction of shale oil are relatively insignificant compared with geothermal utilization and coal combustion, liquefaction, and gasification.

Noise—Jacobs Environmental, a Division of Jacobs Engineering Group Inc.

The noise impacts of oil shale development apply to various primary and secondary aspects of the industry. The aspects of oil shale development causing the most concern are the following: Surface processing plant construction and operation, mining, reservoir operation, pipeline construction, transmission line construction and operation, highway construction and operation, railway construction and operation, and community expansion. A summary of the anticipated noise impacts caused by these activities is presented in this section.

TABLE 3-36. ESTIMATED RADIONUCLIDE EMISSIONS TO THE AIR FROM A 13,600-TONNE/DAY (100,000-bbl/DAY) OIL SHALE FACILITY[a] (μ Ci/day)

Radionuclides	Fugitive dust	Gases	Particulates
Uranium-238	0.64	—	4.9
Thorium-234	0.64	—	4.9
Protactinium-234	0.64	—	4.9
Uranium-234	0.64	—	4.9
Thorium-230	0.64	—	4.9
Radium-226	0.64	—	4.9
Radon-222	—	32,800	—
Polonium-218	0.64	—	4.9
Lead-214	0.64	—	4.9
Bismuth-214	0.64	—	4.9
Polonium-214	0.64	—	4.9
Lead-210	0.64	—	4.9
Bismuth-210	0.64	—	4.9
Polonium-210	0.64	—	4.9
Thorium-232	0.16	—	1.3
Radium-228	0.16	—	1.3
Actinium-228	0.16	—	1.3
Thorium-228	0.16	—	1.3
Radium-224	0.16	—	1.3
Radon-220	—	8,300	—
Polonium-216	0.16	—	1.3
Lead-212	0.16	—	1.3
Bismuth-212	0.16	—	1.3
Polonium-212	0.10	—	0.9
Thallium-208	0.06	—	0.4
Potassium-40	40	—	310.0
Total	50	41,100	385

[a] Source: Reference 105.

Noise Generation—

Construction Activities—The largest amount of noise will be generated during construction of the mine, surface processing facility, reservoir, pipeline, transmission line, rail line, highway, and community expansions. The construction of these facilities will cause a large amount of heavy equipment to be moved into an area which has been historically very quiet. The operation of this heavy equipment and the blasting that occurs during construction of the mine will have the greatest impact on the environments that surround oil shale developments.

The main source of noise from community expansion is due to road and house construction. The extent to which this noise affects human activity depends on the proximity of the construction to local population centers and also on the local topography and meteorological conditions.

Plant Operation—During operation of a surface processing plant, the greatest sources of noise are the retort vessels, compressors, heat exchangers, cooling fans, pumps, control valves, air and steam pipe leaks, and transportation vehicles to and from the plant. Noise from retort vessels and stacks used in an oil shale processing facility will have an average decibel rating of 95 to 100 dB (A) at 7.5 m (25 ft) (107).

The major sources of noise in the operation of an underground mine are associated with the crushers, mining and transportation equipment, ventilation systems, and blasting. The noise levels from operation of equipment at the mine will be the same as those cited in the construction phase.

Noises from the operation of a plant-associated water reservoir results from spillway and outlet operation, dredging, aeration, recreational use, maintenance, and engine noise.

During operation of a pipeline, compressors and pumps are the main sources of noise.

During operation, the outer conductor of a transmission line will be the main source of noise and should produce a negligible impact on human activities and wildlife (106).

Noise Impacts—

According to guidelines set out in a 1974 EPA document (108), a 24-hr average exposure to 70 dB (A) and 55 dB (A) may contribute to hearing loss and speech interference, respectively. Current knowledge is insufficient to determine whether these decibel levels apply to wildlife protection. A large number of laboratory experiments have shown that physiological stress is experienced by certain animals at varying decibel and sound pressure level exposures. Intermittent exposure to sound pressure levels of about 80 dB or more have been associated with increased blood pressure, increased adrenocortical activity, increased levels of serum cholesterol, decreased fertility, induction of seizures, and various other physiological stresses and behavioral abnormalities in laboratory animals (109,110). Based on this evidence, the following impact determinations have been made.

Construction Activities—The greatest noise impact to local wildlife will be experienced during construction. Based on the estimated noise levels of heavy duty construction equipment and the results of the laboratory noise stress tests mentioned previously, it can be assumed that construction of the mine, processing plant, transmission lines, pipeline, water reservoir and road may cause a temporary local displacement of wildlife. The noise impact of construction activities during oil shale development would be very similar to that of community expansion activities, which produce the same noise levels attributed to heavy-duty construction equipment. Under EPA accepted threshold limits for humans, these levels may cause temporary discomfort to human residents. But no displacement of wildlife would be expected from community expansion activities, since a large portion of the local animals would have already been removed by community establishment.

Plant Operation—It is anticipated that noise-related impacts resulting from the operation of oil shale processing facilities and directly related support activities will displace certain species of animals but will have a negligible effect on local communities of people, assuming that population centers are built at sufficiently safe distances.

The noise levels that may be experienced 7.5 m (25 ft) from a processing facility such as an oil shale surface processing facility might displace local wildlife populations. Operation of the mine should create low-profile noise levels; however, blasting will impose a sharp peak on background. The operation of a pipeline, water reservoir, and access road may cause wildlife to relocate, thus perpetuating biological stress and possible consequential population decrease in local ecosystems.

The extent to which noise created by vehicles traveling on a highway affects the environment will depend on the number of vehicles using the road, the speed of the vehicles, local topography and meteorological conditions, and proximity to population centers. Noise impacts to communities can be minimized by locating the highway away from noise-sensitive areas such as hospitals, schools, residences, and various species of wildlife.

Socioeconomic Impacts—Jacobs Environmental, a Division of Jacobs Engineering Group Inc.

The oil shale region contains approximately 10 counties in three States, including five counties in Northwest Colorado, two in Northeast Utah, and three in Southwest Wyoming. The counties that are considered illustrative of all ten are Rio Blanco, Colorado, and Uintah, Utah. Generally, employment in the Oil Shale Region is mainly based on agricultural and mining enterprises. In terms of value of production, the primary industry category is dominated by mining (111). The illustrative oil shale counties are very thinly populated, with an average density of .77 persons/km^2 (two persons per sq mile). Most of the residents live in single unit houses located in small towns. Most of the land in this area is used for either grazing, agriculture, or wildlife habitat.

Water availability in the Upper Colorado River Basin depends on physical availability, State water laws, and the law of the river (a combination of Federal laws, interstate contracts, and court decisions that divide the Colorado River waters among the States through which it flows). Presently, the largest use of water in the oil shale region is irrigation.

The major socioeconomic impacts of any proposed commercial oil shale development in the oil shale region will be due to: (1) the population growth resulting from the new work force required for the construction and operation of the proposed project; (2) the demand for housing, municipal, and human services generated by the new population; (3) the impacts on the local and regional economy, including new employment opportunities at higher wage scales, new public revenues, and changes in the structure of the economy caused by shifts in the relative importance of the basic economic sectors (112).

The analysis of these social and economic impacts was designed to consider effects created during project development, operation, and project end. During project development, a series of economic, demographic, social, and land use impacts would be created. Some of these impacts can be traced with reasonable reliability to characteristics of the new primary industry itself—in particular its size, and the characteristics of its workforce (occupation, earnings, etc.). Given this information and a knowledge of socioeconomic profiles and relationships in comparable situations, preliminary estimates can be made of total employment, female employment, employee earnings, total income, retail sales and service receipts, total population, population age distribution, school age population, household characteristics, housing requirements, land requirements (for residential, business, and community facility purposes), community development costs (capital and operating) and revenues, and other impacts associated with the new primary industry.

Relationships drawn from socioeconomic profiles of mining-dominated counties have been assembled in a straightforward community development programming model, which was used to estimate the impacts of the construction and operation of a synthetic fuels plant (113). A summary of these estimates as they relate to a unit oil shale facility is quantitatively presented in Tables 3-37 and 3-38. Some socioeconomic effects of synthetic fuels development, however, cannot be quantitatively estimated from characteristics of the primary industry alone, even in preliminary form. These potential effects would be determined by the interplay of primary industry development impacts with each prospective community. Examples of such interplay include the effects of synthetic fuels development on traditional local economic functions, job opportunities for local residents, local government finances, the local crime rate, local prices for essential goods and services, and the creation or exacerbation of many social and political problems. The results of this interplay are termed "end impacts," and they define many of the key socioeconomic issues in synthetic fuels development. Since end impacts would be the result of the interplay between the development impacts and a particular pre-

impact situation, the outcomes would be almost as variable as local communities.

Socioeconomic Impacts of Oil Shale Development on Tracts U-a, U-b—

Because of a recent court case involving land ownership at Tracts U-a and U-b, development on those sites has been postponed for an indeterminate time.

The development of an oil shale complex in the White River area of Utah will produce positive economic impacts on the surrounding local communities and on the county as a whole. The areas to be most intensely affected are the cities of Rangely, Colorado, Vernal, Utah and Roosevelt, Utah and to a smaller extent, Duchesne, Utah.

Approximately 3,450 persons will move into the area to provide services for the primary work force of 2,300 so that the total employment in the tenth year of development will be approximately 6,000 workers. The ultimate population in the fifteenth year will be 12,535, which represents an increase of 30 percent over baseline projections. The total income in the fifteenth year will ultimately be $147 million, which represents a 56 percent increase over baseline projections. The impact on demand for land and municipal, health, and education services will be negative in the short term. However, the community is expected to benefit in the long term from extensive local expenditure and net tax revenues (Table 3-38).

A detailed summary of the projected social and economic impacts is presented in Table 3-39. The table assumes that no new town will be built, and the impacts have been presented as areawide impacts, nonspecific to individual townships.

TABLE 3-37. ESTIMATED SOCIO-ECONOMIC IMPACTS OF OIL SHALE DEVELOPMENT[a,b]

Impact	Time periods	
	Peak construction phase	Operational phase
Employment (total)	3,140	2,530
Primary	2,000	1,100
Secondary	1,140	1,430
Female employment (total)	610	760
Primary	40	40
Secondary	570	710
Employment earnings (total), 1975 $(000)	46,700	28,700
Primary	26,400	15,700
Secondary	10,300	13,000
Average annual income		
Per employee, 1975 $	11,700	11,300
Total income, 1975 $(000)	40,300	34,500
Total local business income, 1975 $(000)	Not Available	20,000
Total induced population	5,760	5,260
Total induced families	2,270	1,700
Housing needs:		
Single family	1,120	1,070
Multi-family	500	270
Mobile homes	870	450

[a] Source: Reference 108.

[b] Estimates are based on a 45,000-bbl/day unit oil shale facility.

TABLE 3-38. ESTIMATED COSTS FOR COMMUNITY EXPANSION RESULTING FROM DEVELOPMENT OF A 45,000-bbl/DAY UNIT OIL SHALE FACILITY[a]

Type of Cost	Amount (in thousands)
Recreation costs	
Capital	$ 670
Operating and maintenance	50
School Costs, 1975 $(000)	
Capital	6,960
Operating and maintenance	1,540
Community facilities, 1975 $(000)	
Capital	3,340
Operating and maintenance	40
Utilities, 1975 $(000)	
Capital	12,470
Operating and maintenance	1,040
Annual revenue, 1975 $(000)	3,300
Total adjusted annual cost, 1975 $(000)	5,310

[a] Source: Reference 108.

Socio-Economic Impacts of Oil Shale Development at Tract C-a —

Development on Tract C-a is expected to affect the towns of Rangely and Rifle most intensely, with smaller-scale impacts occurring in Meeker. These communities would be most seriously affected by the increased demand on municipal services and the reorganization of the community infrastructure that would be caused by an increase in the local population.

Direct employment at Tract C-a began in 1977 with the construction of support facilities such as powerlines. Construction employment rose to 175 during early 1977 and increased to 230 near the end of the year. It is expected to stay at or above that level of employment (+300) until late 1979. Construction will continue in 1980, and employment will gradually decrease and level off at about 100 employees through 1982. Employment projections beyond 1982 will be made when the decision to continue commercial development is made. Ninety percent of these Rio Blanco Oil Shale Development Corporation (RBOSC) employees are expected to be local, with the remainder being new area residents. Of the total employees, 80 percent are expected to be married, with an average family size of 3.8 members. A summary of the anticipated employment and population increase is presented in Table 3-40.

Original estimates set employment at the White River Shale Project (WRSP) at a peak of 3,500 in year eight. That projection has been increased to 4,800 (personal communication with Rees Madsen, White River Shale Project, Environmental Coordinator, October 1979). But since no official revision has been made to other social and economic impact projections dependent on that figure, all figures reported for Tracts U-a and U-b are based on original projections of the DDP. These figures will probably be revised when development activity commences.

TABLE 3-39. SUMMARY OF PROJECTED SOCIO-ECONOMIC IMPACTS OF OIL SHALE DEVELOPMENT AT TRACTS U-a AND U-b[a,b,c]

Item	Year	Annual employment		Total induced population	Total wages earned annually (in thousands)	Average employee wage[d,e]	Total net tax revenue[d]	Total annual tax revenue[d]	Projected housing requirements (housing units)			School room requirement
		Primary	Secondary						single family	multi-family	mobile homes	
Phase I:												
Commercial development stage	1	400	120	924	$ 12,220	$27,400	—	—	—	—	—	—
	2	400	120	924	12,220	27,400	—	—	—	—	—	—
	3	300	120	1,218	5,700	14,800	—	—	—	—	—	—
	4	300	150	1,305	6,015	14,800	$1,662,100	$1,906,000	218	25	145	—
50,000 bbl/day production	5	1,300	650	4,538	38,665	24,492	—	—	—	—	—	34.5
	6	1,800	900	6,218	54,990	25,300	—	—	—	—	—	—
	7	2,300	1,380	8,277	25,756	—	—	—	—	—	—	—
	8	3,500[f]	2,450	13,780	102,725	22,000	8,369,500	10,931,000	1,769	203	2,489	—
	9	2,500	2,250	11,310	66,925	17,320	—	—	—	—	—	—
	10	2,300	2,300	10,902	58,190	14,800	—	—	—	—	—	87.0
Phase II:												
100,000 bbl/day production	15	2,300	3,450	12,535	70,265	14,800	—	—	—	—	—	93.5
	20	2,300	3,450	12,535	70,265	14,800	17,248,600	19,522,000	1,972	227	1,643	—

[a] Source: Reference 108.
[b] All numbers in this table reflect original projects of Tracts U-a, U-b to be found in the DDP Document. Employment figures and other subsequent numbers are subject to future revision.
[c] Assumes no new town development.
[d] 1975 dollars.
[e] Determined by multiplying the number of employees in each working class by their respective wages, and dividing this number by the total number of employees.
[f] This figure has been changed to 4,800. Verification is through eeitorial comments by Rees Madsen.

(continued)

TABLE 3-39 (continued)

Item	Year	Natural gas utilities capital cost[d]	Electrical utilities capital cost[d]	Water utilities demand (MGD)	Hospital bed reqm'ts	Doctor reqm'ts	Dentist reqm'ts	Nurse reqm'ts	Firemen reqm'ts	Fire station reqm'ts	Fire pumper reqm'ts	Fire truck reqm'ts	Police-men reqm'ts	Police vehicle reqm'ts
Phase I:														
Commercial development stage	1	$ 375,600	281,700	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—	—
	3	—	—	—	—	—	—	—	—	—	—	—	—	—
	4	19,200	9,900	—	—	—	—	—	—	—	—	—	—	—
50,000 bbl/day production	5	1,146,000	859,500	0.104	—	—	—	—	6.6	0.4	0.4	0.4	6.7	18.5
	6	440,400	442,800	—	—	—	—	—	—	—	—	—	—	—
	7	—	—	—	—	—	—	—	—	—	—	—	—	—
	8	—	1,222,000	—	—	—	—	—	—	—	—	—	—	—
	9	—	—	—	—	—	—	—	—	—	—	—	—	—
	10	—	—	2.82	—	—	—	—	13.6	—	—	—	—	—
Phase II:														
100,000 bbl/day production	15	—	—	—	—	—	—	—	—	—	—	—	—	—
	20	—	—	3.28	—	—	—	—	16.0	1.2	1.2	1.2	28.7	45.6
Total		—	—	—	44.5	7.0	5.0	—	14.0	—	—	—	—	—

TABLE 3-40. PROJECTED EMPLOYMENT AND POPULATION INCREASES RESULTING FROM OIL SHALE DEVELOPMENT AT TRACT C-a[a]

Year	Maximum RBOSC employment	Maximum RBOSC new-resident employees[b]	Maximum secondary employment[c]	Maximum employment	Maximum new-resident population[d]
1977	230	207	104	334	631
1978	300	270	135	435	851
1979	300	270	135	435	851
1980	100	90	45	190	274
1981	100	90	45	190	274
1982	100	90	45	190	274

[a] Data presented are unofficial; they are based on projections, data, and criteria submitted to the U.S. Area Oil Shale Supervisor as manpower estimates and housing surveys(115).
[b] Equals 90 percent of total employment at RBOSC.
[c] Equals 50 percent of new-resident employees.
[d] Equals 80 percent of new-resident employees multiplied by average number of family members (3.8) per married employee.

The number of persons employed as service employees to meet the needs of population increases in the community as a consequence of RBOSC development (secondary employees) is estimated to be 50 percent of the total new-resident persons directly employed. Fifty-two percent of the service employees are projected as locally based residents, and 48 percent as new residents. Eighty percent of the service employees are projected as being married with a family size of 3.8 members.

It should be pointed out that the documents available for socioeconomic impact review of C-a development did not quantify the anticipated community impacts. However, a discussion of the existing facilities and their ability to expand and meet rising demands is available, and from this, rough impact assessments can be drawn. The increased population induced into the area by the C-a oil shale project will affect the community infrastructure in the following manner.

Schools in both Rangely and Meeker have additional student-carrying capacity in the elementary, junior high, and high school levels. The local college, Northwestern Community College, had an enrollment (as of March 1979) of 300, with a resident capacity of 500. Rangely and Meeker school districts have bonding capacities of $15.7 and $2.9 million, respectively.

All of the housing units available for occupancy in Rangely and Meeker are filled and new homes are sold before they are completed. A 400-unit housing subdivision is presently under construction in Meeker and a few houses are available for sale.

To help remedy this situation, RBOSC has devoted much time, effort, and money to the development of a new master plan for Rangely and has assisted Rangely in its application to acquire 6,177 ha (2,500 acres) of BLM land adjacent to the town. Tract C-a has also been instrumental in the development of a new road connecting the Tract to Rangely and is assisting the development of a mobile home park, and a mass transportation system.

Rangely, Meeker, and Rifle all have modern hospital facilities and full-time resident doctors. A clinic at Colorado Northwestern Community College provides all the dental hygiene needs in Rio Blanco County.

The water delivery and sanitary waste treatment systems at Rangely, Meeker, and Rifle have all undergone significant improvements in the past 2 years. These improvements have been designed to accommodate the increased populations that are expected to result from oil shale development at Tracts C-a and C-b.

Major funding support for the water systems and sewage treatment plant expansions comes from the State of Colorado's oil shale trust fund. This trust fund is the State's share of the bonus money paid for the two Federal oil shale leases in Colorado. Although to date (1979) some $21 million has been committed to funding these and other projects geared to mitigate impacts of the oil shale developments, more than $60 million remains in the fund.

Socioeconomic Impacts of Oil Shale Development on Tract C-b—

The impacts of development on Tract C-b are expected to be centralized in Garfield County, with less significant impacts occurring in Rio Blanco County. This is largely due to the facts that property tax revenues will accrue largely in Rio Blanco County, while at the same time population increases will mostly impact Garfield County. The main impact originates from economic and physical growth in the rural areas of Rio Blanco and Garfield Counties.

All local physical and economic growth will originate from the increase in population resulting from direct and indirect employment for the oil shale development. The total peak population during the mine development phase and plant construction phase (including direct employees, their families, service workers, and their families) is estimated to be 1,400 and 13,500, respectively. The total permanent population, once the proposed project is in operation, is estimated to be between 6,000 and 6,500.

At present, municipal services such as schools, health services, water sanitation, utilities, roads, housing, and police and fire protection are all operating at full

TABLE 3-41. SUMMARY OF SOCIO-ECONOMIC IMPACTS OF OIL SHALE DEVELOPMENT AT TRACT C-b[a]

Item	Year	Average Annual employment[b] Primary	Average Annual employment[b] Secondary	Total induced population	Total wages earned annually[c]	Average employee wage[c,d]	Total annual tax revenue[c,e]	Total number of families	Projected housing requirements (housing units) Single family	Projected housing requirements (housing units) Multi-family	Projected housing requirements (housing units) Mobile homes	School room requirement
Phase I:												
Mine	1											
Development	2	320	212	1,413	7,091,362	—	902,603	354	96	51	349	19
	3	350	195	1,304	7,419,948	—	1,189,258	328	94	50	314	17
	4	59	30	229	940,344	18,270	341,371	62	40	20	18	4
	5	59	30	229	940,344	—	176,945	62	40	20	18	4
Phase II:												
Plant	6	512	387	2,579	11,349,278	—	1,558,645	649	176	94	636	35
Construction	7	1,446	1,463	7,200	32,367,041	—	5,014,425	1,813	528	280	1,762	95
	8	2,947	3,325	13,461	66,467,821	21,824	11,275,710	3,403	1,023	540	3,305	179
	9	2,331	3,040	12,361	49,133,861	—	12,349,615	3,133	979	514	2,970	166
	10	1,145	1,563	5,953	17,908,133	—	10,162,858	1,575	795	398	927	83
	11	1,093	1,640	5,860	16,049,172	—	10,712,419	1,585	951	470	656	83
	12	1,123	1,640	5,860	16,049,172	—	10,817,850	1,585	951	470	656	83
	13	1,123	1,640	5,860	16,049,172	—	10,795,792	1,585	951	470	656	83
	14	1,123	1,640	5,860	16,049,172	—	10,795,792	1,585	951	470	656	83
	15	1,123	1,640	6,018	16,493,052	15,985	10,852,164	1,528	951	483	674	86
	16	1,145	1,718	6,137	16,818,564	—	10,931,411	1,660	977	492	687	89
	17	1,154	1,731	6,185	16,951,880	—	10,975,600	1,673	996	496	692	89
	18	1,154	1,731	6,185	16,951,080	—	10,987,186	1,673	1,004	496	692	89
	19	1,154	1,731	6,185	16,951,080	—	10,987,186	1,673	1,004	496	692	89
	20	1,172	1,758	6,280	17,216,112	—	11,020,846	1,699	1,020	504	703	90
	31	1,172	1,758	6,280	17,216,112	—	11,044,191	1,699	1,020	504	703	90

[a] Source: Reference 113.
[b] Derived by adding the monthly employment figures for each year and dividing by 12.
[c] 1975 dollars.
[d] Derived by taking the average yearly wage for all employee classes.
[e] Total excess tax revenue over 31 years is 37.6 million.

capacity. The total front-end capital costs associated with municipal expansion for 6,300 new permanent residents would be roughly $36 million (1975 dollars), excluding highways. Total annual operating and maintenance costs for the same services would be $7.5 million. In per-capita costs, these figures translate to $5,751 capital and $1,200 operating and maintenance costs. Housing costs are not included.

Once the project is operational, it will generate more than $11 million per year in public revenues. Total tax revenues over the 60-year life of the project will be $273.3 million, which represents an excess, after expenditures (excluding highways), of $27.4 million. More than $549 million will be paid in wages over the life of the project.

Details of the projected socioeconomic impact of oil shale development on Tract C-b have been summarized in Tables 3-41 and 3-42.

TABLE 3-42. AVERAGE ANNUAL MUNICIPAL AND HUMAN SERVICE COSTS FOR TRACT C-b FOR A 31-YEAR PERIOD[a,b]

Item	Capital costs	Operating and maintenance costs
Total per-capita municipal and human service cost	$ 7,997.47	$ 1,204.41
Vocational/technical needs	5,424,000	1,097,200
Higher education needs	1,995,000	744,800
Water requirements	2,540,000	184,499
Sewage requirements	2,770,000	135,200
Solid waste collection requirements	90,200	100,500
Open space and recreation needs	2,419,544	179,065.50
Government regulation needs	224,830	505,300
Police protection needs	192,134	201,200
Fire protection needs	962,810	247,700
Basic health requirements	1,367,531.50	741,653

[a] Source: Reference 113.
[b] 1975 dollars.

Socioeconomic Impacts of Oil Shale Development at Colony—

The major impact of oil shale development on the Colony Tract will be due to the physical and economic change caused by induced populations of direct and service employees for the operation. The impacts have been analyzed by Colony using three case situations, each one assuming different locations and intensities of growth. Original estimates showed that 1,200 people would be employed at Colony during Phase I (construction), and 1,050 during Phase II (operation) (115). These figures have now been revised, and peak construction employment is now estimated at 2,500 to 2,700 employees (personal communication with Max Legatski, ARCO Colony Development Operations, Environmental Coordinator, October 1979). Since these revised figures and all social and economic quantifiable impacts dependent on those numbers have not been published, the impacts in this

TABLE 3-43. SUMMARY OF SOCIO-ECONOMIC IMPACTS OF OIL SHALE DEVELOPMENT AT THE COLONY DEVELOPMENT OPERATION[a]

COLONY

Impacts	Year	Annual employment: Primary[b]	Annual employment: Secondary	Total induced population	Total annual revenue[c]	Projected housing requirements: Single family	Projected housing requirements: Multi-family	Projected housing requirements: Mobile homes	Total induced student population	School facility expansion requirement	Projected detail of upgrading health and municipal service facilities in surrounding counties: Natural gas utility requirement	Water utility requirement	Electrical utility requirement
Phase I:													
Construction	1	—	—	—	2,129	—	—	—	—	—	—	—	—
	2	—	—	—	7,943	—	—	—	—	None	—	—	—
	3	1,200	450	3,438	2,940	405	270	675	810	—	—	—	—
Phase II:													
50,000 bbl/day operation	4	—	—	—	3,036	—	—	—	—	—	—	—	—
	5	—	—	—	4,438	—	—	—	—	—	—	—	—
	6	—	—	—	5,907	—	—	—	—	—	—	—	—
	7	—	—	—	7,049	—	—	—	—	—	—	—	—
	8	—	—	—	7,433	—	—	—	—	—	—	—	—
	9	—	—	—	7,404	—	—	—	—	—	—	—	—
	10	—	—	—	7,477	—	—	—	—	—	—	—	—
	11	—	—	—	7,605	—	—	—	—	—	—	—	—
	12	—	—	—	7,693	—	—	—	—	—	—	—	—
	13	1,050	975	4,875	7,779	975	325	325	1,625	Expansion	Expansion	Expansion	Expansion
	14	—	—	—	—	—	—	—	—	—	—	—	—
	15	—	—	—	—	—	—	—	—	—	—	Significant	—
	16	—	—	—	—	—	—	—	—	—	—	Impact	—
	17	—	—	—	—	—	—	—	—	—	—	—	—
	18	—	—	—	—	—	—	—	—	—	—	—	—
	19	—	—	—	—	—	—	—	—	—	—	—	—
	20	—	—	—	—	—	—	—	—	—	—	—	—
	21	—	—	—	—	—	—	—	—	—	—	-	-
	22	—	—	—	—	—	—	—	—	—	—	—	—
	28	—	—	—	—	—	—	—	—	—	—	—	—

[a] Source: Reference 116.
[b] These figures have been revised to 2,500 to 2,700. (Personal communication with Max Legatski, ARCO Colony Development Operations, October 1979.)
[c] 1974 dollars.

discussion were based on original estimates published in the Colony Environmental Impact Analysis (115). This analysis projects the migration of 2,438 persons during peak construction, and 4,875 persons during peak operation. Because of this large influx of new local residents, municipal health and utility services are expected to be strained if no expansion programs are employed. A certain amount of expansion has already been planned because of the high growth rate expected, regardless of oil shale development. To assist in the economic completion of these expansion programs, tax revenues and income distributed throughout the surrounding localities will be available from the oil shale project.

In Phase I, the annual salaries and wages from the project are estimated to be $20 million. In Phase II, the annual salaries and wages from the project are estimated at $12 million. In addition, increases in annual revenues per 1,000 increase in population are estimated to be $432,733.

A summary of the anticipated impacts is presented in Table 3-43. Information in this table is derived under the assumption that growth resulting from the development of the Colony tract will take place according to Case I. This case assumes scattered growth along the Glenwood Springs/Grand Junction corridor.

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SECTION 4
POLLUTION CONTROL TECHNOLOGY

This section reviews the applicability and shortcomings of technology for control of particulate matter, gaseous emissions, wastewater, and solid waste leachates resulting from oil shale processing. Although proven control techniques for many pollutants in process effluents are available, they generally need to be demonstrated in a large-scale oil shale processing plant.

A wide variety of techniques is cited regarding their potential applicability for control of particulate matter and gaseous emissions. Many of the techniques have been successfully used in industries with similar problems, but without the probable wide variety of pollutants, particularly trace elements, resulting from handling enormous quantities of raw shales.

Wastewaters are characterized, insofar as possible, from the limited information available. Standard primary, secondary, and tertiary water treatment methods will be applicable to waste streams, but some of the more highly polluted wastewaters will require research on process methodology to ensure that priority pollutants and toxics are removed. Numerous modes of treatment, recycling, and control should be explored to optimize water utilization at each processing site.

Control of pollutants resulting from solid waste disposal will be an immediate and long-term problem that will require monitoring during operations and perhaps several years after shutdown of an operation because of potential leachate problems. This section reviews control techniques for surface and underground disposal sites, stabilization of *in situ* spent shale, and leachate treatment and recycling.

Also reviewed in this section are controls for refinery sludges and vapor losses from storage tanks. Refinery experience should be directly applicable to these problems.

AIR EMISSION CONTROLS

Robert Thurnau

The commercialization of the oil shale industry will have a significant impact on air quality of the Piceance Valley and possibly on the nearby wilderness areas. Federal, State, and local air pollution statutes will require the process developer to take a hard look at the air pollution control options available, so that the above-mentioned statutes are not violated.

Control of Particulates—Mining, Crushing, Screening, Transportation, Retorting and Spent Shale Disposal

As mentioned earlier, development of the oil shale industry will probably result in significant particulate emissions which may increase the particulate load in ambient air beyond allowable limits. The impact of particulate emissions on ambient air is emphasized because of the newly enacted legislation (the Clean Air Act Amendments of 1974).

Particulates, many of which are fugitive dusts, result from all phases of oil shale industry operations. The need for control of particulates generated from mining, crushing, screening, transportation, retorting and disposal will be one of the significant pollution control problems faced by the industry. A wide variety of con-

trol strategies is available for the removal of particulate matter from ambient air or the process gas stream. These control techniques offer many differences in collection efficiency, initial cost, operating and maintenance cost, waste products, and space requirements.

Water Sprays—

The oldest and simplest control technique is the water spray. Water sprays can be used where evaporation is possible, and if adjusted properly, the operation has no runoff. Water sprays have potential application to: (a) spent shale disposal, (b) grinding and screening operations, (c) mining and blasting activities, and (d) fugitive dusts from surface vehicles and surface retort feeder systems.

The efficiency of water sprays without wetting chemicals is about 80 percent for particles the diameter of which is 5 mm ($2x10^{-4}$ in) or greater. Removal efficiency drops off as particle size decreases and has been reported at 25 percent for particles in the 1 mm ($4x10^{-5}$ in) range (1).

The addition of a wetting agent helps to reduce surface tension and improve the wetting, spreading, and penetrating characteristics of water. Reduced surface tension allows the particles to agglutinate and increases the removal efficiency.

Spray systems have the advantage of suppressing the particulate, and the solids are carried along with the oil shale, thereby reducing one of the waste disposal problems by incorporation of the dust into the shale. However, minimizing a problem in one area of particulate control could intensify the control problems of another—namely, retorting. Additional advantages of water sprays are that they are economical and easy to operate. The disadvantages of spray systems are that they can clog or cause other machinery to clog, and they can freeze in cold weather.

Several oil shale developers have estimated the particulate emissions from their mining, blasting, crushing, transfer, and disposal operations, along with the projected degree of air pollution control achievable by a water spray technique utilizing a wetting agent (2) (Table 4-1).

Chemical Binders—

Chemical binders are an effective tool for the control of fugitive dust emissions. Chemical solutions are deployed over the desired area, and upon drying, they form a protective coating over the exposed area. The treatment has the net effect of reducing the surface area that would be exposed to weathering and erosion, and it greatly reduces the amount of particulate that would be released from the storage area. The materials used as binders can range from inorganic salts to polymeric material. Note that several of the oil shale development areas are rich in carbonates and bicarbonates, and these compounds might be useful as chemical binders.

The costs for binders vary with the type of material chosen. Estimates have been set at about $56.65/ha ($140/acre), but these costs can increase rapidly when manpower and equipment costs are factored into the operation (1).

No data are available to illustrate the effectiveness of chemical binders as a pollution control device for oil shale particulate emissions.

Cyclones—

Cyclones have been used as air pollution control devices for particulates. They are a form of inertial separators that utilize centrifugal force and an abrupt change in direction of the gas stream to reduce the concentration of the dust in the gas. Cyclones are designed so that the incoming gas stream forms a double vortex, one of which spirals downward on the outside, and the other of which spirals upward on the inside. The centrifugal force that moves the particles toward the edge of the outside wall is a function of the square of the inlet velocity and of the inverse of the radius of the cyclone. The collection efficiency depends on the amount of energy expended; thus cyclones with high inlet velocities, small diameters, and long cylinders are usually the most efficient.

TABLE 4-1. WATER SPRAY AS A CONTROL TECHNIQUE FOR PARTICULATES[a]

Activity	Estimated uncontrolled emission rate (kg/hr)					Estimated controlled emission rate (kg/hr)					Estimated control efficiency (%)				
	Paraho Ref. 3	C-b Ref. 4	Anvil Points Ref. 4	Colony Ref. 4	C-a Ref. 4	Paraho Ref. 3	C-b Ref. 4	Anvil Points Ref. 4	Colony Ref. 4	C-a Ref. 4	Paraho Ref. 3	C-b Ref. 4	Anvil Points Ref. 4	Colony Ref. 4	C-a Ref. 4
Mining	79.5	2136	840	665	1783	1.2	43	17	13	35	98.5	98	98	98	98
Blasting	165.7	—	—	—	—	2.5	—	—	—	—	98.5	—	—	—	—
Primary crushing	165.6	—	—	—	—	24.9	—	—	—	—	98.5	—	—	—	—
Transfer	165.7	37	—	—	—	2.5	4	—	—	—	98.5	90	—	—	—
Retorted shale disposal	—	166	353	278	742	—	17	35	28	37	—	90	90	90	95
Transfer	245.7	—	—	—	—	12.3	—	—	—	—	95.0	—	—	—	—
Traffic	519.8	—	—	—	—	131.4	—	—	—	—	75.0	—	—	—	—
Wind erosion	207.9	—	—	—	—	41.6	—	—	—	—	80.0	—	—	—	—
Coarse ore storage	—	—	320	253	450	—	—	16	13	23	—	—	95	95	95

[a] Based on a 50,000-bbl/day operation.

Single cyclones are generally considered to be efficient only for particles with large diameters. As the particle size begins to approach 10 mm ($4x10^{-4}$ in.), the efficiency of the cyclone decreases. To improve efficiency, several cyclones can be integrated into the dust collection system, and collection efficiencies of up to 90 percent have been achieved for particles of 5 mm ($2x10^{-4}$ in) in diameter. However, the greater the desired efficiency of cyclones, the higher the costs, and for particles less than 10 mm ($4x10^{-4}$ in) in diameter, cyclones are not generally the recommended collection procedure.

Cyclones have potential application to these oil shale gaseous effluent streams: Grinding off-gases, screening off-gases, mining dusts, and retorting off-gases.

Fabric Filters—

When high efficiency on small particles (smaller than 5 to 10 mm or 2 to $4x10^{-4}$ in) is required for air pollution control, one of the most widely used methods is the fabric filter. The fabric is usually constructed in bag form, and the entire system is called a baghouse. As the effluent gas stream passes through the baghouse, the dust is removed by one or more of the following phenomena: interception, impingement, diffusion, gravitational settling, or electrostatic attraction. The initial filtration builds up a layer of dust or cake on the bag, and as more contaminated air passes through the system, the dust cake acts as a filter. The cloth serves mainly as a support structure, and the dust itself is responsible for the high levels of removal efficiency.

In addition to the high filtering capability of the dust, efficiencies of fabric filters are also dependent on particulate size distribution, density, chemical composition, and moisture. Under most conditions, a properly designed and operated baghouse operates with efficiencies of 99 percent or better on a mass basis for particles as low as 1 mm ($4x10^{-5}$ in) in diameter.

Table 4-2 summarizes the performance estimates for fabric filters that are proposed as particulate air pollution control devices at several planned oil shale operations. As the table shows, baghouses have potential application for particulate control of many oil shale gaseous effluent streams.

TABLE 4-2. FABRIC FILTER AS A CONTROL TECHNIQUE FOR PARTICULATES

Activity	Paraho Ref. 3	Rio Blanco Phase I Ref. 5	Rio Blanco Phase II Ref. 5	Anvil Points Ref. 4	Colony Ref. 4	C-a Ref. 4
	Estimated uncontrolled emission rate (kg/hr)					
Raw shale storage	333	—	—	—	—	—
Primary crushing	—	408	1,474	780	632	1,683
Primary stockpiling	—	141	—	—	—	—
Primary ore reclaiming	—	454	—	—	—	—
Subore crushing	—	—	227	—	—	—
Overburden crushing	—	—	1,111	—	—	—
Secondary crushing	1,866	3,107	6,577	2,403	1,904	3,367
Fine ore storage	—	610	—	320	253	450
Storage bins	919	—	1,497	—	—	—
Transfer operations	—	—	—	79	63	167
Tertiary crushing	8,398	—	7,484	—	—	2,225
Retort feed	8,396	—	—	—	—	—
Spent shale disposal						
Direct heat	10,659	—	—	—	—	—
Indirect heat	11,382	—	—	—	—	—
Combined heat	10,840	—	—	—	—	—

TABLE 4-2. (continued)

Activity	Paraho Ref. 3	Rio Blanco Phase I Ref. 5	Rio Blanco Phase II Ref. 5	Anvil Points Ref. 4	Colony Ref. 4	C-a Ref. 4
	Estimated controlled emission rate (kg/hr)					
Raw shale storage	0.9	—	—	—	—	—
Primary crushing	—	0.8	6.5	2.3	1.9	5.0
Primary stockpiling	—	1.4	—	—	—	—
Primary ore reclaiming	—	0.9	—	—	—	—
Subore crushing	—	—	0.5	—	—	—
Overburden crushing	—	—	4.9	—	—	—
Secondary crushing	5.6	6.2	29.0	7.2	5.7	168.0
Fine ore storage	—	1.2	—	1.0	0.8	1.4
Storage bins	2.8	—	6.6	—	—	—
Transfer operations	—	—	—	0.4	0.3	0.8
Tertiary crushing	25.2	—	33.0	—	—	6.7
Retort feed	25.2	—	—	—	—	—
Spend shale disposal						
Direct heat	22.8	—	—	—	—	—
Indirect heat	22.8	—	—	—	—	—
Combined heat	22.8	—	—	—	—	—
	Estimated control efficiency (%)					
Raw shale storage	99.7	—	—	—	—	—
Primary crushing	—	99.8	99.8	99.7	99.7	99.7
Primary stockpiling	—	99.0	—	—	—	—
Primary ore reclaiming	—	99.8	—	—	—	—
Subore crushing	—	—	99.8	—	—	—
Overburden crushing	—	—	99.8	—	—	—
Secondary crushing	99.7	99.8	99.8	99.7	99.7	95.0
Fine ore storage	—	99.8	—	99.7	99.7	99.7
Storage bins	99.7	—	99.8	—	—	—
Transfer operations	—	—	—	99.5	99.5	99.5
Tertiary crushing	99.7	—	99.8	—	—	99.7
Retort feed	99.7	—	—	—	—	—
Spent shale disposal						
Direct heat	99.8	—	—	—	—	—
Indirect heat	99.8	—	—	—	—	—
Combined heat	99.8	—	—	—	—	—

Wet Scrubbers—

Many different kinds of particulate collection devices use water as the medium for removing entrained dusts. Spray chambers, wet cyclones, mechanical scrubbers, orifice scrubbers, venturi scrubbers, and packed towers have all been used in the past. The new Federal and State air pollution regulations have, in essence, required that wet scrubbers operate at high particulate removal efficiency, and the consensus seems to be that venturi high-energy scrubbers are the only type of scrubber that will give the desired performance.

The mechanism of particulate removal by a scrubber entails wetting the particle by exposing it to a spray or mist and removing it from the gas stream. Contact of

the particle with the scrubbing liquid is important, because the removal efficiency is related to the number of droplets contacted and the energy imparted to them. Dust particles can also act as condensing nuclei when a gas is cooled below its dew point.

Venturi scrubbers have high efficiencies because of the intimate contact between the scrubbing liquid and the particulate. Water is sprayed into the throat of the scrubber, where gas velocities are very high and the pressure drop may be as high as 1.27 m (50 in) of water gauge. The turbulence created by these conditions can result in removal efficiencies of 99.8 percent on samples of dust smaller than 5 mm ($2x10^{-4}$ in) in diameter. The high efficiency is not without its price, however; high-energy scrubbers are, in most cases, considerably more expensive to operate than baghouses.

Scrubbers have been proposed as a control device for several streams associated with the Paraho process (Table 4-3).

TABLE 4-3. ESTIMATED PERFORMANCE OF THE SCRUBBER AS A CONTROL TECHNIQUE FOR PARTICULATES

Type of shale moisturizer	Uncontrolled emission rate (kg/hr)	Controlled emission rate (kg/hr)	Control efficiency (%)
Directly heated	4,105	41	99
Indirectly heated	4,384	44	99
Combination	4,175	42	99

Source: Reference 3

Electrostatic Precipitators—

Electrostatic precipitation is suitable for the collection of a wide range of dusts and fumes, and electrostatic precipitators have been successfully employed in a large number of industrial applications since the early 1900's. Electrostatic precipitators are often favored because they are efficient, possess a low maintenance characteristic, can handle large flow rates, require low pressure drop, and generally have lower energy requirements.

The incoming gas stream is ionized by means of a high voltage corona discharge, and the particles in the gas stream are, in turn, ionized by contact with the gas or bombardment from the gas. The induced electric field causes the particles to migrate to the electrode of opposite polarity, where they are neutralized. The dust must be periodically removed from the collecting electrode to maintain maximum collection efficiency, and usually a technique of rapping the plates with a striker is employed. Care must be taken not to re-entrain all the dust that was previously removed. The collected dust is then removed for disposal.

The application of electrostatic precipitators to the effluents from oil shale operations is not well defined at this time. It is expected, however, that they will be employed as a control device on some aspects of oil shale processing. For example, a "wet" electrostatic precipitator has been used for years at the Paraho demonstration plant for combined removal of condensed shale oil product and particulate.

Control of Gaseous Emissions

The gaseous emissions stipulated in the legislation pertain to sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, and photochemical oxidants. Sulfur dioxide emissions were broadened to include hydrogen sulfide, since that is the form from which much of the sulfur dioxide is generated.

Hydrogen Sulfide Removal Processes—

The sulfur content of oil shale can be as high as 7 percent by weight, but a more

typical shale contains less than 1.0 percent. Normally this amount would be considered quite small, but the vast amount of oil shale rock that must be processed to produce significant amounts of oil makes the release of sulfur an important problem. If (a) the yield of the shale is assumed to be 104 l/tonne (25 gal/ton), (b) the size of the operation is assumed to be 50,000 bbl/day, and (c) the release of the sulfur occurs as stated in *A Preliminary Assessment of the Environmental Impacts from Oil Shale Development*, then up to 68.2 tonnes (75 tons) of sulfur in the form of H_2S could be generated each day (6). A potential emission of this magnitude needs to be attenuated by an appropriate control technology. Some persons in the oil shale industry feel that the hydrogen sulfide technology could be transferable from other petroleum applications, and thus, they do not plan to conduct significant research and development studies. The Environmental Protection Agency does not totally dispute this claim, but would like to see the sulfur control technologies successfully demonstrated before agreeing with the premise.

The Stretford Process—The Stretford process is a developed technology with numerous plants in operation in the United States and Europe. The process was developed for coal gas treatment but was found to be transferable to other technologies as well. Hydrogen sulfide is dissolved in a mixture of sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) and the pH of the solution is adjusted to a range of 8.5 to 9.5. The dissolved hydrogen sulfide is weakly ionized ($Ka_1 = 1.0x10^{-7}$) and forms a small amount of hydrosulfide (HS^-). The oxidation of hydrosulfide was originally carried out with air, but the slow reaction kinetics seriously influenced the applicability of the process. Therefore vanadium (V) and sodium salts of anthraquinone disulfonic acid (ADA) were added to promote the oxidation. The hydrosulfide (HS^-) reacts rapidly with the vanadium, allowing the equilibrium, to be pushed to the right.

$$H_2S = H^+ + HS^- \quad [1]$$

This shift allows more hydrogen sulfide to dissolve in the scrubbing solution, and improves the removal efficiency. Hydrogen sulfide concentrations in the exhaust gas of 100 ppmv are achievable with the Stretford Process. The overall oxidation-reduction reaction for the process is:

$$2H_2S + O_2 = 2H_2O + 2S \quad [2]$$

A number of problems are associated with the chemistry of the Stretford scrubbing solutions:

a. Carbon dioxide (CO_2) is usually absorbed in alkaline systems and converted to bicarbonates and carbonates. The Stretford process is no exception, and carbon dioxide scrubbing can somewhat diminish the efficiency of hydrogen sulfide removal.
b. Thiosulfate (S_2O_3) = can be formed in the regeneration cycle. Oxygen reacts with the hydrosulfide (HS), forming thiosulfate. The higher the pH and temperature, the higher the yield of thiosulfate.
c. Vanadium, oxygen, and sulfur complexes are formed if the concentration of hydrosulfide is higher than the vanadate ion can oxidize. Potassium or sodium tartrate has been used to repress this reaction.
d. The scrubbing solution can also be contaminated by gases containing sizable amounts of tars or hydrocarbons. These compounds can cause foaming and reduce the efficiency of the system, or even plug the reactor.
e. Hydrogen cyanide (HCN) is also collected by the Stretford system and that reaction results in thiocyanates that cannot be regenerated. Large concentrations of HCN could seriously affect the system's efficiency and economics.
f. The Stretford process will not remove carbon disulfide (CS_2) and carbonyl sulfide (COS) from the oil shale processing gas stream, and, if present, will present a serious drawback to utilizing this technology. To date, however,

neither compound has been found in sufficiently high concentrations to preclude the use of the Stretford process on oil shale gaseous effluents.

The problems associated with the performance of the Stretford process can usually be overcome by conscientious monitoring of the scrubbing solution. This process has been selected by the developers for use in several of the planned oil shale sulfur abatement programs.

The potential for the application of Stretford technology to the oil shale industry can be seen by examining the data taken from Paraho's recycle gas. During the retort's operating period, hydrogen sulfide samples were taken and those data were summarized in Table 4-4. It shows that the concentration of hydrogen sulfide fluctuated some but the average value of 1614 ppmv was well within the limits of the process.

TABLE 4-4. CONCENTRATION OF H_2S IN THE PARAHO RECYCLE GAS

Date of Test	Institution performing the test	H_2S (ppm)
5/75	Paraho	1,000
5/75	Gulf	1,500
8/75	LFE	750-1,200
1/76	Paraho	2,200
3/76	TRW	2,600
1/77	Paraho	3,000
10/77	TRW	1,214-1,277
11/77	Battelle-Northwest	802-930
1/78	Paraho	2,900
Average	—	1,614

Source: Reference 7.

The average concentration is 1,614 ppmv H_2S, which corresponds well with the 1,000 ppm reported by Colley *et al.* (8).

Union Oil Company has utilized the Stretford process in treating the off-gas from a laboratory-sized retort and experienced some difficulties (9). Union found that the sulfur produced by the process was contaminated by charred hydrocarbons, which made the resale value of the recovered sulfur low. Union also expressed an interest in the chemistry of the Stretford solution, indicating that they were not entirely satisfied with the performance of the standard materials.

These problems notwithstanding, it is still believed that Stretford technology should be applicable to the oil shale industry, but that the process might have to be fine-tuned to fit the individual retorting process.

The economics of the Stretford process as applied to oil shale are unknown. However, based on past experience and 1977 dollars, it is estimated that the investment costs would be \$60 to \$80/28.32 SCMD (\$60 to \$80/1000 SCFD) (1). The operating costs of the system would vary with the purity and resale value of the sulfur being recovered.

The Claus Process—This sulfur-removing process was pioneered in the 1880's and is still practiced today with very little change. The basic reaction is:

$$2H_2S + SO_2 \xrightarrow{\textit{Bauxite Catalyst}} 3S + 2H_2O \qquad [3]$$

After a thermal conversion step, hydrogen sulfide and sulfur dioxide are brought together over a bauxite catalyst at a temperature of about 238° to 370°C (400° to 700°F). The chemical reaction as written in Equation [3] will occur with a conversion rate of 65 to 85 percent. The lower the reaction temperature, the more effective the conversion.

There are problem areas. Upon initial inspection, the process appears to solve two pollution problems simultaneously and would seem to be an ideal control technology for oil shale processing and retorting. However, the application of this process to oil shale technology is not as straightforward as has been hoped, and might require adjustment to each oil shale system.

The most important variable in the process is the ratio of hydrogen sulfide (H_2S) to sulfur dioxide (SO_2) as they appear in the gas stream at the catalytic converters. If the stoichiometry is less than 2:1 (Equation [3]), the efficiency of the process is significantly diminished, and sizable concentrations of hydrogen sulfide are emitted from the converter.

The achievement of the desired concentrations of H_2S and SO_2 can also present problems if the sulfurous feedstock consists of only one of the reactants. Under these conditions, part of the feedstock requires oxidation or reduction before reaction, and maintaining a ratio of 2:1 can be a problem. Because of the pyrolyzing nature of the oil shale processes, the principal sulfur component of the retort off-gas is hydrogen sulfide. However, the Claus Process, as routinely practiced in the refining industry, includes a hydrogen sulfide and the feed stock to the unit can be accurately controlled.

In addition to the proper stoichiometry, the feedstock to the Claus plant requires relatively high concentrations of the sulfurous compounds. Research in this area indicates that the minimum concentration for efficient operation of a Claus plant is 10 percent H_2S (10). Data collected by Radian and Paraho indicate hydrogen sulfide concentrations of about 5 percent and 0.16 percent for the indirect heating mode of operation at the Paraho site (8). This figure is considerably less than minimum estimate, and for a Claus plant to be applicable, a hydrogen sulfide enricher (concentration step) would have to precede it in the treatment scheme. This is common practice in the refining industry.

A third area of concern relative to utilizing Claus plants for oil shale effluent treatment revolves around their reliability. The maintenance and downtime of the units because of the corrosive nature of the sulfur and the gas, plus the plugging problems resulting from condensed sulfur, necessitate back-up capability. Carbon dioxide (CO_2) is usually present in oil shale process gas, and unless it is removed, CO_2 can lead to the formation of carbonyl sulfide (COS). All of these operating problems influence the economics of the Claus system in a negative way.

The end product of a Claus system is called a tail gas, and it usually contains sizable concentrations of residual H_2S. If incinerated, emissions of 1.0 to 3.0 percent sulfur dioxide (SO_2) are released. Concentrations as high as 0.3 percent would violate most air standards; thus some form of additional tail gas treatment would be necessary.

The sulfur produced by the Claus system has been rated higher in quality than that produced by the Stretford process, but before this factor can be an asset, there must be a market for the produced sulfur.

In summary, the application of a Claus plant to oil shale operations would depend on the operating characteristics of the particular retorting process. If the 10 percent hydrogen sulfide concentration is the minimum required for economical operation, and if the limited amount of published operating data is representative, most oil shale plants would have to install some form of hydrogen sulfide enrichment system upstream of the Claus plant, and tail gas treatment downstream.

Claus Plant Tail Gas Cleanup. The tail gas from a Claus plant usually contains sizable concentrations of H_2S and SO_2. With sulfur emission regulations being quite severe, especially in the oil shale area of Colorado, it is likely that the developers would be required to treat the Claus plant effluent for the removal of sulfurous compounds. Processes developed specifically for Claus plant tail gas treatment (and their removal effectiveness) that may find some application in the oil shale industry are SCOT (300 ppmv before incineration), Beavon (300 ppmv, no

incineration), and the Institute Francais du Petrok (IFP) (2500 ppmv before incineration).

The SCOT (Shell Claus off-gas treating) process was designed specifically to clean up the off-gas from a Claus Plant. The off-gas is heated with a reducing gas or hydrogen, and the mixture is passed through a bed of cobalt-molybdate catalyst where within equilibrium considerations all the compounds containing sulfur are reduced to H_2S. The H_2S is routed to an absorber, where the gas is dissolved and concentrated. Heat is applied to the absorbing solution, and the concentrated H_2S that is liberated from the absorbing medium is returned to the Claus plant.

Both the SCOT and the Beavon processes are adversely affected by high concentrations of CO_2. Since oil shale gaseous emissions are projected to be rich in CO_2, additional operating constraints such as larger recycle gas streams, more fuel consumption, and perhaps steam injection may be necessary.

In the Beavon process, the tail gas from the Claus plant is heated by mixing it with hot combustion products of fuel gas and air. The mixture is passed through a catalyst, where all the sulfur compounds are converted to H_2S. The H_2S-rich gas is cooled by a slightly alkaline buffer solution and then treated by a Stretford unit.

The basic reaction used in the IFP process is the same as that used for the Claus process, except that it occurs in a liquid phase rather than the gaseous phase. The liquid phase is composed of a polyalkylene glycol and a 5-percent by weight catalyst, orthophthalic acid monopolyethylene glycol ester. Hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) are very soluble in this system and, if the operating parameters are held at optimum conditions, efficient conversion to sulfur results. The most important operating variable, like the Claus plant, is that of the H_2S/SO_2 ratio, which must be kept at or above 2:1. The IFP process has several advantages that could make it attractive to the oil shale industry. First, the process shows flexibility in being able to accommodate wide changes in incident loading while being able to maintain constant design conversion rates. Second, the gas can be treated at higher temperatures than other processes, thus reducing the sensible heat loss.

As noted earlier, the ratio of H_2S to SO_2 is very important. If this ratio dips below 2:1, the system can fail completely, requiring a complete replacement of the scrubbing liquor.

Other Applicable Control Systems—Selexol and other physical absorption processes are similar to the IFP system in that they are liquid-based, but they differ in the fact that the hydrogen sulfide is desorbed essentially unchanged in these systems.

Methanol was the initial solvent used, but it has given way to other solvents that have been specifically designed for sulfur removal. Perhaps the most widely known of these systems is Allied Chemical's Selexol solvent process. Dimethyl ether of polyethylene glycol (DMEPG) is a solvent that can be used for the removal of acid gases and for the selective absorption of H_2S. The H_2S can be desorbed and yield a gas stream suitable for the Claus plant feed.

The physical absorption systems can also treat other undesirable gases generated during oil shale retorting. Gases such as COS, CS_2, mercaptan, and thiophene can be dissolved, but they are not reduced to H_2S, and they are not released during the regeneration step. A buildup of these contaminants can adversely affect the efficiency of operation, but today very little evidence has been presented to indicate that any of the above pollutants are present in appreciable concentrations in retort off-gases.

More than 40 selective solvent plants have been built, and it seems likely that the direct application of this technology to oil shale emissions is possible.

Sulfur Dioxide Removal Processes—

The magnitude of the sulfur dioxide (SO_2) emission problems depend on degree of prior sulfur clean-up (H_2S treatment) and the type of fuel used in the processing. Most developers have planned to use desulfurized fuel to meet their heating and air

pollution control needs, and therefore most of the sulfur emissions are generated in the retorting of the shale. As stated earlier, the amount of sulfur liberated by the processing of the shale can be significant, and treatment will probably be required. A Claus plant can recover better than 95 percent of the hydrogen sulfide but a sizable amount of sulfur dioxide (SO_2) and H_2S will also be liberated by the process if tail gas processes are not used. The following technologies are presented to address the problem of SO_2 emission.

Wellman-Lord Process—The Wellman-Lord SO_2 recovery process is a very versatile technology and has enjoyed widespread acceptance among many industries dealing with SO_2 control. It is anticipated that the process will be adaptable to the oil shale industry. This contention is supported by the fact that Colony planned to use this SO_2 treatment process on their emissions of tail gas after Claus (2).

The basic chemical reaction of the process involves the conversion of sulfite $(SO_3)^=$ to bisulfite $(HSO_3)^-$ and can be summarized in Equation [4]:

$$SO_2 + Na_2SO_3 + H_2O \quad 2NaHSO_3 \qquad [4]$$

The bisulfite solution is pumped to an evaporator and heated by steam. The heating reverses the reaction and liberates a concentrated stream of SO_2 that can be used for making either sulfur or sulfuric acid. The sodium sulfite produced by heating is dissolved and recirculated to the absorption column.

The Wellman-Lord process has a number of drawbacks that influence the economics of the process. Oxidizing agents such as sulfur trioxide can oxidize the sulfite $(SO_3)^=$ to sulfate $(SO_4)^=$ and reduce the efficiency of the process. It has been suggested that these problems can be minimized by a prescrubber and by treating a fraction of the absorbing solution for sulfate removal; but both add to the costs of the process. Second, compared to other SO_2 treatment systems, the capital costs are higher, as are the energy requirements for everyday operation.

On the other hand, the Wellman-Lord process is considered to be a second-generation SO_2 removal process. The amount of sludge produced is considerably less, and the scaling tendencies that occur under alkaline conditions have been reduced. This SO_2 process is considered to be an advanced technology transferable to the oil shale industry with little additional research and development.

Citrate Process—The Bureau of Mines has developed an SO_2 treatment process for acid gases that seems to have a very promising application to the oil shale industry. Pilot-plant tests have been successfully carried out on gas containing 5000 ppmv of SO_2 from a smelter and a coal-fired boiler.

Sodium citrate/citric acid is an excellent buffer system and maintains an optimum pH for SO_2 absorption at 4.5. Sodium thiosulfate ($Na_2S_2O_3$) is added to facilitate the formation of the $(SO_2 - S_2O_3)^=$ complex and improve the efficiency of the system. Hydrogen sulfide is generated onsite and added to the system, with the result being an in-solution reaction equivalent to a gas phase Claus reaction. Hydrolysis of the dissolved sulfur dioxide yields HSO_3^-, and the bisulfite reacts with the H_2S in the following reaction:

$$HSO_3^- + H^+ + 2H_2S \rightarrow 3S + 3H_2O \qquad [5]$$

The sulfur is separated by flotation, and the unreacted portion of the thiosulfate absorbing solution is returned to the absorber. A natural consequence of the reaction is the oxidation of thiosulfate $(S_2O_3)^=$ to sulfate $(SO_4)^=$. To maintain acceptable levels of thiosulfate, a portion of the absorbing solution is cooled to form a concentrated sulfate solution that eventually precipitates as $Na_2SO_4 \cdot 10H_2O$. The crystals are removed by filtration, and the liquor is returned to the process.

The economics of the process are still undefined because of lack of data from commercial-sized units, but it has been suggested that the costs will be competitive with limestone scrubbing.

The application of this system to oil shale processes is very attractive. Previous work had necessitated the onsite generation of H_2S as one of the reactants.

Estimates of many of the off-gases of the various oil shale processes already contain this component in sufficient concentrations to sustain the reaction. It naturally follows that if SO_2 control is necessary, a portion of the retort off-gas could be diverted, and both sulfur emission problems could be handled simultaneously.

Alkali Scrubbing—Lime/Limestone Scrubbing. The oldest and probably best known of the alkali scrubbing systems is limestone process. A nonregenerative slurry of 5 to 10 percent of calcium oxide or carbonate is circulated through a scrubber, wherein the slurry contacts the flue gas and removes the SO_2 as calcium sulfite or sulfate. Although the process has been studied in great detail for over 30 years, the chemical reactions occurring in the carbonate slurry are still not completely defined. Basically, the reactions involve the absorption of SO_2, hydrolysis to sulfurous acid (H_2SO_3, Ka = 1.7×10^{-2}), ionization to sulfite $(HSO_3)^-$, and reaction with calcium to form calcium sulfite ($CaSO_3$) and calcium sulfate ($CaSO_4$).

It has been suggested that because of the lack of predictability of the limestone scrubbing chemistry and the effect of different flue gas characteristics, results of pilot-scale activities are required for each new potential application. Oil shale operations would fall into this category, and it might be anticipated that each process would need to be evaluated individually before limestone scrubbing could be optimized.

In operations where the heat content of the product gas is low or where it is decided not to utilize its heat content, gas combustion followed by alkali scrubbing may be the best economic solution to the sulfur dioxide emission problem. Best estimates by the utilities is that limestone slurry scrubbing will cost $50 to $70/kw to install and 3.9 to 5.5 mills/kw-hr to operate (11). These costs may be difficult to translate into costs for the oil shale industry, but the fact that they are the lowest of the competing SO_2 removal processes is of primary importance.

Regardless of how advanced the alkali scrubbing technology has become, it is not without its problems. The question of the system's reliability has surfaced on more than one occasion, but recent successful tests have helped to reduce this criticism. However, the problem of large volumes of scrubber sludge has not been resolved .

Dual Alkali. The Dual Alkali process, as the name suggests, is a system that incorporates several alkaline compounds for scrubbing sulfur dioxide out of stack gases. The process has several potential advantages over the conventional lime slurry scrubbers. Higher reliability coupled with lower maintenance and improved sludge characteristics and capital costs are the features that could make it attractive to the oil shale industry for sulfur dioxide removal.

The process uses sodium hydroxide (NaOH) and sodium sulfite (Na_2SO_3) to absorb the SO_2 from the gas and convert it to sodium bisulfite ($NaHSO_3$). The scrubbed gases pass on to the stack, and the scrubbing solution is circulated to the regeneration tank. Calcium is added in the form of lime or limestone and reacts with the bisulfite to regenerate sodium hydroxide and sodium sulfite. The precipitated calcium solids are removed in a clarifier.

The costs of the double alkali systems are difficult to estimate for the oil shale industry and can only be compared to other industrial applications and utilities. Green (12) has estimated the capital costs of the double alkali systems at $86.87 to $819.31/cmm ($2.46 to $23.2/cfm) for industrial applications and $43.2 to $189.0/kW for electric utilities. The operating costs were also reported as 5.5 to 6.5 mills/kWh.

The environmental aspects of the sludge handling problems are not as severe with double alkali as with limestone scrubbing; however, the volume of sludge is still significant and could cause problems if not handled properly.

Magnesium Oxide. The magnesium oxide process is similar to other alkaline flue gas desulfurization processes in that the reaction products are bisulfite and sulfate. The process is different in that the magnesium oxide used for the scrubbing solution has a higher affinity for SO_2 than lime, and the process is regenerable.

Magnesium oxide hydrolyzes to form magnesium hydroxide, $Mg(OH)_2$, and the hydroxide $(OH)^-$ reacts with the SO_2 to form magnesium sulfite ($MgSO_2$) or sulfate ($MgSO_4$). Both reaction products have a low solubility and can be easily crystalized out of solution. The magnesium sulfite/sulfate is routed to a regeneration calciner, where heat and coke (a reducing agent) are added. The desulfurization reaction is reversed, and a concentrated stream of SO_2 (10 to 20 percent) is liberated. The gas can be made into sulfuric acid or sulfur, and the calcined magnesium (MgO) is returned to the make-up slurry.

Philadelphia Electric has reported capital costs for a magnesium oxide system on a 120-MW boiler at $90/kW and operating costs at 4.7 mills/kWh (13).

The main environmental problems deal with the manufacture of sulfuric acid and the process byproducts.

Nahcolite Ore—Nahcolite is a naturally occurring mineral that contains 70 to 90 percent sodium bicarbonate. If the bicarbonate is subjected to heat, carbon dioxide is driven off and the remaining sodium carbonate (Na_2CO_3) is available for reaction with sulfur dioxide.

There are several important implications of sulfur dioxide control by nahcolite that should be investigated by the oil shale industry. First and most important is that sizable amounts of nahcolite are available near some of the oil shale deposits, and this resource could offer an economic advantage to the sulfur control strategy for that oil shale process. A second advantage of the system is that the nahcolite is injected dry, and the water pollution problems are thereby minimized. A third plus for the system is its simplicity. The simpler a control system, the smaller the capital, operating, and maintenance costs, generally.

To date, operations of the nahcolite system have been carried out on a small scale, and the results should be viewed in that light. Preliminary data indicate that capital and operating costs may be lower than limestone scrubbing.

NO_X Control—

Oxides of nitrogen are a natural product of the combustion of conventional fuels, and they are expected to be a significant air pollution emission relative to oil shale development. The emission of these substances contributes to secondary chemical reactions in the atmosphere that result in the formation of photochemical oxidants. In addition, the emissions themselves are undesirable from a physiological point of view.

When compared to ordinary laboratory conditions, the requirements for NO_X formation are very severe. Temperatures in excess of 980 °C (1,800 °F) are needed to supply the endothermic energy necessary to break the nitrogen to nitrogen triple bond (225 kcal). However, the conditions experienced by reactants in or near a flame are very extraordinary, and sufficient energy is available to rupture the nitrogen molecule. Unburned oxygen also experiences these conditions, and when the two gases are in proximity in the flame, they will form NO_X according to the equation:

$$N_2 + O_2 \rightleftharpoons 2NO \qquad [6]$$

Control of the NO_X problem is similar to the sulfur problem in that it can be approached in several ways. If combustion conditions can be properly controlled, the amount of nitrogen and/or oxygen available for reaction can be minimized, and the amount of NO_X produced can be kept to a minimum. A second option would be to disregard combustion conditions and clean up the off-gases.

It is common knowledge that engineering solutions designed to minimize an air pollution problem at the source are more effective than retrofitting control devices to a particular process. The oil shale industry is still in the pilot-plant phase of most of its systems and it is still in a position to design low furnace emissions of NO_X into commercial-scale units. In the future, if the need arises for additional NO_X control, appropriate retrofit control systems could be added.

The following discussion centers on combustion modifications and control technologies for NO_X abatement.

Combustion Modifications. Several approaches exist to modifying the combustion conditions to result in lower emissions of oxides of nitrogen. The specific design of a combustion chamber can greatly influence the amount of NO_X formed. The tighter the burning pattern, the more intense the heat flux and the greater opportunity for oxides of nitrogen to be formed. In general, it has also been found that the more turbulent the combustion conditions, the higher the NO_X emissions. Research has been undertaken to minimize the NO_X emissions, but in most cases, it has resulted in lower combustion efficiency.

Two-Stage Combustion. To address the problem of combustion efficiency and NO_X emissions, a two-stage burning system was developed. In the first stage, only 85 to 95 percent of the stoichiometric air needed for combustion was supplied. The remaining air was injected above the burners to complete the combustion. Systems of this type have reduced NO_X emissions by about 50 percent.

Tangential Firing. As stated earlier, the interaction between closely-spaced burners tends to elevate the NO_X emissions. Tangential firing removes some of the burner proximity, and firing is carried out on a tangent to a circle at the center of the furnace. The result is less flame interaction, more radiant heat transfer to the cooling surface, and lower concentrations of NO_X produced.

Flue Gas Recirculation. Flue gas recirculation has been applied to combustion sources for NO_X reduction. The gas has some sensible heat associated with it and does not quench the reaction temperature as dramatically as excess air thereby allowing the kinetics of the formation reaction to be reversed toward molecular nitrogen and oxygen. The recirculated gases are lower in oxygen than excess air and present less of the reactant necessary for the formation of NO_X. There are, however, some problems with flame stability, which have limited the application of this technique to NO_X reduction.

Fuel Modifications. In addition to atmospheric nitrogen, fuel-bound nitrogen can be a major contributor to the NO_X problem. Any fuel burned onsite should be of such quality as to assure low oxides of nitrogen emissions. Some operators have suggested the use of a portion of the shale oil as a fuel in the process itself. If this option is exercised, pretreatment of the oil should be done to reduce the high levels of nitrogen contained in the shale oil.

Low NO_X Burners. Low NO_X burners have reduced the thermal and fuel-derived NO_X emissions by various methods. One method employs a thin flame and good mixing to promote rapid combustion, thereby reducing levels of NO_X. A second method utilizes an internal recirculation of the combustion gases to reduce NO_X emissions, and a third method uses stratified combustion. The combination of one or more of these techniques is usually employed in the low NO_X burners available on the market today. The performance of these units usually results in NO_X emissions low enough to be in compliance with the air pollution regulations, but data from operating experience are limited.

Control Technologies. If sizable quantities of NO_X are formed as a result of combustion or processing of oil shale, removing them by some form of add-on NO_X control technology could be a reasonable alternative. To date, however, very little has been done in this area, because it is generally believed that NO_X emissions are not going to be a very significant problem. It may be possible to combine NO_X abatement with SO_2 control, and it seems logical, from a presumed cost-effective viewpoint, that the problem should and could be approached in this manner.

Limestone Scrubbing. The limestone slurry employed for SO_2 control will also remove NO_2 or an equimolar mixture of NO/NO_2 from flue gases. The process is the same as outlined for alkaline scrubbing of sulfur dioxide, except that an additional end product, calcium nitrate, is quite soluble in solution and will build up. Work done at Wisconsin Electric's Oak Creek power plant (12) indicated about a 20-percent reduction in NO_X emissions using limestone slurry scrubbing.

Chiyoda Thoroughbred 102 Process. The Chiyoda Thoroughbred 102 process utilizes ozone to oxidize NO_X to NO_2 and thereby enhances its absorptive properties. After oxidation, the flue gas is introduced into a packed tower and treated with dilute sulfuric acid containing a ferric catalyst. Pilot-plant studies have indicated NO_X removal efficiencies of 60 percent. Again, the build-up of calcium nitrate could be an operational problem.

Selective Catalytic Reduction Processes. Several nitrogen oxide processes have been developed by the Japanese for the selective reduction of NO_X. The Kurabo process mixes the flue gas with ammonia and reacts the mixture over a bed of copper and alumina. Pilot-plant data indicate about a 90 percent conversion of NO_X to N_2. The Hitachi shipbuilding process and the Sumitomo process both use ammonia injection and subsequent reduction over a metal catalyst. Based on experience with these systems, a number of very large denitrification plants are being built.

Air Emission Controls for Hydrocarbons and Carbon Monoxide—**Prepared for Dale Denny and Bruce Tichenor by Radian Corporation**

This section describes hydrocarbon and carbon monoxide emission control technologies that are currently applied to distillation, cracking, and other process sources in natural crude oil refining and that might be applied in oil shale retorting or shale oil refining. The four basic approaches to hydrocarbon and carbon monoxide control that are discussed here include: destruction, recovery and recycling, containment, and conversion.

Direct flame incineration and catalytic incineration are two methods of control by destruction. These control techniques are applicable for combustible hydrocarbons that do not have a high recovered product market value, or that are too dilute to be economically recovered. The recovery and recycling control technologies include compression-condensation, condensation, and adsorption systems. Each of these systems allows recovery of the controlled hydrocarbons; they are most economical for hydrocarbons with a high market value. The third approach to hydrocarbon control is vapor containment, the principle behind adsorption systems. In adsorption systems, hydrocarbon emissions are trapped on the surface of an adsorbent such as activated carbon. These adsorbed hydrocarbons must later be removed or recovered by one of the other hydrocarbon emission control technologies. The last approach, conversion, involves utilizing the shift conversion process to react carbon monoxide with steam to form carbon dioxide and hydrogen.

In addition to the above control technologies, fugitive emission controls are also discussed.

Direct Flame Incineration—Emission control by direct flame incineration (also termed thermal combustion) is widely used to control combustible gaseous materials such as hydrocarbon vapors, aerosols, and particulates. These systems are also used extensively in removing odors and in reducing the opacity of visible plumes from ovens, dryers, stills, cookers, and refuse incinerators. The principle of operation consists of ducting the exhaust process gases to a combustion chamber that employs direct-fired burners to combust the process gases to their appropriate oxides. A well-designed plant flare system is a good example of control by direct incineration.

In direct flame incinerators, the combustible process gases are delivered to a refractory-lined incinerator by either the process exhaust system or by a self-contained blower. If the process gases do not have a sufficient heating value to sustain combustion, a metered fuel stream is combined with a portion of the process gases in the burner and then allowed to combust in the combustion zone. If the process gases have a high heating value, air must often be introduced at the burner instead of fuel. The remaining process gases are then introduced into the mixing zone where they are combusted. For maximum destruction of contaminants, the combusted gases are retained briefly in a reaction zone where additional oxidation

occurs before being vented to the atmosphere. When sized and operating properly, most direct-flame incinerators will obtain 99+ percent destruction of hydrocarbon compounds. Most units are sized to operate at efficiencies between 95 and 99 percent.

Many components in the process gas stream form hazardous combustion products such as nitrogen oxides, sulfur oxides, hydrogen chloride, hydrogen fluoride, trace elements, and particulates. When required, the most common means of controlling these secondary pollutants is aqueous solution scrubbing. Noise can also be a problem in high turbulence incinerators and is normally reduced through the application of standard acoustical technology.

Catalytic Incineration—Catalytic incineration is a widely used alternative to direct flame combustion for the control of combustible gaseous materials such as hydrocarbon vapors and aerosols. These systems are also used extensively in removing odors and in reducing the opacity of visible plumes from ovens, dryers, stills, cookers, and refuse incinerators. The principle of operation consists of ducting exiting process gases to an incineration chamber filled with a catalyst. Upon contact with the catalyst, the selected components of the process gases are oxidized. The use of a catalyst allows more complete combustion at lower temperature, resulting in lower fuel costs and more economic materials of construction. However, catalysts are generally selective and may not destroy as many components of the process gases as direct flame incineration. In addition, because of catalyst fouling and poisoning, pollutants must be free of smoke, particulates, and heavy metals and other catalyst poisons.

When sized and operated properly, catalytic incinerators will obtain 95 to 99+ percent destruction of selected compounds. Many catalysts are highly selective as to the reactions they promote. Although relatively reliable and simple to operate, catalytic incinerators are more complex than direct flame incinerators. Accurate, dependable fuel and/or air controllers are required to maintain close control of catalyst bed temperature in the midst of highly variable process gas heating values and flow rates. Catalyst beds are also highly susceptible to fouling and poisoning by halogens, heavy metals, and sulfur species. As a result, catalyst beds must be routinely cleaned and eventually replaced.

As in direct incineration, aqueous scrubbing may be required to remove secondary pollutants resulting from combustion. Likewise, standard acoustical technology may be required in high turbulence incineration.

Compression/Condensation—Compression/condensation systems are desirable for recovering concentrated hydrocarbon vapors from relatively small gas streams. The compression/refrigeration/absorption (CRA) recovery system is based on the absorption and condensation of compressed hydrocarbon vapors with cool liquid from storage. Compression/refrigeration/condensation (CRC) vapor recovery systems are based on the condensation of hydrocarbon vapors by compression and refrigeration.

In both systems, incoming vapors are first passed through a saturator, where they are sprayed with fuel to insure that the hydrocarbon concentration of the vapors is above the explosive limit. This step is performed as a safety measure to reduce the hazards of compressing hydrocarbon vapors. The saturated vapors are then compressed and passed through a condenser or heat exchanger. In the CRC system, most of the hydrocarbons are condensed in a condenser. Essentially hydrocarbon-free air is vented from the top of the condenser. In the CRA system, the compressed vapors are cooled in a heat exchanger before entering an absorber. In the absorber, the cooled vapors are contacted with chilled liquid product drawn from storage and are condensed and absorbed into the liquid. The remaining air, containing only a small amount of hydrocarbons, is vented from the top of the absorber.

The vapor collection efficiencies of both CRA and CRC systems are dependent on the inlet hydrocarbon concentration. Current CRA systems can surpass 90 percent recovery for inlet hydrocarbon concentrations of greater than 20 percent by volume. The CRC units can recover 96 percent of the hydrocarbons in saturated gasoline vapors, and 88 to 90 percent in subsaturated gasoline vapors.

No secondary pollutants are generated, but vent streams from a compression/condensation system may require incineration.

Condensation—Condensation is usually applied in combination with other air pollution control systems. Condensers located upstream of afterburners, carbon beds, or absorbers can reduce the total load entering the more expensive control equipment. When used alone, condensation often requires costly refrigeration to achieve the low temperatures needed for adequate control.

Condensers employ several methods for cooling the vapor. In surface condensers, the coolant does not contact the vapor or condensate; condensation occurs on a wall separating the coolant and the vapor. Most surface condensers are common shell-and-tube heat exchangers. The coolant normally flows through the tubes, and the vapor condenses on the outside tube surface. The condensed vapor forms a film on the cool tube and drains away to storage or disposal.

Contact condensers usually cool the vapor by spraying a liquid at ambient temperature or slightly cooler directly into the gas stream. Contact condensers also act as scrubbers in removing vapors that normally do not condense. The use of quench water as the cooling medium results in a waste stream that must be contained and treated before discharge.

Equipment used for contact condensation includes simple spray towers, high-velocity jets, and barometric condensers. Contact condensers are generally less expensive, more flexible, and more efficient in removing organic vapors than surface condensers. On the other hand, surface condensers recover marketable condensate and present no waste disposal problem. Surface condensers require more auxiliary equipment and have greater maintenance requirements.

Condensers have been widely used (usually with additional control equipment) in controlling organic emissions from petroleum refining, petrochemical manufacturing, dry cleaning, degreasing, and tar dipping. Condensation processes with significant refrigeration requirements are being used for the recovery of gasoline vapors at bulk gasoline terminals and service stations.

Control effectiveness depends on hydrocarbon contaminants and condenser operating parameters. In the removal of gasoline from saturated vapors, removals of about 99 percent can be obtained. Efficiencies for recovering heavy hydrocarbons with nonrefrigerated condensers can exceed 99 percent.

Secondary environmental problems include the disposal of noncondensibles and the treatment of the liquid effluent from contact condensers. The noncondensible gas effluent can be vented to the atmosphere or further processed (e.g., incinerated), depending on the effluent composition. The liquid effluent from contact condensers must be treated or separated before disposal or reuse.

Absorption—Absorption is the process by which certain constituents of a gas stream are selectively transferred to a liquid solvent. Absorption may be purely physical, with the solute simply dissolving in the absorbent, or it may be chemical, with the solute chemically reacting with the absorbent or with reagents dissolved in the absorbent. Typical absorption equipment includes plate towers, packed towers, spray towers, and venturi scrubbers. After absorption, the vapor-laden absorbent may be regenerated, used as make-up to nearby processes, or disposed. The most common absorbents used for the removal of hydrocarbons are nonvolatile petroleum liquids ("lean oils"). Other commonly used absorbents are water and aqueous solutions of oxidizing agents, sodium carbonate, or sodium hydroxide.

Several lean oil absorption systems are in service at pipeline terminals for the control of loading emissions. These systems treat gas flows of less than 0.5 m^3/sec

(1,000 scfm). Absorption is quite commonly used in petroleum and petrochemical operations for treating gas streams with relatively high concentrations of organic vapors. Organic vapors removed include alcohols, ketones, amines, glycols, aldehydes, phenols, organic acids, and light hydrocarbons.

Control effectiveness depends on inlet hydrocarbon concentration. Lean oil absorption systems routinely achieve removal efficiencies in excess of 95 percent for inlet hydrocarbon concentrations of 24 percent or greater. Lean oil absorbers have little impact on methane. Higher removal efficiencies are achieved with larger oil flow rates attained at greater cost.

Secondary emissions depend on the fate of the solute-laden absorbent. If the absorbent is regenerated, a regeneration gas is produced that consists of the stripped solute and the stripping gas (usually steam or air). If this regeneration gas stream is incinerated, hazardous combustion products may be produced. If the stripped vapors are condensed, the condensate may pose a liquid disposal problem. If the solute-laden absorbent is simply disposed, further treatment or neutralization is required. Another secondary pollutant is absorbent carried into the "clean" exit gas.

Adsorption—Adsorption is the process by which components of a gas are retained on the surface of granular solids. The solid adsorbent particles are highly porous and have a very large surface-to-volume ratio. Gas molecules penetrate pores of the material and contact the large surface area available for adsorption. Vapors retained on the adsorbent are subsequently desorbed. Both the vapors and the adsorbent can be recovered for reuse.

Activated carbon is the most widely used adsorbent because it can selectively adsorb hydrocarbons from gases even in the presence of water. Because of their strong affinity for water, other adsorbents such as silica gel, activated alumina, and molecular sieves are better suited for the treatment of "dry" gases. Soda lime alone or combined with activated carbon has also been used to adsorb certain hydrocarbon vapors.

After completion of the adsorption cycle, the used adsorbent may be either regenerated or replaced. Regenerative systems reactivate the adsorbent by desorbing the adsorbed vapors. The desorbed vapors may then be reused or disposed. Nonregenerative systems usually return the used adsorbent to the vendor for regeneration. The adsorbent is most commonly regenerated by steam stripping, although air stripping and vacuum stripping are also used. The steam and pollutant vapors may then be directly incinerated or routed to a condenser, after which they can be separated by gravity decantation or by distillation. Although two-unit adsorber systems have been proven efficient, a third unit may be desirable to allow a freshly regenerated bed to cool after steam stripping.

Adsorption is highly efficient (in excess of 99 percent) in removing hydrocarbons. The process is technically feasible for controlling hydrocarbon emissions from: (a) tail gases from sulfur recovery processes, (b) streams produced in the regeneration of acid gas removal systems or, (c) other waste streams containing hydrocarbons. However, adsorption is normally used for treating streams of low hydrocarbon concentrations. Particulates and condensibles must be removed in a pretreatment step.

Secondary pollutants arise during gas pretreatment and regeneration. Particulates and condensibles in the inlet gas to the adsorber must be removed in a pretreatment step; the removed particulates and condensibles must then be safely disposed. Regeneration gases typically consist of steam, nitrogen, oxygen, and desorbed vapors. If the regeneration gas stream is incinerated, hazardous combustion products may be produced. If the steam and vapors are recovered by condensation and separation, the water stream may require further treatment because of the presence of soluble hydrocarbons.

Shift Conversion—In the shift conversion process, steam is reacted with carbon monoxide to form carbon dioxide and hydrogen. This endothermic process is con-

ducted in a fixed-bed catalytic reactor. External cooling is usually employed between multiple catalyst beds to maintain an optimal temperature range for the equilibrium conversion. Excess carbon dioxide formed in the shift conversion process can be separated and vented to the atmosphere.

The shift conversion process is used to remove carbon monoxide formed during steam reforming or partial oxidation methods for hydrogen production; it is also used to remove carbon monoxide from acid-gas streams. It would be applied when CO emissions were high enough to make it cost effective.

There are no secondary pollutants from the shift conversion process. However, if the chromium/iron oxide catalyst used in the shift conversion is regenerated rather than sent to disposal or metal recovery, impurities that blind or poison the catalysts may be released to the atmosphere. The most likely types of contaminants, in addition to hydrocarbons, will be trace elements such as nickel, vanadium, iron, arsenic, and selenium, which may be present in the feedstock gases.

Fugitive Emissions—In contrast to the previous air pollutant categories, which are classified by pollutant type, fugitive emissions are defined by their origins.

Fugitive hydrocarbon emissions have two principal sources: leaks and evaporation from open surfaces. Unlike fugitive dust, which arises in a diffuse pattern over an area, many fugitive hydrocarbon losses occur from specific points, such as valves, flanges, pump seals, compressor seals, and drains. However, these sources are so numerous in most plants processing hydrocarbon liquids that the emissions can be considered diffuse for practical purposes.

Fugitive emission controls are primarily based on good plant design and maintenance procedures rather than equipment. Plant design items that help reduce fugitive emissions include:

Confinement, diversion, and flaring

Dual seals

Sparing of critical pumps, compressors, and valves

Use of surface condensers rather than direct-contact units (barometric or low-level jet)

Probably the most important item in preventing fugitive emissions is the institution of a good preventive maintenance program. Such a program would include making use of outages and normal downtimes for repairing and testing potential fugitive emission sources on a systematic basis.

WASTEWATER TREATMENT CONTROLS

Thomas Powers

The chief EPA concern about environmental control technology for oil shale wastewaters is that the environment be protected by the best practicable methods available at the time of implementation. Water sources, their quantities and characteristics, water uses, wastewater treatments particularly for reuse, and final water disposal alternatives must be considered to arrive at an optimum environmental control system for each process facility.

Existing water pollution control technology may be applicable to most of the waste streams encountered in oil shale processing. However, several of the more highly polluted wastewaters will require research on process methodology to ensure that priority pollutants and toxics are removed to ensure safe reuse or discharge. Process wastewaters, spent shale compaction wastewaters, and mine dewatering wastewaters may pose significant problems that will have to be resolved before commercialization by the industry. The data used in this evaluation of treatment controls for the oil shale industry are based on oil shale process pilot-plant studies and projections by developers.

Water pollution problems at a specific site will depend on the oil recovery process used, the quality and quantity of available raw water, and final reuse or disposal objectives. Figure 4-1 shows a generalized water flow and options.

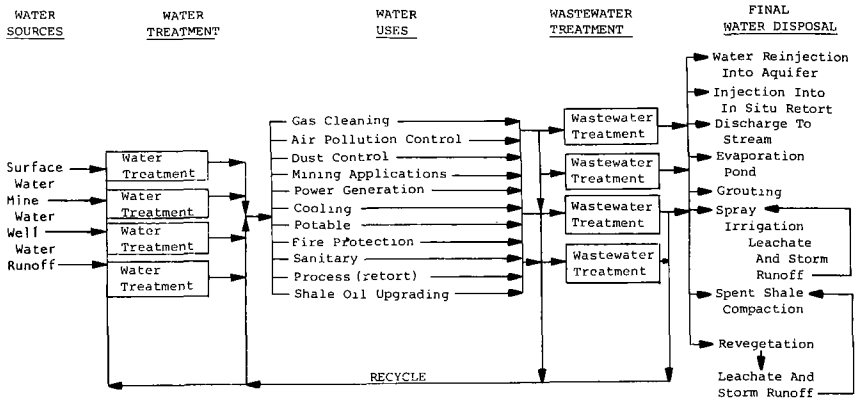

Figure 4-1. Oil shale water and wastewater utilization.

For treatment, options must be designed to produce water acceptable for use in the process (recycled wastewater) or water acceptable for discharge, or both. Typical techniques available for this application are as follows:

Physical:

Sedimentation
Flotation
Filtration-Microscreening
Ammonia Stripping
Evaporation Ponds
Carbon Adsorption

Chemical:

Ion Exchange
Coagulation
Oxidation-Reduction
-Ozonation

Biological:

Activated Sludge
Trickling Filter-Rotating
Biological Contactor
Aerated Lagoons
Oxidation Ponds
Anaerobic Filters

Wastewater Treatment Methods

As additional data on waste streams become available, it will be possible to determine the optimum process for a specific application. In some cases, it may also be necessary to apply tertiary methods for the removal of refractory organics, residual nutrients, trace metals, dissolved solids, or trace quantities of organics that present a problem in either reuse or discharge of the wastewater. Tertiary methods may play a role in permitting maximum utilization and minimum discharge of water by the oil shale industry.

Wastewater Sources, Quantities, and Characteristics

The utilization of water and wastewater for oil shale development is forecast as a complex problem. The optimum system would be one with a zero discharge, that is, total recycling. To project such a system applying these principles to each oil shale process, it is necessary to identify and quantify the raw water supply and aqueous wastes from oil shale processes. The major wastewater streams from oil shale processing are summarized in Table 4-5.

Process Wastewaters from Retorting Operations—

Process wastewaters have been classically defined by EPA as . . ."any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product or waste product" (15). The term "process wastewater pollutants" means pollutants present in process wastewater.

The characteristics of wastewaters produced during retorting (Operations 1a through 1i in Table 4-5) vary considerably. Retort wastewaters can, however, be generally characterized by the use of water quality parameters (as in Table 4-6), organics content (Table 4-7), and trace element content (Tables 4-8 and 4-9). The quantities of the constituents listed in Tables 4-6 through 4-9 are the determining factors in the choice of treatment method or methods used to achieve water quality design.

Shale Oil Upgrading Wastewaters—

Oil cooling wastewater (2a through 2e in Table 4-5), upgrading process wastewater (2f through 2i), and wash waters (2j through 2m) constitute the major process discharges from upgrading operations that convert shale oils to refined products. Except for the rates given in Table 4-5, little information is available on oily cooling wastewaters and upgrading process wastewaters. At present, Union plans to process the sour water stream in the ammonia separation unit for the removal of light hydrocarbons by degassing and the removal of hydrogen sulfide and ammonia by stripping. Wastewater reuse is forecast by other developers as well and will ultimately be demonstrated on full-scale facilities. Portions of the sour water have been characterized, but information is generally not available as to the specific trace organics and toxic substances that could be present to cause problems.

Regarding the characteristics of wash wastewaters, the Union Oil Co. has estimated the generation rates of some constituents in boiler blowdown for a 50,000-bbl/stream day crude shale oil plant (Table 4-10) (26).

The Union Oil Co. has also described the characteristics of wastewater from backwashing and water rinsing operations upstream of treatment for boiler feedwater by ion exchange (Table 4-11) and the characteristics of wastewater from regeneration of ion exchange resins (Table 4-12) for a 50,000-bbl/stream day plant (26).

Wastewater from Process Gas Cleaning and Air Pollution Control—

Air pollution control technologies are expected to use water for removing pollutants from the air. Examples of similar wet collection devices are numerous in industrial applications. Mining dust control, retort gas cleaning, tail gas cleanup and foul water stripping operations generate major waste streams (3a through 5b in Table 4-5). Major constituents in such waters include shale dust particulates, hydrocarbons, H_2S, NH_3, phenols, organic acids and amines, thiosulfate, and thiocyanate. Quantities of wastewater anticipated have been estimated in several cases (2). Data are not complete, however, on the quantity and quality of water required for air pollution control devices to be utilized in the developing oil shale industry. Air scrubbers, elutriation scrubbers, moisturizer scrubbers, and ammonia recovery units are anticipated as principal sources of wastewater.

TABLE 4-5. UTILIZATION OF WATER AND WASTEWATER FOR OIL SHALE DEVELOPMENT[a]

Water use	Barrels of water per barrel of shale oil		
	Requirement	Consumption	Discharge
Total utilization (for surface retorts)[b]	3.776 to 4.38	2.85 to 2.88	0.926 to 1.5
1. Process	—	0.25 to 0.31[c]	1.5 to 22[d]
(a) Retort pyrolysis water	—	—	0.103 to 0.120
(b) Combustion of organics	—	—	0.192 to 0.32
(c) Dehydration of minerals	—	—	—
(d) Groundwater *(in situ)*	—	—	1 to 22[d]
(e) Coker steam condensate	—	—	0.021
(f) Product gas cooling condensate	—	—	0.151
(g) Pyrolysis steam condensate	—	—	0.151
(h) Oil storage	—	—	0.06
(i) Product gas cleaning (retort)	—	—	0.123
2. Upgrading shale oil (hydrogenation)	—	0.62 to 0.93	0.629
Oily cooling wastewaters	—	0.72	0.170
(a) Quenching	—	—	—
(b) Vessel cleanout	—	—	—
(c) Spills cleanup	—	—	—
(d) Coker blowdown	—	—	0.007
(e) Process steam condensation	—	—	—
Process wastewaters	—	—	0.335
(f) Stripping condensed steam	—	—	—
(g) Drum cleaning wash water	—	—	—
(h) Chemical reaction wastewaters	—	—	—
(i) Spent caustic streams	—	—	—
Wash wastewaters	—	—	0.124
(j) Plant storm water runoff	—	—	—
(k) Hydraulic decoking	—	—	0.05
(l) Steam boiler bloxdown	—	0.21	0.025
(m) Boiler feedwater treatment blowdown	—	—	—
Backwashing and water rinse	—	—	0.03
Regeneration	—	—	0.019
3. Air control and gas cleaning	—	—	0.205
(a) Ammonia	—	—	0.017
(b) Moisturizer scrubber	—	0.343	0.027
(c) Elutriation scrubber	—	—	0.038
(d) Gas cleaning (upgrading)	—	—	0.123
4. Dust control	—	—	—
(a) Shale ash	—	0.171	—
(b) Scrubber	—	0.452	0.490
5. Mine applications (dewatering)	—	c	1.0 to 6.8-8.3
(a) Dust control	—	0.24	—
(b) Crushing	—	0.15	—
6. Power generation blowdowns	—	0.63	0.02 to 0.089
7. Cooling, non-contact	1.3	0.69	0.20 to 0.25
8. Potable and fire water protection	0.18	0.12	0.03 to 0.069
9. Sanitary	—	—	0.0 to 0.02
10. Revegetation	—	0.048 to 0.3	—
11. Moisturized spent shale runoff	—	0.925 to 1.87	—
12. Storm water runoff	—	—	Variable
13. Spent shale leachate	—	—	Variable
14. Spray irrigation leachate and runoff	—	—	Variable

[a] Data from References 2, 5 and 16 through 29.

[b] The "Total utilization" figures are those reported by certain surface developers as their combined, lump-sum, water flow rates; the individual unit-process wastestream rates shown come from a variety of other data sources, some from *in situ* operations. Consequently, the sum of the individual rates do *not* equal the total rate. It must be noted that many sources of water utilization are shown for illustrative purposes only.

[c] Union estimates 2.12 barrels water/barrel oil consumption for all uses; mining, crushing, retorting, shale cooling, leaching revegetation, sanitary, etc in a 10,000 TPD experimental plant.

[d] Upper level of this range is a result of groundwater infiltration into *in situ* retorts.

TABLE 4-6. WATER QUALITY PARAMETERS FOR *IN SITU* RETORT WATERS[a]

Parameter	Concentration range (ppm)
Alkalinity	18,200 to 110,900
BOD_5	350 to 5,500
Carbon, bicarbonate (as HCO_3^-)	4,200 to 42,000
Carbonate (as $CO_3^=$)	0 to 7,500
Inorganic	1,960 to 19,200
Organic	2,830 to 19,000
Chemical oxygen demand	8,500 to 43,000
Nitrogen, ammonia (as N)	1,700 to 13,200
Ammonium (as N)	930 to 24,450
Organic	73 to 1,510
Oil and grease	580 to 3,800
Phenols	2.2 to 169
Solids, total	6,350 to 121,000
Sulfur, sulfate	42 to 2,000

[a] Source: references 16 and 17.

TABLE 4-7. MAJOR ORGANICS IN RETORT WATERS*

Compound	Concentration (ppm)
Acetic acid	600
Propanoic acid	210
n-Butanoic acid	130
Acetamide	230
n-Pentanoic acid	200
Propionamide	50
n-Hexanoic acid	250
Butyramide	10
Phenol	10
n-Heptanoic acid	260
o-Cresol	30
m & p—cresols	20
n-Octanoic acid	250
n-Nonanoic acid	100
n-Decanoic acid	50

*Major organic components in retort water from the Laramie Energy Technology Center (LETC) 150 ton retort. Reference 30.

Wastewater from Mine Dewatering—

Water from aquifers encountered during mining and *in situ* retorting operations must be removed by dewatering systems. The quality and quantity of such waters will vary with the location and the processing technique employed. Surface retorting process developers reportedly intend to use this mine water for wetting and compacting retorted shale, and for dust control. *In situ* developers are working toward reinjection of a portion of the mine dewatering flows and/or toward using these wastewaters for spray irrigation. The major constituents of concern in mine water are sodium, bicarbonate, and chlorides.

The major potential oil shale developments are located in the Piceance Creek Basin of Colorado, Utah, and Wyoming. The Piceance Creek Basin area contains groundwater that is normally discussed in terms of lower and upper aquifers (even though there is a multiple aquifer system) separated by the Mahogany Zone of oil shale. The mine drainage is not uniform throughout the Piceance Basin. The south end of the basin near the rim will produce little or no mine water.

The characteristics of the groundwater for the C-a and C-b lease tracts are expected to change as water enters the mine, moves downward, and travels horizontally to the sumps where it will be collected. There is presently information on groundwater leaching of raw shale but not on surface stored raw shale. It is anticipated that water soluble inorganic salts (particularly sodium bicarbonate) and organic materials can be leached (see Section 3, Leaching of Solid Wastes). Information is not now available to ascertain the characterization of organics actually present in the mine drainage. The level of organics may not be greater than 10 mg/l (8.34×10^{-5} lbs/gal) and may not be significant in oil shale process water utilization (Table 3-32).

The treatment of mine drainage waters for onsite use and possible above-ground disposal will require information on both the organics and inorganics contained in the waters. Values for the major inorganic constituents of the groundwaters that will enter the mines are shown in Table 4-13. Table 4-14 summarizes Tract C-a and C-b flow rates.

TABLE 4-8. TRACE ELEMENT CONCENTRATION (ppm) IN WATERS FROM SURFACE AND *IN SITU* RETORTS

	Surface retorts			*In situ* retorts				
Element	Refs. 2,25,29	Ref. 31	Ref. 32	Ref. 33	Ref. 34	Ref. 35	Ref. 36	Ref. 32
Be	—	—	—	—	—	—	—	—
Hg	—	—	—	0.01	0.01	0.39	0.01	0.02
Cd	—	—	—	—	—	—	0.001	0.003
Sb	—	—	—	0.007	0.07	0.016	—	—
Se	0.96	0.7	0.1	0.005	0.1	0.98	—	—
Mo	0.06	0.1	0.006	0.47	0.1	—	—	—
Co	0.005	0.04	0.004	0.37	0.07	0.65	—	—
Ni	0.03	0.2	0.034	0.26	1.0	—	—	—
Pb	0.002	0.2	—	0.01	0.1	—	0.03	0.1
As	1.0	1.0	—	0.26	6.0	6.0	2.0	0.3
Cr	0.007	0.3	0.004	0.012	0.02	0.02	—	—
Cu	0.16	0.2	0.16	0.003	0.007	—	0.2	5.0
Zr	0.003	—	—	0.02	0.07	—	—	—
B	0.44	5.0	0.55	0.26	6.0	—	—	—
Zn	0.045	0.4	0.045	0.04	0.4	0.43	5.0	1.0
Li	0.006	1.0	—	—	0.3	—	—	—
V	0.002	0.03	—	1.2	0.7	—	—	—
Mn	0.019	0.3	0.02	0.023	0.1	—	—	—
F	0.3	7.0	3.1	—	25.0	—	—	—
Ba	0.09	2.0	—	0.03	0.05	0.13	—	—
Fe	5.7	5.0	—	0.49	25.0	1.0	—	—

TABLE 4-9. TRACE ELEMENTS IN SURFACE AND *IN SITU* RETORT WATERS[a]

Element	Concentration range (ppm)			Element	Concentration range (ppm)		
Ag	0.002	to	0.23	Mg	3.2	to	350
Al	0.024	to	0.8	Mn	0.019	to	0.3
As	0.0	to	10.0	Mo	0.006	to	0.47
B	0.26	to	8.8	Na	8.3	to	1300
Ba	0.002	to	2.0	Nb	0.001	to	0.005
Be	0.0[b]		—	Nd	0.001	to	0.055
Bi	0.001	to	0.009	Ni	0.034	to	2.6
Br	0.009	to	0.66	P	0.58	to	9.2
Ca	0.41	to	36	Pb	0.002	to	0.37
Cd	0.00	to	0.0[b]	Pr	0.0006		—
Ce	0.001	to	0.1	Rb	0.036	to	0.59
Cl	0.023	to	2.0	S	14	to	310
Co	0.002	to	0.65	Sb	0.004	to	0.047
Cr	0.004	to	0.3	Sc	0.0003	to	0.0004
Cs	0.002	to	0.01	Se	0.003	to	3.1
Cn	0.003	to	0.2	Si	1.7	to	48
Dy	—		—	Sm	0.00031	to	0.003
Er	0.0015		—	Sh	0.11	to	100
Eu	0.00029	to	0.010	Sr	0.003	to	3.0
F	0.3	to	54	Tb	0.0011	to	0.002
Fe	0.49	to	77	Th	0.004	to	0.013
Ga	0.02		—	Ti	0.2	to	21
Gd	0.02		—	Tm	0.003		—
Ge	0.001	to	0.007	U	0.002	to	4.6
Hf	0.002	to	0.004	V	0.004	to	11
Hg	0.01	to	0.39	W	0.003	to	0.024
Ho	0.00008		—	Y	0.002	to	0.050
I	0.003	to	0.33	Yb	0.00036		—
K	3.4	to	70	Zn	0.037	to	14.4
La	0.0017	to	0.010	Zr	0.003	to	0.39
Li	0.004	to	1.0				
Lu	0.00009	to	0.003				

[a] Data from References 2, 7, and 24-27.
[b] Not detected to these levels of concentration.

TABLE 4-10. CHARACTERISTICS OF STEAM BOILER BLOWDOWN, UNION B PROCESS[a]

Constituent	Generation rate kg/hr	Generation rate lb/day
TDS	2.7	145.1
Hardness (as $CaCO_3$)	0.3	14.5
Sodium	0.5	28.9
Chloride	0.8	43.4
Sulfate	0.8	43.4

[a] Source: Reference 26.

TABLE 4-11. CHARACTERISTICS OF WASTEWATER FROM BACKWASHING AND RINSING OPERATIONS, UNION B PROCESS[a]

	Colorado River			White River		
	Concentration	Generation rate		Concentration	Generation rate	
Constituents	(mg/l)	kg/hr	lb/day	(mg/l)	kg/hr	lb/day
TDS	454	4.6	242	551	5.5	293
SS	25	0.2	13	32	0.3	17
Hardness	214	2.2	114	300	3.0	160
Chloride	119	1.2	63	42	0.4	22
Sulfate	129	1.3	69	188	1.9	100
Calcium	60	0.6	33	84	0.9	45
Magnesium	17	0.2	9	24	0.2	13

[a] Source: Reference 26.

TABLE 4-12. CHARACTERISTICS OF REGENERATION WASTEWATERS, UNION B PROCESS[a]

	Concentration	Generation rate	
Constituent	(mg/l)	kg/hr	lb/day
TDS	20,430	129	6,830
SS	2,043	13	680
Hardness	9,889	63	3,310
Chloride	2,780	18	930
Sulfate	4,500	28	1,510
Calcium	2,190	14	730
Magnesium	1,130	7	380

[a] Source: Reference 26.

A great variation can be found by sampling at different levels and locations within the aquifers and by sampling at different times of the year. The extent to which leaching in the mine will add to the contaminants will depend on the volume of flow, the contact time with raw shale, and the extent to which dust and particulates are cleansed from the mine environment.

Power Generation Blowdowns—

Power generation blowdowns (6 in Table 4-5) include blowdowns to minimize scaling and blowdowns from boiler feedwater systems, but they exclude steam stripping wastewaters as proposed in other reports. The Union Oil Co. has estimated some characteristics of boiler feedwater before and after blowdown in Table 4-15 (26). Blowdown waters will require complete characterization.

TABLE 4-13. SOME WATER QUALITY CHARACTERISTICS FROM GROUNDWATERS IN PICEANCE BASIN[a]

	Aquifer concentrations (ppm)								
	Alluvial			Upper			Lower		
Characteristic	Low	Mean	High	Low	Mean	High	Low	Mean	High
Potassium	0.8	2.5	6.8	0.2	1.5	6.0	0.4	11	78
Sodium	66.0	490.0	2900.0	55.0	210.0	650.0	230.0	3980	16,000
Calcium	2.4	57.0	120.0	7.4	50.0	110.0	2.8	8	15
Magnesium	3.6	80.0	160.0	9.8	60.0	187.0	3.0	10	26
Bicarbonate (Na)	336.0	1220.0	3560.0	307.0	550.0	918.0	493.0	9100	40,000
Chloride	5.2	42.0	270.0	3.4	16.0	63.0	1.3	690	2,900
Sulfate	41.0	430.0	1500.0	24.0	320.0	850.0	4.2	80	350
Fluoride	0.1	5.0	33.0	0.0	1.0	12.0	5.0	28	66
Dissolved solids	469.0	1750.0	6720.0	345.0	960.0	2180.0	491.0	9400	38,900

[a] Source: Reference 18.

TABLE 4-14. SOURCES AND FLOW RATES OF WATER FROM TRACT C-a

Source	Estimated flows (gpm)[a,b]	Water-to-Oil Ratio (bbl/bbl)
Dewatering wells:	1,350[c]	0.812[c]
Upper aquifer	3,900[d]	2.35[d]
Dewatering wells:		
Lower aquifer	6,300[c]	3.79[c]
Mine seepage water	3,600[c]	2.17[c]
Total Tract C-a	11,250[c]	6.772[c]
	13,800[d]	8.31[d]

[a] Source: Reference 18.

[b] The estimate of dewatering flows for Tract C-a is given in the modified detailed development plan for a 57,000 bbl/stream day shale oil production rate (18). The *in situ* mine drainage volume for Tract C-b is estimated between 1.0 and 1.68 bbl of water/bbl of oil (20).

[c] Original estimate.

[d] Current upper aquifer dewatering rate included.

Cooling Water Discharges—

Cooling water is used in retorting and shale oil upgrading to absorb heat that cannot be economically recovered. Noncontact cooling water (7 in Table 4-5) should be essentially pollution free. Noncontact cooling water, as defined by EPA, is water used for cooling that does not come into direct contact with any raw material, intermediate product, waste product, or finished product. On the basis of several different raw water supply sources, the Union Oil Co. has estimated the characteristics of cooling tower blowdown as given in Table 4-16 (26). It is anticipated that the presence of biocides and other pollutants in cooling tower blowdown may require special treatment.

Potable and Fire Treatment Discharges—

The contaminants in water treatment discharges (8 in Table 4-5) will be primary coagulants and chemical sludges, backwash solids from the filtration system, and blowdown from the zeolite softening system. Characteristics of water treatment discharges have not been forecast specifically for an oil shale processing facility. It is anticipated that blowdown from the potable water treatment system could be treated by the domestic sewage system. Other wastewater treatment blowdowns may also be amenable to treatment in the domestic treatment plant if toxic and other materials are not present.

Storm Water Runoff and Leachate from Spent Shale Disposal—

Three types of solid wastes are produced from oil shale retorting operations: carbonaceous spent shale, burned spent shale, and raw shale itself. The surface retorts consume most of the raw shale fed to them, whereas *in situ* retorts will require larger quantities of raw shale above-ground storage. True *in situ* retorting results in very little solid waste for disposal above ground. Different leachate and runoff characteristics will result from each solid waste. Other sludges and solid wastes from oil shale processing will perhaps be added to the shale for onsite, above-ground disposal and may also change the leachability characteristics of the combined solid wastes.

TABLE 4-15. CHARACTERISTICS OF UNION B BOILER FEEDWATER AND BLOWDOWN[a]

Characteristic	Boiler feedwater[b]	Boiler blowdown
TDS (mg/l)	50	331
Conductivity (μ mhos/cm)	75	496
Hardness (mg/l)	5	33
Sodium (mg/l)	10	66
Chloride (mg/l)	15	99
Sulfate (mg/l)	15	99

[a] Source: Reference 26
[b] Low pressure steam generation equipment only.

TABLE 4-16. CHARACTERISTICS OF UNION B COOLING TOWER BLOWDOWN[a]

Characteristic resulting concentrations	Raw water supply source			
	Colorado River	White River	Upper aquifer	Lower aquifer
TDS (mg/l)	1,589	1,929	3,360	32,900
Conductivity (μ mhos/cm)	2,490	2,968	5,250	50,750
Hardness (mg/l)	749	1,050	1,295	203
Sodium (mg/l)	333	273	735	13,615
Chloride (mg/l)	417	147	56	2,415
Sulfate (mg/l)	452	658	1,120	280
Fluoride (mg/l)	—	1	4.9	98
Chromium (mg/l)	53	53	53	53

[a] Source: Reference 26.

The quantities of leachate and storm water runoff (12 and 13 in Table 4-5) that will result from shale disposal are unknown. Numerous factors affecting wastewater volumes and qualities are discussed elsewhere in this document. Available data on experimental leachate from shale disposal indicate that it will be highly polluting. The volume of wastewater from leaching and storm runoff will be variable.

Application of Treatment Methods to Oil Shale Wastewaters

The methods of wastewater control technology that yield the greatest potential for water recycling and that meet final disposal criteria should ultimately be chosen by the developers of oil shale. Each developer will have an opportunity to explore the recycling methodology available to produce zero discharge and thus complete control of environmental pollutants. The optimum system for each process is yet to be determined.

Numerous modes of treatment, recycle, and control should be considered in trying to optimize each process developer's water utilization scheme. The concept of complete recycle will require maximum reuse, and some degree of treatment. The extent to which this concept must be reached will be determined on a case by case basis through existing regulatory mechanisms.

In order to solve the water utilization problems facing the oil shale industry, it is necessary to consider all of the pollutants to be controlled and provide for appropriate handling. Since a zero discharge water system is currently the goal of several developers, detailed information on pollutant characteristics and process water quality requirement is needed. It should be noted that, in the past, wastewater streams have been characterized and reported on in a combined manner, rather than as individual unit process streams. Judgments on selected treatment options for specific wastewaters cannot be made in the absence of data on specific pollutant characterization.

The following descriptions of treatment options consider clusters of combined wastewater streams to the extent supportable by the data. Oil shale wastewaters are known to contain dissolved and suspended solids, oil, trace elements and metals, trace organics, toxic substances, dissolved gases, and sanitary wastes (e.g., see Tables 4-6 through 4-10). The basic approach will be to provide water of a quality for recycling and when necessary, discharge to the environment.

A hypothetical schematic diagram for oil shale wastewater treatment is presented in Figure 4-2. The idealized processing scheme depicted does not necessarily reflect optimum design recommendations, but rather an avenue of approach since the treatments have not been demonstrated.

Regarding pretreatment and/or wastewater blending possibilities, the following generalizations can perhaps be made. The wastewaters containing dissolved solids (greater than 1,000 mg/l or 8.34×10^{-3} lbs/gal) and suspended solids (those grouped on the left half of Figure 4-2) should be essentially free of oil and trace organics and can be collected and flow-equalized in large holding lagoons before treatment. The oily wastewaters (above 10 mg/l or 8.34×10^{-5} lbs/gal) from all wastewater sources should be collected and processed by the API separator before receiving further treatment. Trace element and metal-contaminated wastewaters should be essentially free of oil and dissolved solids, thereby allowing separate treatment. Wastewaters containing trace organics are not anticipated to be great in volume, but highly diverse as far as the types of organic pollutants contained therein. Toxic wastewaters are anticipated to be small in volume and to require careful control. Wastewaters coming from scrubbers that treat common oil shale process gases such as H_2S, NH_3, and CO_2 will require specific controls and treatment before water reuse or discharge. The sewage and water treatment wastes should be examined to determine the advantages of separate treatment as compared with beneficial and safe use of the nutrient, organic, and water content.

Dissolved and Suspended Solids Wastewater Treatment System—

A scan of the available data previously summarized indicates that the following wastewater streams are candidates for the solids treatment system (see Table 4-5 for the stream numbering key):

(1d) Groundwater (*in situ*, not organically contaminated)
(2j) Plant storm water runoff (diversion)
(2l) Steam boiler blowdown
(2m) Boiler feedwater treatment blowdown
(4b) Dust control scrubber wastewater
(5) Mine drainage or mine dewatering wastewater
(6) Power generation blowdowns
(7) Non-contact cooling water blowdown

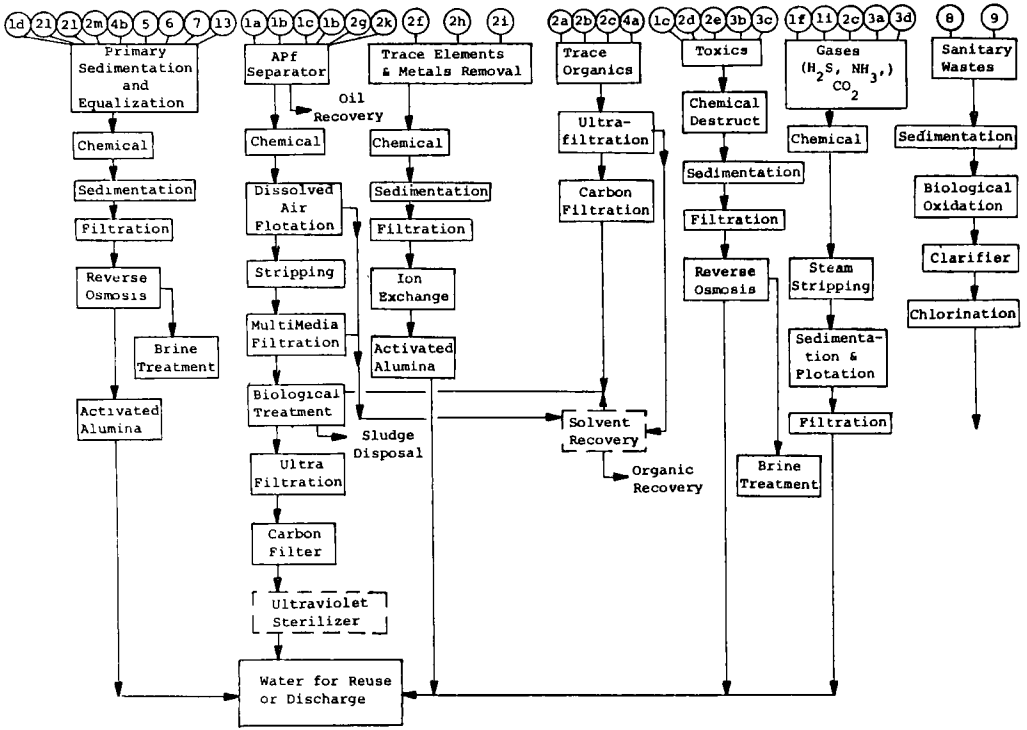

Figure 4-2. Comprehensive hypothetical schematic diagram for oil shale wastewater treatment. No one plant would utilize all treatments shown. The degree of treatment will vary dependent on reuse purpose. (See Table 4-5 for key to wastewater streams indicated in the circles above.)

(13) Spent shale leachate

The *in situ* process groundwater may be high in organics and oil contents. If oil and other organics are present, these wastewaters should be considered as candidates for the oily wastewater treatment system. Figure 4-2 indicates some of the potential treatment processes which may be applicable to these streams (37,38,39).

Oily Wastewater System—

Special considerations should be exercised when designating a candidate waste stream for treatment in the oily wastewater treatment system. The aqueous stream should contain more than 10 mg/l (8.34×10^{-5} lbs/gal) oil, and certain toxic elements and organics should not be present in concentrations above the treatment capabilities of the system. The candidate wastewaters for the oily wastewater treatment system include the following (see Table 4-5 for the stream numbering key):

(1a) Retort pyrolysis water

(1b) Combustion of organics water

(1c) Dehydration of minerals water

(1h) Oil storage water

(2g) Drum cleaning wastewaters

(2k) Hydraulic decoking wastes

It is probable that *in situ* retort groundwater may be added to the volumes of oily discharges mentioned earlier. The volume of groundwater could be substantial. The system may also have to be modified to reduce specific pollutants before the indicated treatment. Figure 4-2 indicates some of the potential treatment processes which may be applicable to these streams (40,41).

Trace Elements and Metals Removal System—

Wastewater streams that contain some trace elements and metals of concern may be controllable by use of a small treatment system. The waste streams identified as potential candidates are (see Table 4-5):

(2f) Stripping condensed steam

(2h) Chemical reaction wastewaters

(2i) Spent caustic streams

Other plant wastewaters could be added if they are shown to be high in trace elements and metals of concern and low in oil and organics. It is anticipated that the design of this system will be site-specific and will depend upon effluent volumes and required recoveries for each individual wastewater. Figure 4-2 indicates some of the potential treatment processes which may be applicable to these streams (40,42,43).

Trace Organics Treatment System—

The trace organics of environmental concern present in oil shale wastewaters are suspected to be present primarily in the upgrading process area. The major sources of trace organics may include (see Table 4-5):

(2a) Quenching

(2b) Vessel cleanout

(2c) Spills cleanup

(4a) Shale ash dust control

Other waste streams may contain only organics and be amenable to this system. Only a process-by-process analysis will indicate which specific candidate effluents may be appropriate. Figure 4-2 indicates some of the potential treatment process which may be applicable to these streams (40,44,45,46).

Toxics Treatment System—

Toxic components of oil shale wastewater can be treated in a variety of ways, depending on the nature of the problem and the appropriate solution for each specific case. Oil shale processing is known to produce carcinogens, mutagens, priority pollutants, and other hazardous wastes. The specific system capable of handling toxic liquid wastes will possibly receive the following candidate wastewater discharge streams (see Table 4-5 for the stream numbering key and Figure 4-2 for the flow sequence):

(1e) Coker steam condensate

(2d) Coker blowdown

(2e) Process steam condensation

(3b) Wastewater from moisturizer operations

(3c) Elutriation scrubber wastewaters

The toxic substances anticipated will include trace and concentrated organics, metals, and other concentrates that may present a health problem. High temperature incineration is a thermal destruction method successfully employed by industry to render many organic compounds in byproduct effluents innocuous. Alternatively, chemical techniques could be used to destruct or chemically tie up toxic substances found in oil shale wastewaters. Figure 4-2 indicates some of the potential treatment processes which may be applicable to these streams.

Treatment System for Wastewater Containing Dissolved Gases—

The treatment systems needed to remove contaminants from off-gases wetscrubber effluents are not new, but they have not yet been applied to the oil shale industry. As an example, a liquid-phase process (Stretford) to remove hydrogen sulfide from gaseous effluents is planned but little applicable work has been done on the liquid effluent. Until the complete system of air controls has been demonstrated, the treatment system for wastewaters containing these dissolved gases can only be hypothesized.

The main effluents to be controlled include wastewaters from the following unit operations (see Table 4-5 for the stream numbering key):

(1f) Product gas cooling condensate

(1i) Product gas cleaning

(2c) Spills clean-up

(3a) Ammonia control

(3d) Gas cleaning

Figure 4-2 indicates some of the potential treatment process which may be applicable to these streams.

Domestic Wastewater Treatment System—

The domestic wastes which include laundry, sanitary kitchen wastes, etc. should be given careful considerations as to the role they may play as a source of nutrients for biological systems, for revegetation, etc. For these uses the public health aspects must be considered (see Table 4-5 and Figure 4-2).

SOLID WASTE CONTROLS

Edward Bates

Surface Disposal of Overburden, Lean Shale, and Spent Shales

Surface disposal of at least some spent shale as well as possible surface disposal of overburden, lean shales, raw shale fines, and chemical solids will occur as part of any oil shale operation. However, overburden handling is expected to approach significant size only for surface mining operations. Control technology for mining,

handling, and disposal of overburden would be similar to that for other extractive industries, although application to specific oil shale localities needs to be demonstrated. Techniques employed in the surface mining of coal should generally be applicable to surface mining of oil shale. Disturbance of the minimum area necessary, use of water sprays and chemical binders to control dust, conservation of existing soil, and use of arid area revegetation techniques would be applicable. The major problems anticipated are in the huge size of any operation envisioned, bulking effects, prevention of leachates that might affect surface or groundwater quality, and retention of adequate moisture in the root zone to establish and maintain vegetative growth. Selective placement, sizing, and compaction of backfilled overburden materials would assist in controlling the leachate and moisture retention problem. Lean shales could possibly be disposed of along with the overburden in the mine cuts if their leachates are demonstrated to be free of contaminants that would affect water quality. Disposal of other process wastes, including spent shales in the mine cuts, may prove troublesome because of the risk of leachates impacts on groundwater quality. Because of bulking effects, it would also be impossible to return all mined material to the cut.

Surface Disposal of Spent Shale and Raw Mined Oil Shale

Any oil shale operation other than a true *in situ* operation must include disposal of some spent oil shale on the surface, either in the form of disposal piles or as canyon fills. Studies to date by EPA and others indicate that revegetation of spent oil shales is possible if properly conducted. Numerous studies have been conducted including those by Colony Development Operation (47), TOSCO Corporation (48), and Union Oil Company (49). Since 1973, EPA has been investigating the environmental impacts and possible control technologies for surface disposal of spent shale. Field test plots have been constructed and studies made on coarse-textured USBM spent shale, fine-textured TOSCO II spent shale, and coarse-textured Paraho (direct mode) spent shale. The plots were constructed in Colorado at a low elevation (1,700 m or 5,700 ft), very dry site near Anvil Points and at a higher elevation 2,200 m (7,200 feet), moister site in Piceance Basin near Black Sulfur Creek. The most significant results of these ongoing studies to date may be summarized as follows (42,50):

If spent oil shales such as the ones used in these studies are to be quickly stabilized with native vegetation, they will require careful management which may include leaching, N and P fertilization, and irrigation for establishment. Nitrogen application will be required for a few years after establishment.

The infiltration rate of the fine-textured spent shale is very slow, and thus the erosion potential may be high when this material is subjected to high-intensity summer storms. The slow infiltration rate must be considered when planning stabilization of this spent shale.

Resalinization of leached fine-textured spent shale with resultant vegetation kill occurred in these studies probably because a water table was established. If a water table is not established, then resalinization should not occur.

Application of leach water on a continuous basis (100 cm or 39 in. over 10 days) proved more effective in preparing the shale for revegetation than intermittent application.

A surface stabilization alternative indicated by these studies consists of use of soil over unleached spent shale (30 cm or 12 in. soil in the cited study). This alternative would work only for lower pH spent shales into which roots of adapted species can grow, thus utilizing stored water. High pH (11-12) spent shales, into which roots will not grow, would require thicker soil cover. Even with soil cover, irrigation and fertilization during the first year would still be required for fast cover establishment. Table 4-17 presents a summary of vegetative cover established on test plots for TOSCO II, USBM, Paraho and Union B spent

TABLE 4-17. PERCENT OF VEGETATIVE COVER ESTABLISHED ON SPENT OIL SHALE TEST PLOTS

	Year and % slope						
	1973	1974	1975	1976	1977		1978
Site	25%	25%	25%	25%	2%	25%	25%
EPA low elevation site (1,700 m), seeded 1973:[a,b]							
TOSCO spent shale	50	42	67	72	—	29	66
15 cm soil cover/TOSCO	80	60	78	80	—	32	76
30 cm soil cover/TOSCO	80	61	74	75	—	46	70
USBM spent shale	56	55	82	77	—	53	65
15 cm soil cover/USBM	70	68	84	87	—	38	72
60 cm soil cover/USBM	70	64	78	84	—	42	78
Soil control	64	58	80	85	—	36	75
Paraho spent shale	—	—	—	—	5	5	66
20 cm soil cover/Paraho	—	—	—	—	70	85	66
40 cm soil cover/Paraho	—	—	—	—	70	80	62
60 cm soil cover/Paraho	—	—	—	—	85	80	65
80 cm soil cover/Paraho	—	—	—	—	80	80	64
Soil control	—		—		80	75	83
EPA high elevation site (2,200 M), seeded 1975:[a,b]							
TOSCO spent shale	—	—	58	84	—	60	63
15 cm soil cover/TOSCO	—	—	44	82	—	52	69
30 cm soil cover/TOSCO	—	—	56	—	—	50	62
USBM spent shale	—	—	54	80	—	60	61
15 cm soil cover/USBM	—	—	54	73	—	52	78
30 cm soil cover/USBM	—	—	48	65	—	42	70
Soil control	—	—	50	79	—	46	67
Paraho spent shale (seeded 1977)[c]	—	—	—	—	15	10	44
20 cm soil cover/Paraho	—	—	—	—	65	75	66
40 cm soil cover/Paraho	—	—	—	—	65	75	60
60 cm soil cover/Paraho	—	—	—	—	80	65	53
80 cm soil cover/Paraho	—	—	—	—	80	75	53
Soil control	—	—	—	—	60	55	98
Union Oil Co. site (1,770 m), seeded 1975:[b,d]							
Union B spent shale	—	—	38	59	—	45	80
15 cm soil cover/Union B	—	—	73	56	—	37	87
30 cm soil cover/Union B	—	—	75	69	—	40	78
Soil control	—	—	65	65	—	41	79
Union Oil Co. site (2,300 m), seeded 1975:[e]							
Union SGR spent shale	—	—	—	42	—	18	36
15 cm soil cover/Union SGR	—	—	—	49	—	29	64
30 cm soil cover/Union SGR	—	—	—	51	—	29	71
Soil control	—	—	—	65	—	41	79
Union Oil Co. site (2,300 m), seeded 1975:[e]							
Union SGR spent shale	—	—	—	7	—	13	16
15 cm soil/Union SGR	—	—	—	47	—	46	33
Soil control	—	—	—	76	—	54	69

[a] 1978 data are mean of 2% and 25% slopes.

[b] 1973-76 data for EPA plots are from Reference 42.
1977-78 data for EPA plots are from Reference 51.

[c] The Paraho high elevation lysimeter was actually located at Anvil Points, Colorado but irrigation was used to simulate at site elevation of 2,200 m.

[d] Union data are from Reference 49, Tables 5 and 6, west aspect.

[e] West aspect, Reference 52, Tables 6 and 14.

shales. The table shows that with proper management, it is possible to vegetate spent shale successfully. The figures for 1977 and 1978 are especially significant. The year 1977 was very dry and resulted in substantial reductions in vegetative cover. The vegetation did, however, survive the drought of 1977 and shows a good recovery in the moist year 1978. Thus it appears that once established, vegetative cover will survive without irrigation.

The presence of deer and domestic livestock on disposal areas must be carefully controlled to prevent grazing before establishment of a strong, permanent vegetation cover. Such control may initially require exclusion by fencing.

Pocket gophers and other burrowing animals can be expected to move into the revegetated areas. This control is difficult or impossible, and thus the site stabilization scheme must be sufficiently resilient to allow for such disturbances.

Disposal sites on south aspects at the lower elevations (F2,000 m or 6,560 ft) have very dry microclimatic conditions and require more intensive management than more moist locations.

Erosion is a continuous natural process. Thus soil cover or spent shale modified for plant growth eventually erode, particularly from steep upper slopes. This process must be considered in future waste stabilization research and planning.

On the basis of the studies, it is recommended that high pH spent shale (such as Paraho direct mode) be covered with soil to insure that an adequate vegetative cover is quickly established. Tables 4-17 and 4-18 illustrate the importance of soil cover in initial establishment of vegetation. More study is needed on soil-cover treatments before a recommendation on the depth of soil cover can be made.

TABLE 4-18. PERCENT OF PLANT SURVIVAL AFTER 1 YEAR, BY SITE TREATMENT AND TOPOGRAPHICAL ASPECT, ROAN PLATEAU[a]

	Aspect			
Treatment	North	Level	South	Treatment Mean
Topsoil	79	89	79	82
Rock mulch	62	69	53	61
Straw amendment	35	38	36	36
Subsoil only	76	74	76	75
Aspect mean	63	67	60	

[a] Source: Reference 41.

Since the pollution potential from soluble salts is high, water should not be allowed to leach through retorted oil shale and enter the hydrological system. Possible alternatives for preventing water movement through retorted shale include revegetation, compacting the material to make it impervious to water flow, if possible, and/or covering the material with a sufficient depth of soil material to hold the seasonal precipitation, particularly from spring snowmelt. Surface runoff from soil covered disposal sites may be of much better quality but should be evaluated on an individual site basis.

Results from EPA's Paraho spent shale lysimeter study (50) suggest that water moved into and through the compacted shale in the leached treatments. Therefore, additional research is needed to insure that the material can be made impervious, before a compacted zone is used to prevent water movement through the commercial disposal pile.

Additional research is needed on the rates of cooling of retorted shale under commercial disposal pile conditions. If elevated temperatures are maintained in a disposal pile, a very dry site could result because of warmer surface temperatures and the resulting higher evaporation potential.

Additional research is needed to assess the dust control problems from retorted shale disposal piles. Dust control measures such as water sprays may in turn pose their own environmental problems.

Initial surveys of two vegetation species successfully grown on spent shale and soil-covered spent shales show higher levels of some trace elements than vegetation grown on the soil controls. Some trace elements may inhibit plant growth or prove harmful to animals feeding on the vegetation.

Canyon fills or disposal piles should be protected from the effects of severe storm events, especially flash flooding.

Since 1976, the U.S. Forest Service has been studying the effects of soil amendments, drip irrigation, containerized plants versus seeding, and species survival in revegetating surface spent shale piles. Test sites for revegetating TOSCO II spent shale are located at Sand Wash, eastern Utah, within the Salt Desert shrub zone (very dry) and on the Roan Plateau, western Colorado, in the upper mountain brush zone (more moist). Preliminary recommendations by the U.S. Forest Service resulting from these EPA-sponsored studies may be summarized as follows (48):

Disposal embankments of processed oil shale should be covered with 30 cm (1 ft) or more of local topsoil that has shown good capability for supporting vegetation. Use of topsoil increases the number of species adapted for revegetating disposal embankments and greatly reduces the need for fertilizers. Topsoil was superior to broken rock fragments, which in turn were superior to barley straw as a soil amendment.

Several native saltbushes and two introduced Chenopodiaceae species that showed excellent performance in these studies should be considered for use in revegetating processed oil shale disposal embankments in the arid salt desert shrub zone. Grasses that should be considered for use in that zone include four native species (Indian ricegrass, galleta, blue grama, alkali sacaton) and two introduced grasses (crested wheatgrass and Russian wildrye). Galleta, blue grama, and alkali sacaton are warm-season grasses that require adequate summer moisture for successful establishment.

In the more mesic mountain brush zone, the Chenopodiaceae and other shrubs that performed well in these studies should be considered for revegetating processed oil shale disposal areas that have been covered with 30 cm (1 ft) or more of topsoil. Native grasses that should be considered for use in the mountain brush zone include beardless bluebunch, streambank, thickspike, and western wheatgrasses, and Great Basin wildrye; introduced grasses include smooth brome, fairway, intermediate, tall, and pubescent wheatgrasses.

Use of container-grown plants on arid and semiarid sites can ensure successful revegetation of disposal areas where fall planting of seeds has failed. One liter (.26 gal) or more of water per plant should be applied at the time of planting and as needed during the first growing season.

Whereas supplementary water might not be required beyond the first growing season for plant survival, additional moisture stored in the processed shale underlying a covering layer of topsoil would enhance plant growth. Surface configurations such as contour furrowing and/or pitting should be employed on disposal areas to increase water infiltration and prevent runoff and erosion.

Site treatment such as the use of soil cover appears to be more significant to plant survival and growth than either aspect (north, south, etc.) or slope (Table 4-18).

Trace Element Uptake by Vegetation—

Little work has been done to date to determine if vegetation grown on spent shale disposal areas contains increased levels of trace elements, especially metals. Increased levels of some elements, such as boron and fluorine, may be toxic to plants, and others such as molybdenum, selenium, and arsenic may be toxic to animals. Table 4-19 summarizes results from trace element uptake studies of plants grown on spent shale revegetation plots. Although data are still very meager, some initial conclusions and tentative findings can be stated as follows:

Conclusions:

Plants grown on some spent oil shales have increased levels of some trace elements compared to plants grown on native soils. Implications of these increased levels are not known.

Uptake of trace metals is influenced by the type of spent shale.

Uptake of trace metals may vary with the type of vegetation.

Tentative findings:

Plants grown on TOSCO II spent shale tend to have increased levels of fluoride, iron, molybdenum, and zinc.

Plants grown on USBM spent shale tend to have increased levels of boron, fluoride, molybdenum, selenium, and zinc.

Plants grown on Paraho spent shale tend to have increased levels of iron, lithium, and molybdenum.

Plants grown on Union B process spent shale tend to have increased levels of copper, molybdenum and zinc.

Use of 15 to 20 cm (6 to 8 in.) of soil cover over the spent shale produced mixed results on trace metal uptake; concentration of some metals in plants decreased, and others increased.

Spent or Raw Shale Leachate—

Some leachate could probably be produced from any surface disposal of spent or raw oil shale, and this leachate could probably adversely affect surface and groundwater quality. A discussion of the nature of solid waste leachates and their possible impacts on surface and groundwater quality was presented earlier in Section 3. Some provision for collection, treatment, and/or reuse of this leachate will likely be necessary. Use of an impermeable lining below the disposal pile, coupled with installation of a drainage system to collect the leachate for treatment or reuse, may be desirable. The surface retorting technologies are tending toward a zero discharge concept, which would necessitate the collection, treatment, and reuse of this leachate. If an impoundment structure is used for the collection or evaporation of this leachate, it will be especially important to insure that leachate will not seep through the bottom lining of the impoundment and enter the groundwater system. As in the case of the disposal piles, provision should be made to protect the impoundment structure from the effects of severe storms, especially flash floods.

Spent shale leachate of poor water quality may possibly be produced for many years beyond the period of time that any particular oil shale facility would be in operation. Therefore, a technology needs to be developed and employed to prevent leachate from causing surface and groundwater pollution after cessation of retorting operations. Such a technology could perhaps take the form of an essentially maintenance-free evaporation pond to contain the leachate that is produced.

Process-generated solid wastes such as spent catalysts, lime sludges, coke, and other solids from water and wastewater treatment systems may contain highly toxic substances such as arsenic and require disposal as toxic substances. Disposal of these wastes by burying them in the spent shale pile would probably result in increased levels of toxic pollutants in the spent shale leachate and impacts on surface

TABLE 4-19. TRACE METAL UPTAKE BY PLANTS GROWN ON EPA SPENT OIL SHALE TEST PLOTS (ppm)

Shale type	Plant	As	B	Cd	Cr	Cu	F	Fe	Hg	Li	Mn	Mo	Ni	Pb	Se	V	Zn
TOSCO II[a]	Fourwing		69.7				4.13					4.71					
[b]	Saltbush	<0.02	c	0.07	<0.1	1.4	c	70	<0.1	<0.05	18	1.3	4.6	<0.1	1.1	0.4	404
TOSCO II[a]	Western wheat grass		126.59				4.71					4.25			0.22		
15 cm soil over TOSCO II	Fourwing Saltbush	<0.2	c	0.1	0.2	0.9	c	76	<0.1	<0.05	18	2.4	3.8	<0.1	3.2	<0.2	289
USBM[a]	Fourwing		53.69			6.36	2.0					22.71					
[b]	Saltbush	<0.2	c	0.04	<0.1	0.8	c	57	<0.1	<0.05	16	2.8	2.2	<0.1	4.5	<0.2	49
USBM[a]	Western wheat grass		29.13				2.85					5.07			0.45		
15 cm soil[b] over USBM	Fourwing Saltbush	<0.2	c	0.02	0.1	0.4	c	72	<0.1	1.0	21	6.4	1.9	<0.1	3.8	<0.3	22
Paraho[b]	Fourwing Saltbush	<0.2	c	0.04	0.1	<0.1	c	114	<0.1	1.5	16	2.6	0.2	<0.1	1.0	<0.2	4.3
20 cm soil over Paraho	Fourwing Saltbush	<0.2	c	0.05	<0.1	0.2	c	108	<0.1	<0.05	28	8.4	2.0	<0.1	2.0	<0.2	7.8
Union Process B shale[d]	Fourwing Saltbush	1	39.0	0.22		6.2						1.3		5	1.0		22.5

[a] Reference 45. Mean of North and South aspects, high and low elevation plots, 1976 and 1977.
[b] Reference 46. Samples collected 11-1-78.
[c] Value questioned.
[d] Data from application of Union Oil Company to Colorado Mined Land Reclamation Board, March 26, 1979.

(continued)

TABLE 4-19 (continued)

Shale type	Plant	As	B	Cd	Cr	Cu	F	Fe	Hg	Li	Mn	Mo	Ni	Pb	Se	V	Zn
Union Process B shale[d]	Grass mixture	1.8	39.5	0.04		6.7						6.7		2	1.0		28.5
Union Process B shale[d]	Winterfat	2.2	22.5	0.23		9.6						7.6		2.5	1.0		47
15 cm soil over[d] Union Process B shale	Fourwing Saltbush	1	34	0.20		5.6						5.7		6	1		48
15 cm soil over[d] Union Process B shale	Grass mixture	2.0	34	0.06		5.9						4.8		1.5	1		26
15 cm soil over[d] Union Process B shale	Winterfat	1.5	27	0.20		8.7						7.1		3	1		41.5
Soil control[a] Anvil Points[b]	Fourwing Saltbush	<0.2	66.98 c	0.12	0.2	4.3	1.91 c	57	0.1	<0.05	18	5.53 0.7	3.1	<0.1	0.5	0.2	0.0
Soil control[a] Anvil Points	Western wheat grass		9.19				2.17					2.69			0.19		
Soil control[d] Union	Fourwing Saltbush	1.0	44.5	0.26		5.6						4.7		4.5	1.0		27
Soil control[d] Union	Grass mixture	2.2	7.5	0.05		4.8						3.9		1.5	1.5		18.5
Soil control[d] Union	Winterfat	2.5	22.5	0.33		8.2						2.7		3.5	1.0		27.5

[a] Reference 53. Mean of North and South aspects, high and low elevation plots, 1976 and 1977.
[b] Reference 54. Samples collected 11-1-78.
[c] Value questioned.
[d] Data from application of Union Oil Company to Colorado Mined Land Reclamation Board, March 26, 1979.

and groundwater quality. Disposal of some process wastes along with the spent shale may be possible after it is demonstrated that they do not themselves produce a leachate and that they do not facilitate production of additional pollutants in the spent shale leachate. A future alternative method for handling potentially toxic wastes such as spent catalysts may be to return them to the manufacturer for regeneration and subsequent reuse.

Underground (Mine) Disposal of Spent Shale—Bob Newport

A single commercial surface retorting operation will generate a minimum of 45,000 tonnes/day (50,000 tons/day) of spent shale. Particle size of this waste depends on the retorting process used and ranges from finely divided residues to boulders more than 20 cm (8 in.) in diameter. Water passing over this waste produces a leachate of extremely low quality. Total dissolved solids have been measured at 130,000 mg/l (0.108 lbs/gal). In addition, spent shale contains up to 5 percent organic carbon. Some fractions of this organic material have been found to contain polycyclic aromatic hydrocarbon compounds that have carcinogenic components. These figures are used only to indicate the potential pollutants that could be made available during shale disposal.

To answer the concern about disposing of spent shale in a manner that is environmentally acceptable, various methods have been considered: Surface disposal, mine backfilling with dry spent shale, and backfilling with spent shale slurry. The preferred method depends on whether the mine is wet or dry. Because of potential chronic leaching, spent shale should not be returned to a wet mine. Adverse leachate problems are much easier to control on the surface than in a subsurface environment. Numerous research studies indicate that, except for stabilization and revegetation, shale spoil, because of its adverse leaching potential, should be protected from moisture to the extent practical.

Groundwater is the ultimate recipient of shale leachate from surface disposal or mine backfill. Because of potential leaching of organic and inorganic compounds by groundwater, a concerted effort should be made to minimize leachate volumes entering the groundwater system.

In the case of a dry mine, however, the return of the dry spent shale to the mined areas may be acceptable pending further study and the promulgation of future regulations. This system creates support, reduces subsidence potential, and reduces surface storage of spent shale by approximately 60 percent.

Current research indicates that potential adverse environmental and operational problems can result from pumping spent shale in a slurry form back into an oil shale mine or abandoned retort. Low compressive strengths of shale slurry, the potential for chronic leaching of slurry backfill and surface storage of slimes created by slurry production and application all pose a potential serious threat to groundwaters of the Piceance Basin and should be critically investigated prior to the initiation of the shale slurry backfill operations. For these reasons, hydraulic backfilling of spent shale is not recommended at this time.

Stabilization of In Situ *Spent Shale*—by Edward Bates

True and modified *in situ* retorting processes leave the retorted shale below the ground, which avoids many of the problems of surface disposal but also creates a greater potential for groundwater pollution. In addition, any subsidence that may occur could fracture overlying aquifers and result in water movement between aquifers and probable lowering of groundwater quality. Dealing with these potential impacts would require development and implementation of new control technology not available at this time.

Control of Leachate—

The prevention of groundwater and surface water (from groundwater recharge of surface streams) pollution by true or modified *in situ* retorting is an unsolved

problem. Some possibilities that have been proposed include the use of high retorting temperatures, slurry backfilling, exhaustive leaching and treatment, and hydrologic barriers or bypass.

High Retorting Temperatures—Maintaining high retorting temperatures (approximately 1,000° to 1,200°C or 1,832° to 2,192°F) encourages the restructuring of shale minerals into insoluble igneous or metamorphic mineral complexes. The formation of such complexes at temperatures of approximately 900° to 1,200°C (1,650° to 2,192°F) under laboratory conditions has been demonstrated and reported by Smith, Rubb, and Young (55). If the results of such laboratory studies are applicable to field retorting conditions, then this approach might serve as a primary control technology. However, several questions must be answered before applicability of this approach can be assessed. First, it must be determined that the mineral complexes produced by field conditions are similar to those indicated by laboratory studies under controlled conditions. Second, the spent shale mineral complexes produced in the field must be shown to remain insoluble under conditions that exist years after backflooding of modified or true *in situ* retorts. It must be established that the water quality of backflooded retorts will not cause a breakdown of these mineral complexes. And, third, and perhaps most difficult, it will be necessary to demonstrate that retorting conditions can be controlled to produce a spent shale that is uniform in respect to its insolubility. This step may be difficult, since one of the retorting problems is maintaining a uniform retorting front. Portions of the retort, especially fringe areas, may not reach temperatures high enough to produce the mineral complexes reported in laboratory studies.

Slurry Backfilling for Cementation—It has been suggested that finely crushed surface-retorted shale grout could be hydraulically injected into burned out modified *in situ* retorts to fill void areas and cement the retorts to make them impermeable to water flow.

Surface-retorted shale has been shown to have some cementation properties under controlled conditions (56,57,58). However, several questions must be answered before this can be considered as an applicable control technology to prevent leachate generation from modified *in situ* retorts. It must be demonstrated that injected spent shale slurry will develop adequate cementation strengths and very low permeability values when injected into the environment of burned out retorts. The question of whether injected spent shale itself would produce a troublesome leachate must be addressed. As discussed in Section 3 under Solid Waste Impacts, the leachates from surface-retorted shale (Table 3-27) may affect water quality. It is possible that such injection may compound the problem of groundwater pollution rather than solve it. The mechanics of injecting the slurry so as to obtain a uniform distribution within the retort may prove very difficult. Permeabilities to flow of injected slurry may be highly variable within the retort, making uniform dispersion to seal the retort impossible. Preliminary cost estimates for grouting retorts with spent shale slurry have been stated by Persoff and Fox as being $2.70/bbl of oil for the C-a lease tract and $3.80/bbl for the C-b tract (59). However, the Rio Blanco Oil Shale Company has stated that they believe the actual costs will be much lower (personal communication from Kay Berry, Rio Blanco Oil Shale Company).

Exhaustive Leaching and Treatment—If it is found that spent shale within true or modified *in situ* retorts does indeed produce a leachate that can significantly lower groundwater quality and if efforts to seal the retorts to prevent water movement through them fail, then a serious water pollution hazard could exist.

One possible approach to resolving such a problem would be to intercept and remove the leachate and contaminated groundwater near the retorts by pumping followed with adequate treatment and reinjection downgradient from the retorts. In addition to the obvious problem of cost, a major unanswered question affecting this approach is the length of time that such a program might have to be main-

tained before the retorts would be adequately leached to permit safely discontinuing the pumping and treatment process. Pumping and treating would likely be necessary for a number of years following retorting. Analysis of water samples from the Rock Springs, Wyoming Site 6 of the Laramie Energy Technology Center showed some improvement, but they were still far from restored to the background water quality 50 months after retorting (59). Possibly, the leaching process could be deliberately accelerated to reduce the treatment period, but such technology has yet to be developed. Preliminary cost estimates for collecting leachate and treating it on the surface by activated carbon and reverse osmosis have been estimated by Persoff and Fox at $1.20/bbl of oil production, based on treating six pore volumes of leachate (59).

Hydrologic Barriers—The use of hydrologic barriers such as barrier pillars to control the inflow of water into the retort area and prevent the spread of leachates from the retort area has been suggested as a partial solution to the problem. However, barrier pillars alone cannot be expected to be very effective, since the retort zones often intersect aquifers or other zones of water movement. Effectiveness of barrier pillars could be substantially increased by use of grouting to seal more permeable zones and fractures. Barrier pillars properly designed and supplemented by grouting could reduce the magnitude of the rate of leachate plume development under favorable hydrogeologic conditions, but they are not by themselves likely to solve the problem. Preliminary cost estimates for construction of a grout curtain around the retort area have been estimated by Persoff and Fox at $1.70 to $2.80/bbl of oil for the C-a and C-b lease tracts, respectively (59).

Hydrologic Bypass—The use of a hydrologic bypass to divert a major portion of the groundwater flow around the retort area has been theorized (59). Essentially, a hydraulic bypass would capture most of the groundwater flowing toward the retort area, carry it around the retort zone, and return it to the groundwater flow system downgradient from the retorts. The design of such a system would vary with the local hydrology but would likely involve use of numerous wells.

A hydraulic bypass system carefully designed for local hydrology could possibly make a substantial reduction in the quantity of leachate produced, but will not by itself solve the problem. In addition, a hydraulic bypass system may permit the mixing of waters between aquifers of differing quality. Preliminary cost estimates for constructing a hydrologic bypass system for the C-a and C-b lease tracts have been estimated by Persoff and Fox at $0.25 and $0.50/bbl of oil produced, respectively (59).

Prevention of Subsidence—

Modified *in situ* retorting, conventional underground mining, and possibly true *in situ* retorting may pose fracturing and subsidence problems unless subsidence control technology is provided. For conventional underground mining, some control technology presently exists for other mineral commodities that could probably be modified and applied to the specific hydrologic and geologic environment of a particular underground oil shale mine. Backfilling of mine voids with spent shale could provide additional support, though groundwater pollution could be a concern. Weakening of pillar strength by spalling and weathering would require special attention to avoid long-term problems.

For modified and true *in situ* retorting an acceptable control technology has not been demonstrated. Both these technologies depend on fracturing the oil shale to be retorted. Technology to fracture the shale and yet not seriously fracture or weaken surrounding rock and support pillars has not been perfected. Recent experience of the Occidental Oil Shale Company at their Logan Wash site indicates that problems in controlling the nature and extent of fracturing still exist.

Subsidence need not reach the surface to have serious impacts on the environment. Fracturing of overlying water-bearing strata may result in loss of this water

resource to the retort zone, compounding the problem of leachate production and doubly affecting groundwater resources. Injection of spent shale or other cementing material into burned out retorts may provide additional support and help prevent fracturing of overlying strata. However, the key to controlling subsidence or fracturing of surrounding strata will likely lie in learning to control the rubblization process and developing a technology for providing adequately-sized and appropriately-spaced support pillars capable of supporting overlying strata. The possible effects of heat on the strength of support pillars and overlying strata should be investigated to assure that adequate support will remain after retorting.

OTHER PROCESS CONTROLS

Prepared for Dale Denny and Bruce Tichenor by Radian Corporation

Storage Tank Vapor Controls

Floating-roof tanks and internal floating covers are two tankage alternatives to standard fixed-roof storage tanks that offer substantial hydrocarbon emission control. These alternatives lower both diurnal breathing losses and filling losses associated with fixed roof tanks by eliminating the vapor space inside the tank.

Floating-roof tanks consist of a welded or riveted cylindrical steel wall equipped with a deck or roof that is free to float on the surface of the stored liquid. The roof rises and falls according to the depth of stored liquid. To insure that the liquid surface is completely covered, the roof is equipped with a sliding seal around its circumference, which fits against the tank wall. Additional emission control is provided by employing double sliding seals. Roof drains are also provided to protect against excessive loading by rain and snow.

Internal floating covers are floating roofs or floating decks provided inside a standard fixed-roof tank. They are equipped with sliding seals and are free to float on the product surface in the same manner as floating roofs. A primary advantage of internal floating covers is that they are protected from the weather and do not require provisions for rain and snow removal.

Floating roof and internal floating cover technology is well developed, having been applied by the petroleum and chemical industries for many years. Internal floating covers are more applicable for locations with very high wind, rainfall, or snowfall, than are floating roof tanks. Also, internal floating covers may be retrofit to fixed-roof tanks. Both are available as prefabricated units in a variety of styles for tanks ranging in size from smaller than 400 m^3 or 14,126 ft^3 (2,500 bbl) to more than 95,000 m^3 or 3,354,894 ft^3 (600,000 bbl). Costs for floating covers vary with the size of the storage tank. A recent report (60) indicates installed costs of $40-50,000 for floating roofs on tanks with capacities of 16,000 m^3 or 565,040 ft^3 (100,000 bbl).

Floating roofs and internal floating covers are very reliable and require only a minimum of maintenance. Sliding seals exposed to harsh weather must be routinely inspected and occasionally replaced. Heavy snows must be removed from exposed floating-roof tanks.

Standing storage emissions from floating-roof tanks and internal floating covers are approximately 15 percent of comparable fixed-roof tank emissions, and working emissions (those resulting from level changes after filling or discharging) are less than 1 percent of comparable fixed-roof tank emissions. Actual emission reductions are a function of tankage operations, but, in general, net emissions from floating-roof and internal floating-cover tanks average less than 10 percent of emissions from comparable fixed-roof tanks. No secondary pollutants are associated with floating-roof tanks or internal floating covers.

Refinery Sludge Controls

The most common sources of refinery sludges are as follows:

Cooling water sludge	API separator bottoms
Alkylation sludge	Treating clays
Biological sludge	Storm water silt
Tank bottom sludge	

Existing practices in refineries that are employed to limit or reduce these sludges and other solid wastes consist primarily of source control methods.

The initial step in applying source control techniques involves identifying and monitoring sources of oil, water, and other contaminants. Two policies that can be implemented to help monitor and control solid wastes are:

Refinery permit systems that allow oily streams to be released to drains only with the approval of the environmental department, and

Shutdown planning that provides for prearranged disposition of oils and wash waters.

After solid waste sources have been identified and monitored, the next step is to implement in-plant operating procedures or equipment changes to reduce the amount of wastes from these sources. Operating procedures that might be employed include water re-use and segregated drains for process and storm water. These methods introduce less water into oily drains and also result in reduced amounts of soluble contaminants and biosludges. Treatment methods such as aerobic digestion, incineration, settling, and centrifugation significantly reduce the quantity of sludge for final disposal and help recover oil and remove water from solid wastes.

Equipment which can be utilized to reduce the amount of contaminants to oily drains and the oil content of API separator solid wastes include mechanical seals for pumps and flow-by sample valves. In addition, the installation of mixers in storage tanks to keep solids suspended in the oil will diminish tank bottom sludge formation.

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SECTION 5
SAMPLING, ANALYSIS AND MONITORING

This section discusses the sampling, analysis, and monitoring techniques and programs that should be a part of any commercial oil shale activity. It describes analytical methods and the application of those methods to air, surface and ground water, and solid waste leachates.

This section cites the need for baseline sampling, analysis, and monitoring prior to oil shale recovery and processing in order to maintain the environment as nearly as possible in its original condition. It also cites the need for monitoring programs to predict and thus to aid in preventing environmental damage. Finally, it considers the need for long-term monitoring, particularly around shale disposal sites, after conclusion of oil shale processing activities.

Monitoring needs may be satisfied by the oil shale developer, the government, and by other organizations. It may be useful, therefore, to distinguish between regulatory requirements which the developer must meet and environmental answers which may be answered through government research. It may also be in the best interests of the industry to perform some limited screening research monitoring.

After a discussion of ambient and stationary air monitoring techniques, a discussion of water pollutants of concern is presented, but with greater emphasis on monitoring, including siting and frequency of sampling. This discussion cites the need for biological monitoring in addition to the use of physical and chemical tests.

Predictive capability is emphasized in the discussion of solid waste disposal sites because of the potential need for corrective action at these sites during and following processing activities to control leachate movement. The discussion of solid waste disposal also cites the need to inspect shale disposal sites regularly for stability and integrity.

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This section incorporates both stationary and ambient air monitoring techniques. Table 5-1 summarizes the accuracy and precision of data for all methods discussed here.

Gases

The contribution of gaseous pollutants to the atmosphere by oil shale processes is a very important aspect of the environmental problem associated with oil shale. The analytical determination of these compounds is important from a process as well as from an environmental point of view. Gaseous emissions are discussed relative to stationary source testing and ambient air monitoring. Actual data from several testing occasions have been included to illustrate concentrations encountered and variability of results.

SO_2, Stationary Source Method—

The method for SO_2 determinations is Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources (1). In this method, a gas sample is passed through an impinger train containing a 3-percent hydrogen peroxide absorbing solution. The sulfur dioxide is measured as a sulfate by barium-thorin titration.

TABLE 5-1. PRECISION AND ACCURACY RANGES FOR MONITORING METHODS USED IN THE ANALYSIS OF OIL SHALE EFFLUENTS

Pollutant and method	Accuracy and/or precision
1. Sulfur dioxide, SO_2:	
A. Ambient:	
1. Std method (Schiff)	(Avg. value) 41 ± 6 μ/m^3
2. Flame photometric	—
3. Pulsed fluorescent	NR[a]
B. Source:	
1. Std method (sulfate titration)	18.9 ± 4.3 ppmv
2. Oxides of nitrogen, NO_X:	
A. Ambient:	
1. Arsenite method	Range: 60 to 300 μ/m^3 ± 11μ/m^3 SD[b]
2. Chemiluminescence	Precision: 5 ppb
B. Source:	
1. Std method (phenoldisulfuric acid)	217.3 ± 39.6 ppmv
3. Carbon monoxide, CO:	
A. Ambient:	
1. Std method (nondispersive infrared)	+3 ppm bias
2. GC (THC method)	Range: 3.43 to 40.6 Average difference: 3.2%
B. Source:	
1. GC	2.60 ± 0.2% (v)
4. Combustion gases:	
A. Source:	
1. Carbon dioxide (GC)	25.93 ± 1.45% (v)
2. Nitrogen N_2 (GC)	60.89 ± 3.50%
3. Oxygen O_2 (GC)	NR
5. Suspended particulate (Std hi-vol method)	3.7% Precision
6. Ozone:	
A. Ambient:	
1. Ultraviolet Absorption (Std method)	1.7% Precision
2. Chemiluminescence	6% Precision; −5% accuracy bias
B. Source:	
1. KI method	NR
7. Hydrogen sulfide, H_2S	
A. Ambient:	
1. Sulfur-specific photometric detector	2.76%, relative SD 0.1 ngs
B. Source:	
1. $Cd(OH_2)$ method	1.764 ± 42.5 mg/m^3
8. Carbon disulfide, CS_2 and carbonyl sulfide, COS:	
A. Source:	
1. $Cd(OH_2)$ for CS_2	NR
2. $CdCl_2$ for COS	NR
9. Ammonia, NH_3:	
A. Ambient:	
1. Indophenol	Range: 1 to 30 ppb; precision: 30%
B. Source:	
1. Impinger method	4,457 ± 891 mg/m^3

TABLE 5-1. (continued)

Pollutant and method	Accuracy and/or precision
10. Trace metals:	
A. Ambient (metals on particulate):	
1. Mercury (silver wool)	NR
2. Lead (3% HPO_3 on filter)	Range: 80 to 125 g/m³; precision: 3.7%
3. Arsenic (glass filter)	Coefficient of variation: 4%
B. Source (metals in gas):	
1. Mercury (impinger)	±10% relative SD
2. Arsenic (GC/MS)	NR
11. Hydrogen cyanide, HCN:	
A. Source:	
1. Hydrolysis to NH_3	81.25±5.81 mg/m³
12. Sulfates, $SO_4^=$:	
A. Ambient:	
1. Methylthymol blue	Recovery: 91% to 99%; relative SD; 2% to 4%
13. Particulate analysis (Inorganics on the particulate):	
A. Ambient:	
1. Nitrate NO_3^- (cadmium reduction)	Recovery: 94% to 103%; relative SD; 2 to 3%
2. Fluoride F^- (ion selective electrode)	5% to 10% relative SD
14. Particulate loading:	
A. Ambient:	
1. Stacked filters	NR
B. Source:	
1. Isokinetic sampling	
15. Organic:	
A. Ambient:	
1. BAP	Range: 10 to 400 ng; coeff. of var. ±0.07
2. PAH GC/UV	NR
3. POH (Ultrasonic collection)	±5% Precision
4. Ambient organics (cartridge method)	NR
B. Source:	
1. C_1 C_6 (GC)	NR

[a] Not Reported.
[b] Standard deviation.

This method was used in two separate testing occasions at the Paraho oil shale retort by TRW. Results, reported as reliable at the Paraho operation are summarized as follows: (2,3)

Date	SO_2 (ppmv)
10/15/77	16.0
10/17/77	22.0
10/17/77	14.5
10/19/77	23.0
Mean and SD	18.9 ±4.3

This method is subject to interferences from free ammonia, water soluble cations, and fluorides. Ammonia and fluorides have been identified as present in oil shale effluents and could interfere with the determination. The TRW Corporation tests added a sulfuric acid trap to remove ammonia and recorded SO_2 concentrations of 11 and 14 ppmv. The lower values might indicate that there could be an interference, but more data are necessary before it can be stated with any certainty. This is the type of work that is envisioned as being done by the methods manual study mentioned earlier. However, until otherwise indicated, Method 6 (1) will be used for the measurement of SO_2.

SO_2, Ambient Methods—

Colorimetric Analysis—By a principle based on the Schiff reaction and West-Gaeke modifications (4) sulfur dioxide is absorbed from ambient air volumes into a solution of potassium tetrachloromercurate (PTCM). The resulting dichlorosulfitomercurate complex is reacted with pararosaniline and formaldehyde to form a colored dye. Absorbance of this colored solution is measured spectrophotometrically.

The EPA reference method (5) is called either manual or automated. A revised standard of test also appears in the *American Society for Testing and Materials (ASTM) Annual Book of Standards,* (6).

The method is applicable to the ambient atmospheres in the range of 5 to 13,000 mg/m^3 (0.002 to 5 ppm). Autoanalyzer techniques, absorption collection efficiency of sampling, and manipulation of sample solution aliquot have lowered the limit of detection to 5 mg/m^3 (7-9).

Flame Photometric Detection—Ambient air can be sampled continuously and supplied to a flame photometric detector. An in-line H_2S scrubber is required by the equivalency method under designation by EPA to remove H_2S and pass SO_2. SO_2 is converted to an S_2 excited molecular species that emits light near the 394 nanometer (nm) wavelength, and intensity is measured with an optically filtered photomultiplier tube. Response is approximately equal to the square of sulfur atom concentration (10,11).

Analyzers that chromatographically separate SO_2 from other gases in ambient atmospheres do not respond to changes in concentration as quickly as those that monitor without prior separation. Concentrations over the range of 0.01 to 1 ppm are measured in atmospheres containing low concentrations of sulfur-containing gas and CO_2.

Pulsed Fluorescent Detection—Ambient air is sampled continuously and supplied to a fluorescent chamber where SO_2 is detected. The method is an EPA-designated equivalent method (12,13). Pulsating ultraviolet (PUV) light is focused through a narrow band pass filter into the fluorescent chamber. SO_2 molecules are excited, and fluorescent light is emitted and measured by a photomultiplier tube. The fluorescent radiation is proportional to SO_2 concentrations in ambient air.

The method is applicable where instrumentation is operated on the 0.5 ppm full-scale range within a temperature range of 20 to 30 °C (68 to 86 °F) and where suitable power is available. Ambient atmospheres with concentrations greater than 5 ppbv over a 24-hr period are measured with a rise and fall time of 4 min as concentration is changed.

NO_x, Stationary Source Method—

The method employed for oxides of nitrogen determinations is Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources (1). Grab samples of the gas are collected in an evacuated flask containing a dilute sulfuric acid/hydrogen peroxide solution. The nitrogen oxides, except nitrous oxide (N_20), are oxidized to nitrate and determined by the phenol disulfonic acid method. This method was used by TRW in the examination of the off-gas of the Paraho oil shale retort and found to be acceptable (2,3). The results of their analysis are as follows:

Date	NO_X (ppmv)
10/15/77	160.0
10/17/77	235.0
10/17/77	250.0
10/19/77	224.0
Mean and SD	217.3 ± 39.6

The amount of scatter for the NO_X data is more severe than for the SO_2 data, but valid conclusions cannot be drawn with this limited information.

NO_2, Ambient Methods—

Bubbler Method—NO_2 is measured in ambient air by specifically removing NO_2 with sodium arsenite reagent solutions through reactions between nitrite ion (NO_2^-) and diazotizing and coupling reagents. Analysis of the colored azo dye is performed with a spectrophotometer at 540 nm of 10-nm bandwidth (14).

The method is applicable to ambient atmospheres for 24 hr and for determination of NO_2 concentration in the range from 0.005 to 0.4 ppm. Interferences are negligible in ambient air quality monitoring when the procedure is applied in underdeveloped areas. NO and CO_2 have been found to be potential interferences in urban atmospheres (15).

Chemiluminescence—The chemiluminescence procedure for measuring NO_2 uses the principle of gas phase reaction of NO_X and O_3 to form NO_2 and light. Detection of NO_X (NO + NO_2) requires conversion of NO_2 to NO, since the reaction is directly proportional to NO in the presense of excess O_3. Typically, NO_2-to-NO converters are capable of quantitative conversion for long periods before needing maintenance (16).

This principle has application in ambient monitoring and automated monitoring networks in the range of 0.005 to 1 ppm with linear response over these concentrations. It is an EPA Federal reference method (17).

CO_2, CO, N_2, and O_2, Stationary Source Method—

These parameters are usually indicative of the process efficiency and can be determined with a gas chromatograph. A column of silica gel and a molecular sieve is placed in series with a thermoconductivity detector, and the gas is separated into its various components. Table 5-2 summarizes the data taken at Paraho during one testing sequence (3).

TABLE 5-2. SUMMARY OF CO_2, O_2, N_2, AND CO DATA TAKEN AT PARAHO

Date	CO_2	O_2	N_2	CO
10/17/77	25.08	—	60.94	2.94
10/17/77	25.71	—	63.89	2.43
10/19/77	25.92	—	54.83	2.81
10/19/77	25.14	—	57.82	2.68
10/20/77	27.36	—	60.93	2.45
10/20/77	28.28	—	63.91	2.68
10/21/77	24.02	0.78	63.91	2.18
Mean and SD	25.93 ±1.45	0.78	60.89 ±3.50	2.60 ±0.2

Workers investigating the emissions from a TOSCO II operation also have reported using a gas chromatograph to determine the composition of the gas by analyzing it for CO, CO_2, O_2, and N_2 (18). Researchers at the Laramie Energy Technology Center have also employed this technique for analysis of the off-gas (19).

CO, CH_4, NMHC, Ambient Methods—

Flame Ionization Detection—Measured volumes of ambient air are delivered 4 to 12 times/hr to a gas chromatographic column where HC, CO_2, and H_2O are separated from methane and CO. Methane (CH_4) is transferred and measured in a hydrogen flame ionization detector . The CO is eluted to a catalytic reduction tube and reduced to CH_4 before passing through the FID. Hydrocarbons (HC) are also transferred quantitatively to the FID, and nonmethane hydrocarbons are determined by subtracting the methane from the total hydrocarbon (THC) value (20).

The method is applicable to the semicontinuous measurement of THC, CH_4, and CO in ambient atmospheres over the range 0.025 to 2 ppm for THC, 0.025 to 1 ppm for CO, and 0.025 to 2.0 ppm for CH_4 (3,21).

Nondispersive Infrared—The principle of nondispersive infrared (NDIR) is based on the absorption characteristics of CO at infrared wavelengths. The spectrometer measures the absorption of CO using two parallel infrared beams and a selective detector over the range of 1 to 100 ppm (0.7 to 115 mg/m^3 or 3.06×10^{-4} to 5.03×10^{-2} grains/ft^3) (22). The procedure is an EPA Federal reference method (17).

Application depends on the ambient atmosphere to be monitored, since the degree of interference by water vapor can be equivalent to 11 mg of CO/m^3 or 4.81×10^{-3} grains/ft^3 (10 ppm) (23).

Hydrocarbons at concentrations found in suburban ambient atmospheres do not ordinarily interfere, since 325 mg methane/m^3 or 0.142 grains/ft^3 (500 ppm) will give a response equivalent to 0.7 mg/m^3 or 3.06×10^{-4} grains/ft^3 (0.5 ppm) (24).

Trace Metals, Stationary Source Method—

A system of four impingers commonly used in Method 5, Determination of Particulate Emissions from Stationary Sources, is usually employed for the collection of trace metals. The first is filled with 3M H_2O_2, the second and third are filled with 0.2M $(NH_4)_2 S_2O_8$ plus 0.02M $AgNO_3$, and the fourth is filled with Drierite*. The peroxide is used for SO_2 removal, and the persulfate solution removes trace metals such as Hg, Se, Sb, As, or Pb that pass through the peroxide solution. The sampling train can also use IC1 as the oxidizing medium when specific tests for mercury are made. It has been demonstrated by Fox (25) that the impinger method is effective for collecting mercury samples. The samples are then brought to the laboratory and analyzed by atomic absorption spectroscopy (AAS).

TRW used the impinger technique described above to evaluate the mercury emissions from the Paraho oil shale retort and reported mercury concentrations of 0.304, 0.120, 0.155, 0.235 and 1.298 mg/m^3 or 1.33×10^{-4}, 5.24×10^{-5}, 6.77×10^{-5}, 1.03×10^{-4}, 5.67×10^{-4} grains/ft^3 (0.304, 0.120, 0.155, 0.235, and 1.298 ppb) (3). This technique was stated by TRW to be accurate to ± 10 percent. Trace metal experiments carried out by Shendrikar and Faudel (18) were conducted by passing the gases from the Fischer Assays through 100 ml (.026 gal) of 1:1 nitric acid x water mixture. The samples were boiled down and diluted to a known volume and used to represent the gaseous fraction of the total trace metal concentration. No data were presented on collection efficiency.

Arsenic was determined by TRW, but the levels were too dilute to be detected by AAS methods (3). An outline of the method used to convert arsenic to arsine (AsH_3) is given, and a gas chromatograph/mass spectrometer (GC/MS) technique for analysis is presented for concentrations of less than 1 ppb.

Fruchter (26) found arsenic in the form of arsine at levels of 0.015 mg/m^3 or 6.55×10^{-6} grains/ft^3 (0.015 ppb) in the off-gas from the LETC 9-tonne (10-ton) retort by using neutron activation analysis and x-ray fluorescence.

Ozone, Ambient Methods—

Ultraviolet Absorption—The analytical principle employed for ozone utilizes the intensity changes of UV energy as the light beam traverses a fixed pathlength occupied by a volume of air containing ozone (27).

Continuous instrumentation utilizing the UV absorption principle has application in the ambient atmosphere and will measure concentrations from 0.003 to 1.0 ppm. It has been projected as an equivalent method.

Chemiluminescence—Chemiluminescence can be used as the analytical technique for ambient ozone measurements. Sample gases containing ozone and reagent ethylene are combined, and the chemiluminescent light produced as a result of the reaction is photometrically detected (28,29). Instrumentation to monitor O_3 continuously in the ambient atmosphere is specified in the Federal Register (30).

Ambient atmospheres are monitored over the concentration range of 10 mg/m^3 to 2 mg/m^3 or 4.37×10^{-6} to 8.74×10^{-4} grains/ft^3 (0.005 to 1.00 ppm). The chemiluminescent detection of O_3 with ethylene is not subject to interference from common gaseous air pollutants such as NO_2, CO, NH_3, and SO_2 at ambient concentrations.

NH_3 and HCN, Stationary Source—

Both NH_3 and HCN can be analyzed using the same sampling train. The sample is drawn through three impingers with 5 percent HCl for ammonia removal and then passed through another impinger that contains concentrated H_2SO_4 for hydrolyzing HCN to NH_3. Samples were titrated by the Los Angeles Air Pollution Control District using this method, and the accuracy was estimated at ±5 percent for the hydrogen cyanide (3). Table 5-3 summarizes the reported data for NH_3 and HCN from the recycle gas of the Paraho Retort.

TABLE 5-3. SUMMARY OF NH_3 and HCN EMISSIONS IN THE RECYCLE GAS FROM PARAHO

	mg/m^3	
Date	NH_3	HCN
10/17/77	5,032.0	Not Reported (NR)
10/17/77	4,093.0	NR
10/17/77	4,987.0	NR
10/17/77	3,519.0	NR
10/19/77	4,560.0	79.50
10/19/77	NR	80.59
10/20/77	6,028.0	75.56
10/20/77	3,611.0	89.33
Mean	4,457.0	81.25
±SD	±890.8	±5.81

Ambient Ammonium Method—

Atmospheric ammonia is collected by drawing a known volume of air through a dilute sulfuric acid solution. Ammonium sulfate is formed and then reacted with phenol and alkaline sodium hypochlorite to form the blue dye, indophenol. Sodium nitroprusside is used as a catalyst to speed up the reaction. After reaction is complete, the solution can be analyzed spectrophotometrically (31). The mechanism of this reaction has been proposed by Rommers and Vissor (32).

The range and sensitivity of the method is reported (33) as 20 to 700 mg/m^3 or 8.74×10^{-6} to 3.06×10^{-4} grains/ft^3 (0.025 to 1 ppm) with a sampling rate of 1 to 2 l/min (.26 to .52 gal/min) over a sampling time of 1 hour. The detection limit is 0.02/mg NH_3/m^3 (8.74×10^{-9} grains/ft^3) (33).

Hydrogen Sulfide, Stationary Source Method—

The method used for hydrogen sulfide is Method 11, Determination of Hydrogen Sulfide from Stationary Sources (34). The method utilizes about 0.20 M solution of cadmium hydroxide ($Cd[OH]_2$) to precipitate the hydrogen sulfide as CdS. The precipitate is oxidized with I_2 and back-titrated with thiosulfate. TRW ran four H_2S determinations at Paraho with this method and got a mean of 1,764.7 mg/m^3 (0.771 grains/ft^3) and an SD of 42.5 (3).

Hydrogen Sulfide, Ambient Method—

A gas chromatographic separation of substances is used in conjunction with sulfur-specific detection by the flame photometric detector. The detector measures sulfur-containing gases at the 399 $\pm$5 nm emission line of sulfur in a hydrogen-rich flame, with a specificity ratio of sulfur to nonsulfur compounds of between 10,000 and 30,000 (35).

Carbonyl Sulfide and Carbon Disulfide, Stationary Source Method—

Carbonyl sulfide and carbon disulfide are collected by passing the gas through a series of impingers. Typically, the first impinger contains $Cd(OH)_2$ to remove any hydrogen sulfide. The second impinger is empty to collect any carryover. The third impinger contains 100 mg (1.54 grains) of 7.5 percent $CaCl_2$ and 1 percent NH_4OH for collection of carbonyl sulfide. The fourth impinger contains 100 mg (1.54 grains) of alcoholic KOH to collect carbon disulfide, and the last impinger contains silica gel. The hydroxide and chloride solutions are normally oxidized to SO_4 by hydrogen perioxide and analyzed by gravimetric methods. TRW used these techniques for the analysis of COS and CS_2 in the gas stream of the Paraho Retort. The results are summarized in Table 5-4 (3).

TABLE 5-4. SUMMARY OF COS AND CS_2 DATA FROM PARAHO

	mg/m^3	
Date	COS	CS_2
9/6/77	32.6	58.3
9/6/77	50.0	ND[a]
9/6/77	ND[a]	ND[a]

[a] None detected.

Based on the range of data, it might be inferred that this method should be a candidate for additional study.

Organics (C_1 - C_6), Stationary Source Method—

Direct measurement of organics in the gas stream is usually limited by the boiling point of the organic compound, and carbon compounds with more than six carbon atoms are usually too dilute to analyze without some separation and/or concentration procedure. Figure 5-1 shows how the percentage of hydrocarbon in the gas stream varies with boiling point and illustrates the point very clearly that the C_6+ fraction is extremely dilute. Note, however, that the concentration of organic material in the gas stream depends on the type of process used to retort the shale, and some systems have produced markedly different gas compositions.

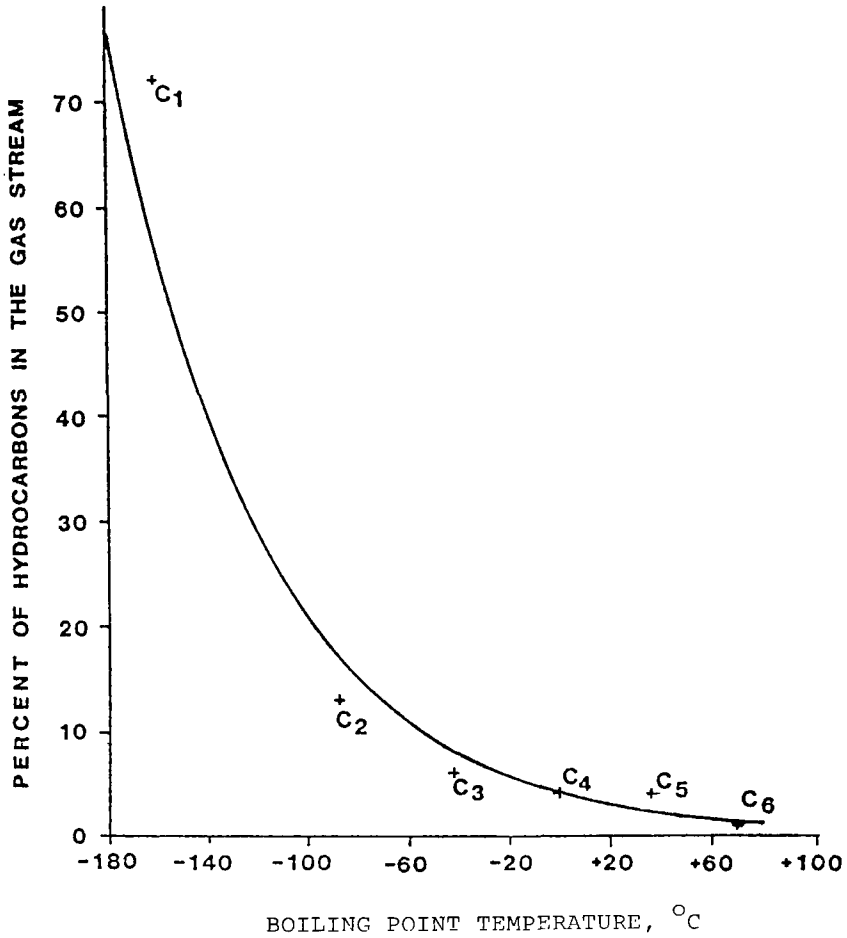

Figure 5-1. Percentage of hydrocarbon in the gas stream versus boiling point of carbons 1-6.

The light-end organic compounds (C_1 - C_6) are usually present in sufficiently high concentrations to be routinely determined by gas chromatographic techniques. The conditions vary to some extent and are summarized for two testing occasions in Table 5-5.

Most of the n-alkanes and n-alkenes can be identified by their retention time data. Other compounds that do not fall into that category can be identified by using mass spectroscopy.

Analysis of the gas stream for organics larger than six carbons requires the addition of more sophisticated equipment, usually a GC/MS system. Since these

TABLE 5-5. SUMMARY OF GAS CHROMATOGRAPH CONDITIONS FOR C_1 - C_6

Source	Column	Detector	Temperature
Level I Assessment (Ref. 36)	Poropak Q in 6′SS columns	Flame ionization	100°C isothermal
TRW (Ref. 3)	Poropak Q in 6′SS columns	Flame ionization	60 to 160°C @ 20°C/min

samples are collected in a cold trap, they are analyzed as the solid fraction. Their analytical description will be covered in a later section.

Organics, Ambient Methods—

Gas Chromatography—Ambient air samples are collected through grab sampling techniques using plastic bags with air valves. Portions of the ambient air in the bag are analyzed for C_1 through C_5 hydrocarbons by GC (37).

The method has applications in atmospheres containing 0.01 ppm. The lower limit for C_3 through C_5 HC can be extended by concentrating 100-ml (2.64×10^{-2} gal) aliquots or more of sample in a freeze trap. This limit is 0.1 ppbv.

Sampling is accomplished by flushing the plastic bag three times with ambient air and then filling the bag for transport to the GC for analysis. Integrated sampling can be done with large-volume bags and appropriate storage times before analysis.

Analysis is performed on a single column at 0°C (32°F), with separated components being detected by a flame ionization detector.

Fluorometric—Samples of benzo(a)pyrene and other aromatic hydrocarbons collected on membrane filters are extracted with benzene for subsequent separation by thin-layer chromatography. The BaP fractions from the TLC separations are extracted, evaporated, and dissolved in sulfuric acid for quantitative fluorometric measurement (38).

The fluorometric final analytical step of the procedure is linear over the range from 10 to 400 ng (10^{-9} g) (1.54×10^{-7} to 6.17×10^{-6} grains), and sample aliquot size from the benzene extraction must be adjusted so that sample concentration falls in this analytical range. Ambient air containing 0.02 to 0.8 mg/m^3 (8.74×10^{-9} to 3.50×10^{-4} grains/ft^3) would correspond to this range.

UV Spectroscopy—Sampling for polynuclear aromatic hydrocarbons is conducted with a suitable air mover and membrane or glass fiber filters, with subsequent GC separation of extraction mixtures. Polynuclear aromatic compounds are collected from GC eluate and analyzed by UV spectroscopy (38).

The method has a range of concentration from 2 to 1000 mg/m^3 (8.74×10^{-7} to 4.37×10^{-4} grains/ft^3), with sample volumes as low as 0.5 m^3 (17.66 ft^3). Ambient atmospheres in oil shale areas will require that large volumes of air be sampled. Detection limits lie in the range of 0.2 to 2.7 mg/sample (3.09×10^{-6} to 4.17×10^{-5} grains/sample) for individual compounds as collected on membrane filters.

FID/GC Method—Filter samples of aromatic HC can be extracted ultrasonically in CS_2 or benzene solvent, and the solvent solution is analyzed by FID/GC. The method is not specific, and analysis is qualitative for classes of compounds as defined in the Federal Register (39,40).

Ambient concentrations of 0.05 to 10 mg/l (4.17×10^{-7} to 8.34×10^{-5} lbs/gal) can be measured with a sufficient volume of sampled air (usually 1 m^3 or 35 ft^3).

Absorption, Purge and Trap Gas Chromatography—Ambient organic concentrations are determined on a semiquantitative basis by sampling through specially designed cartridges mounted in place of the filter on a high volume air sampler. Absorbed organic material is quantitatively desorbed from the cartridge

with separation and identification, first by GC and then by MS (41).

The technique has application in ambient atmospheres with concentrations of organics ranging from baseline levels (low concentrations) to relatively high concentrations when sampling for specific time periods at 100 to 250 ppm. Detection limits are typically 0.1 ng/m^3 (4.37x10^{-11} grains/ft^3) (42).

Particulates—David Sheesley and Michael J. Pearson

The solid material collected at an oil shale retorting operation can be split into two categories: controllable and fugitive emissions.

Controllable emissions are those process emissions that are confined by ducts, pipes, etc. that constrain their movement and direct them to a suitable control device. These types of emissions can be accurately sampled by utilizing isokinetic sampling techniques outlined in Method 5, Determination of Particulate Emissions from Stationary Sources (1). The primary method of analysis is to weigh the filters and correlate the mass to the volume of gas sampled. If taken properly, this value will reflect the concentration of the solids in the process stream at the time the sample was taken.

The uncontrollable, or fugitive, emissions present a severe sampling problem because of their lack of confinement. High volume samplers are usually employed as the method for collecting fugitive emissions. Care must be exercised to space or align the samplers properly in order to collect representative samples. Isokinetic sampling techniques are not employed, but a calibrated orifice allows a reasonably good estimation of the volume of gas that has passed through the filter, and the concentration of the dust in the air can then be determined. Unless some specific experimental conditions are instituted, this technique has the disadvantage of not being able to differentiate between various aspects of oil shale activities. Data on fugitive emissions from mining operations can contain information on blasting operations that are not distinguished from the total. An advantage of the technique is that it allows collection of large amounts of particulates that can be used for additional analysis. The main analytical technique for fugitive emissions is the determination of the mass of particles collected.

Additional analytical procedures can be carried out on the collected particulate, and these techniques can be found under the following section on solid waste sampling and analysis.

Ambient Particulate Sampling Methods—

Hi-Vol Sampler—The principle of the high volume (Hi-Vol) particle sampler is filtration sieving from a moving air stream. The glass fiber collects particles by interception and diffusion mechanisms according to the size of airborne particulate being sampled.

Particles with diameters of less than 100 mm or 3.94x10^{-5} in. (Stokes equivalent diameter) are normally collected over a 24-hr period at a flow rate of 1.1 to 1.7 m^3/min (38.8 to 60.0 ft^3/min). The method is applicable in an ambient atmosphere having concentrations of suspended particulates in the 10- to 1,000-mg/m^3 (4.37x10^{-6} to 4.37x10^{-4} grains/ft^3) (43).

Stacked Filter Unit—Ambient air can be sampled through stacked membrane filters, and particles in the air stream are physically separated into two fractions—12 and 0.2 mm (4.72x10^{-4} and 7.87x10^{-6} in.) (44,45). Typical mass loadings on the two filters suitable for subsequent analyses are 25 mg/m^3 (1.09x10^{-5} grains/ft^3) for the larger and 16 mg/m^3 (6.99x10^{-6} grains/ft^3) for the smaller filter.

The procedures have application where concentrations of the ambient atmospheric constituents are of the order of nanograms per cubic meter (ng/m^3). Sampling flow rate is adjusted according to the face velocity required to meet calculated efficiency of collection on membrane filters (46).

Virtual Impactor—Ambient air is sampled by a dichotomous sampler, and particles in the air stream are physically separated according to size by inertial impaction and collected by filtration. Filter samples are transported to a laboratory where analyses of the size-fractionated particulate matter may be carried out through a variety of analytical procedures. Mass loading on the filters is sufficient for energy-dispersive x-ray fluorescence (EDXRF) spectroscopy, ion chromatography, and spectrophotometric analysis (47,48). Nondestructive EDXRF analysis is followed by sonification extraction and transfer with subsequent analysis (49). Ion exchange chromatography and analyses for hydrogen ion, sulfate ion (by thorin spectrophotometry), and ammonium have been performed (48).

Analytical Methods for Ambient Particulate Samples

Ambient Sulfates Method—

Ambient sulfates are collected by drawing air through a glass-fiber filter with a hi-vol pump (50). The filters are extracted with H_2O and the extract is analyzed for sulfates by the methylthymol blue (MTB) method using a single channel Technicon Autoanalyzer II system equipped with a linearizer (51).

The MTB method is based on the spectral difference that exists in basic solutions (ph 12.5 to 13.0) between the barium ion (Ba^{++}) complex of MTB and the free MTB. At this pH, the barium complex is blue, and free ligand is brownish-red (absorbs light at 460 nm). Thus the color of solutions containing both the free ligand and the complex appears as gray. The amount of free ligand, monitored colorimetrically at 460 nm, is the measure of the amount of sulfate in the sample because the reaction of sulfate with MTB-Ba^{++} results in an equivalent amount of free ligand.

The method is applicable to the collection of 24-hr samples in the field and subsequent analysis in the laboratory.

Nitrates, Ambient Method—

Ambient nitrates are collected by drawing air through a filter with a high-volume pump. The exposed hi-vol filters are extracted with H_2O and analyzed for nitrates by reduction of the nitrate to nitrite by a copperized reductor column. The nitrite is reacted with sulfanilamide in acidic solution to form a diazo compound. This compound then couples with N-1-naphthylenediamine dihydrochloride to form a reddish purple azo dye that is determined colorimetrically at 520 nm using a Technicon Autoanalyzer II.

The method is applicable to the collection of 24-hr ambient samples in the field and subsequent analysis in the laboratory.

Trace Metals—

Lead—Lead is extracted from filter strips by using 3 percent nitric acid (HNO_3) as an extracting solution and then sonifying for 30 min. The concentration of lead in the resulting solution is determined quantitatively using flame atomic absorption (AA) spectrophotometry (52).

Ambient air volumes of 2,400 m^3 (84,746 ft^3) are typical, with a linear range of analysis of 15 mg/ml (8.74×10^{-6} lbs/gal). The method can be used for sample extracts containing between 0.03 and 7.5 mg/m^3 (1.31×10^{-8} and 3.28×10^{-6} grains/ft^3) of inorganic lead. More concentrated solutions can be diluted and the upper limit of the range thereby extended.

Mercury—Ambient air is drawn through silver wool in glass tubing where elemental mercury is collected and then desorbed at high temperature for transfer to AA analysis (53).

The sampling procedure has application for atmospheres with concentrations of 0.02 to 10 mg/m^3 (8.74×10^{-9} to 4.37×10^{-6} grains/ft^3) at collection flow rates of 100 to 200 cm^3/min (6.10 to 12.20 $in.^3$/min) over a 24-hr period.

Arsenic—Air is sampled through glass fiber filters for 24 hours to collect particles containing arsenic. Arsenic and the more natural aerosol, arsenic acid, are extracted from filter strips using 0.5 percent sodium hydroxide (NaOH) as an extracting solution. The concentration of arsenic in the resulting solutions is determined quantitatively using graphite-furnace AA spectrophotometry.

The method can be applied to ambient air samples of at least 10 m^3 (353 ft^3) having concentrations in the range of 0.1 to 1.0 mg/m^3 (4.37×10^{-8} to 4.37×10^{-7} grains/ft^3). The method can be used for sample extracts containing between 0 and 3 mg/ml (0 and 2.50×10^{-8} lbs/gal) arsenic. More concentrated solutions can be diluted and the upper limit of the range thereby extended (54).

Fluoride—Fluoride ion concentrations in H_2O soluble samples extracted from hi-vol filters can be measured directly using a F^- selective electrode in conjunction with a standard pH meter with an expanded millivolt scale. Electrode potentials are measured at 60-, 90-, and 120-sec intervals. Values extrapolated over arbitrarily long times are calculated and compared with the calibration curve determined from standard fluoride solutions (55).

The detection is approximately 0.002 mg F^-/ml (1.16×10^{-9} lbs/gal). The upper range for this procedure is 0.1 mg F^-/ml (5.82×10^{-8} lbs/gal). Samples with fluoride concentrations above this upper working limit can be analyzed using appropriate dilution techniques.

Asbestos—Ambient air is drawn through a membrane filter, and the filter is transformed for optical analysis (56). The method is the test method in the U.S. Public Health Service criteria document on occupational exposure to asbestos (57) and is listed in the 1974 Annual Book of ASTM Standards (58).

The method with suitable sampling periods has application in atmospheres containing concentrations of asbestos and asbestos-like fibers over the range of 1 to 20 fibers/m^3 (.028 to .567 fibers/ft^3). Fibers longer than 5 mm (1.97×10^{-4} in.) are counted.

Meteorological Conditions

Monitoring of meteorological conditions is critical for assessing the environmental impact of new source emissions. It is essential that meteorological data be representative of source conditions and primary receptor areas. The degree to which the data are representative depends on the complexity of the terrain, exposure of the sensors, and the period of data collection. Although onsite data are preferred, offsite data may be adequate for some applications (59). A minimum of 1 year of meteorological data is required. If available, 5 years of data should be used to minimize year-to-year variations.

Most meteorological variables can be measured using standard National Weather Service (NWS) equipment or its equivalent, and data values should meet NWS standards for accuracy. The parameters measured depend on previous data available for the area, representativeness of that data, and its intended application. Extensive information exists on required meteorological inputs for standard computer air monitoring models and guidelines on meteorological siting and instrument exposure. Data-averaging over time periods shorter than 1 hr may be required by certain complex terrain models.

Visibility

The Clean Air Act Amendments of 1977 declared the protection of visibility in mandatory Class I Federal areas as a national goal (60). The NAAQS and PSD standards require that a means of maintaining visibility in such areas be developed. In October 1979, EPA submitted a report to Congress (61) defining visibility, monitoring methods, modeling data requirements, and permit review requirements. This report provided the guidelines required to establish future regulations.

At this time, no universally accepted definition of visibility or visibility monitoring methodology exists (8), but four methods are commonly used for assessing visibility-related parameters: (1) Photography, (2) telephotometry, (3) nephelometry, and (4) transmissometry (62). These methods of visibility monitoring are described in Appendix B.

WATER

Wesley Kinney and Leslie McMillion

Surface Water Monitoring Methodology

The objectives of water quality monitoring programs with respect to oil shale development are to provide:

1. A record of changes from conditions existing before development operations, as established by baseline studies and evaluation;
2. A continuing check on compliance with all applicable Federal, State, and local pollution control laws, regulations, and lease requirements;
3. Predictive capability or timely notice of conditions or developing potential problems that would require correction to prevent environmental damage;
4. Determinations of the effectiveness of mitigating procedures implemented in regard to item (3) above;
5. Observations and calculations on effects in the biological realms resulting from changes in water quality and quantity.

From a water-quality standpoint, surface water and groundwater are closely related in most of the western oil shale regions. As exemplified by conditions in the Piceance Creek Basin, a significant portion of the surface water results from natural groundwater discharges. The quality of the streams likewise reflects the contributions from groundwater. Thus, a total monitoring program must consider both. However, because the methods for sampling and hydrologically investigating the two differ considerably, they are treated separately in the following.

Surface Water Impacts—

It is anticipated that surface water impacts will be attributable to one or more of the following situations, singly or in combination:

1. Point source discharges, such as wastewater outfalls or cooling system discharges;
2. Nonpoint source discharges, such as runoff from stored solids, erosion of construction areas, or overland transport of airborne fallout materials;
3. Accidental discharges such as spills from trucks, leaks in pipelines, or failure of containment structures or embankments around holding ponds or solid waste disposal piles;
4. Flow reductions through consumptive uses and mine dewatering.

Point Sources—Point source discharges from extraction or processing operations are not currently anticipated to contribute substantially to the degradation of surface water quality. Most excess mine waters, water from spent shale piles, and process water will be collected and routed to evaporation ponds or utilized. Slurry waters, if used to transport spent shale, will also be recovered and rerouted to containment ponds or utilized (63).

Because of the diffuse and episodic nature of probable sources of surface water pollution, point source monitoring is not expected to be a major component of the overall monitoring effort. However, if direct discharges to surface water occur, such discharges will be subject to the requirements of the NPDES Permit Program, including self monitoring of the effluents by the discharger. Monitoring requirements with respect to parameters, frequency, sample, and data handling and

analytical procedures will be specified by the regulatory agency issuing the discharge permits. Required monitoring would most likely include measurements of volume, sampling and analysis for selected chemical constituents, suspended solids, temperature, and pH. The frequency, duration, and methods of sampling should be such that a calculated average constituent loading ±50 percent will encompass the true average loading over any period of time.

Nonpoint Sources—It appears that the greatest potential for surface water quality degradation is from nonpoint sources rather than point sources. Thus, in the design of monitoring programs emphasis should be on nonpoint source pollutants, which generally will include: (a) sediments and associated sorbed materials eroded from shale piles, construction sites, access roads, etc, (b) dissolved salts leached from shale disposal sites, unlined catchment, and evaporation ponds, and discharge of saline groundwaters, (c) trace substances, both inorganic and organic, resulting from leaching of solid waste disposal piles or overland transport of airborne fallout materials during periods of high runoff (64,65).

The nonpoint source surface water monitoring effort will focus on instream monitoring networks that incorporate sufficient sensitivity to detect very subtle changes in water quality and flow patterns. The monitoring networks will include stations on permanent streams as well as on all major tributaries draining areas of mining and processing activities, disposal piles, evaporation ponds, and catchment basins. This network includes washes and ephemeral streams that may transport wastes during periods of heavy runoff, as well as intermittent and perennial tributaries that may be receiving wastes from groundwater seepage or atmospheric rainout, or whose flow patterns may be altered by consumptive water uses or mine dewatering processes. Significant springs and seeps should also be included in the monitoring network to determine if the quality or quantity of their flow is altered. Because of the well defined drainage patterns in most of the oil shale region, establishment of monitoring stations should be straightforward. Sampling stations on potentially impacted tributaries will make it possible to identify the sources of any changes detected in mainstreams. However, where large drainage areas are involved, a rationale must be developed for placing the stations in specific locations.

Accidental Discharges—The major potential sources of accidental discharges to surface water include failure of shale disposal piles or embankments around catchment basins or evaporation ponds, and spills associated with the transport of materials via pipeline, truck, or rail.

An integral component of the total monitoring program should include an early-alert system for the detection of potentially stressed or faulty containment structures (ponds, dikes, embankments) or transport systems in the case of spills or leaks. Such a system would signal the need for activation of appropriate monitoring sites and provide sufficient lead-time for the implementation of contingency measures to control, contain, or abate spills and accidental discharges.

Flow Reductions—Possibly of even greater concern than degradation of surface water quality through the introduction of waste materials are the reductions in flows that will undoubtedly accompany development. The industry will require substantial quantities of water for processing, upgrading, dust suppression, irrigation, and a host of associated activities. Since both surface and sub-surface waters will be used, depending on the particular operation (the technology utilized and water sources available), alterations of the hydrological regime are to be expected, becoming more pronounced as the industry matures. Drawdown of the water table as a result of mine dewatering will decrease the rate of recharge to streams. Diversions, impoundments, and consumptive uses of surface waters will alter the hydrology of surface drainages. It is impossible to forecast at this time what the long-term impact of a maturing industry will be on the regional surface and groundwater hydrological regimes because of the many unknowns associated with the development of this new industry. Development of new technologies could

substantially alter current projections of water requirements. However, assuming current projected requirements are reasonably accurate, the developers should be encouraged to return high quality water to aquifers and/or streams to minimize the impacts of withdrawal.

Monitoring Approaches—

Monitoring approaches and procedures most suitable for application in surface waters potentially affected by oil shale development and associated activities are not well defined. Traditional surface water quality monitoring methods successfully applied in industrialized and urbanized areas of humid regions of the country are not necessarily well suited for application in streams of semiarid regions, where oil shale development is occurring. The many unknowns relating to the nature, release potential, transport rates, and pathways of potential pollutants complicate monitoring approaches and reduce the utility of conventional techniques. The monitoring problem is further complicated by the high natural variability in water quality and discharge inherent to surface drainages of the oil shale area.

The surface water monitoring design must be developed in close coordination with the groundwater, terrestrial, and air monitoring networks. And a free exchange of information must be maintained throughout the existence of the program. Since groundwater and surface water hydrological regimes are closely intertwined, a two-way exchange of information is essential to provide a total assessment of qualitative and quantitative changes in the systems and to relate such changes to causative factors. Similarly, meteorological data that provide information on the nature, transport and fallout of airborne particulates are essential to determine the distribution of such materials in the terrestrial environment and subsequent transport to surface water.

Selection of monitoring components for application in surface waters of the oil shale area must be based on the specific requirements and characteristics of the drainages subject to impact. Network design consideration must include station siting requirements, appropriate sampling frequencies, parameters of major and secondary interest, sample collection, handling and *in situ* measurement methodologies most appropriate for a particular situation, laboratory and field analytical techniques that produce the required level of accuracy and precision, data management procedures, and quality assurance safeguards for all phases of the monitoring program. Aspects relating to sample collection, handling and analyses, data management, and quality assurance are addressed in other sections of this report. The remaining network design considerations are addressed below.

Station Locations—The distribution of sampling stations within a monitoring network should reflect the particular objectives of the monitoring program. For example, trend monitoring networks designed to detect changes in water quality or flow for an entire drainage basin generally have stations located in the lower reaches of major tributaries, on the mainstream (downstream from principal sources of input), and in tributaries. Trend monitoring stations established to detect spatial and temporal changes in water quality and in the stream hydrograph should not be expected to identify the causes of such changes. Such monitoring programs must rely on other work to identify pollution sources and associate in-stream changes to causative factors (66).

For purposes of assessing and quantifying the contribution of surface water pollutants generated by oil shale development activities, station siting requirements are somewhat different from those of a traditional trend monitoring network. Permanent stations should be established on major streams both upstream and downstream from the confluences of potentially impacted perennial tributaries, as well as on the tributaries themselves. In addition, permanent stations should be established in washes and gulches that are designated as disposal sites for shale or overburden or that are otherwise potentially impacted. Meteorological and groundwater data should aid in the selection of stations upstream from the development

sites in unimpacted stream reaches as well as in reaches potentially impacted by atmospheric fallout or by groundwater withdrawals.

Sampling Frequencies—All permanent stations established need not be sampled at the same frequencies. Sampling of ephemeral tributaries and washes can, in many instances, be restricted to periods of events such as rainstorms or sudden snow melt, when transport potential is greatest. Optimally, mainstream stations would be sampled at similar intervals and frequencies to assure the statistical validity and comparability of the data; however, it is not necessary to measure all parameters during each sampling. For example, measurements such as temperature, flow, pH, and conductivity, which lend themselves to *in situ* monitoring with automated instruments, would be recorded continuously at mainstream stations.

Sampling frequencies for such parameters as dissolved oxygen, selected nutrients, major anions and cations, and inorganic and organic trace constituents that require treatment in the field and/or analyses in a laboratory should be established based on the natural variability in water quality, intensity of activities in the area, and the stream hydrograph. Ideally, sampling frequencies for these parameters would be greatest during periods of maximum variability in water quality with less frequent sampling during more stable periods. In the semiarid oil shale area, maximum variability in water quality is not necessarily coincident with periods of maximum discharge; in fact, quite the opposite may be true. The periods of greatest variability in water quality frequently occur during the late summer low-flow period, when the assimilative capacity of the stream is minimal and when there is a high frequency and intensity of localized thunderstorms, with subsequent runoff and transport of easily erodible and highly soluble substances to permanent streams through washes and tributaries. In terms of total loading, the contribution of such events may be relatively minor, but in terms of water quality criteria for beneficial uses, the effects are frequently highly detrimental, particularly with respect to biological impacts. Since much of the flow during the periods of peak discharge is derived from snow-pack melt in the upper watershed, the concentration of potentially harmful substances is relatively low during this period, even though the total stream burden is high. Bank and streambed scour, however, is often greatest during the peak flow period, and enormous sediment loads, both suspended and bedload, are characteristic of streams throughout the area during peak flows. The combined effects of streambed deposition, scouring, and frequently, rechannelization, are temporarily devastating to the bottom dwelling macroinvertebrates and attached periphyton. Sampling of these communities would ideally be conducted before peak discharge and again after communities have re-established following a reduction in flow rates.

Daily suspended sediment measurements should be made at key stations during the period of maximum discharge. Techniques are available for obtaining suspended sediment from varying depths with fixed samplers as the hydrograph rises and falls.

Methods for optimizing sampling frequencies for chemical and physical parameters have been proposed by several workers (67-69). In each case, a large amount of *a priori* knowledge is required to apply the sophisticated techniques used to determine when to sample. A basic problem with the stratified sampling approach is that the highest variability in parameter concentration occurs at different times for different parameters and at different stations. The practical considerations of sampling logistics require either considerable compromise, large resources, or both.

Stratified sampling is based on one other assumption—that parameter concentration variability will continue to follow pre-established patterns. Pollutants generated by oil shale development activities may or may not follow historical distribution patterns. The environmental disturbances may be expected to follow

more closely the level of mining or processing activity than hydrographic cycles. In addition, stream flows may be subjected to manipulation through operation of dams, diversions, discharges, etc. These manipulations impose additional elements into the naturally occurring flow regimes and parameter concentration patterns.

Data may not presently be adequate to determine optimum sampling times except for a few parameters such as temperature and conductivity. The method of Sanders and Adrian (68) requires an extensive period of daily parameter records in order to determine the harmonic components of variability. Such records are generally unavailable, but an argument may be advanced for using conductivity to estimate the variability of ionic constituents (66).

In view of the foregoing considerations, it is recommended that sampling initially be conducted at fixed-time intervals until sufficient data have been compiled to establish a statistically sound stratified sampling schedule. A fixed sampling interval greatly simplifies logistics. The selection of an interval without a seven-day component would help assure that the weekly work schedule of personnel will not lead to biased data. (In addition, the time of sampling should not be consistently the same; ideally it should be randomly distributed over the 24-hr period.) A sampling frequency of 8 to 13 days would provide 25 to 50 samples per year for analyses of chemical and physical parameters and should provide sufficient information to allow the development of time-stratified sampling programs.

Selecting Parameters and Setting Priorities—Because of the numerous Federal, State, and local water pollution control laws, regulations and associated monitoring requirements applicable to the oil shale industry (Section 1 and Appendix D), it is impossible to develop a single list of parameters for across-the-board application to all potentially impacted surface waters. The following provides the rationale for identification of parameters of concern along with prioritized listings of chemical, physical, and biological parameters recommended for inclusion in surface water monitoring programs.

Water quality parameters should be selected based on an analysis of the possible pollutants and their toxicity, persistence, concentration, ease of analysis and identification, release potential, and present levels in receiving waters.

Special Problems and Concerns in Parameter Measurement. Detection of some pollutants presents no problem and requires only a straightforward approach. For example, suspended sediments, total dissolved solids, and turbidity will be clearly indicated by major changes in solids loading of streamflow as a result of increased erosion or runoff from raw or spent shale piles. Normal analyses for oil and grease and for dissolved and suspended organic carbon can be used to detect spills and leaks of oil and other organic materials. Fractionation of the dissolved organic carbon can be used to identify classes or origins of pollutants.

However, knowledge of organic compounds associated with oil shale and subject to release to surface water as a result of industrial development is incomplete. The extreme difficulty in conducting organic analyses has discouraged most researchers and has largely limited monitoring efforts to measurement of organic carbon, phenols, oils and grease and a few similar analyses. Thomas (66) summarized the results of a study by Pellizzari (70) that reported organic substances found in process water from oil shale based on analyses of six samples. Thomas listed maximum concentrations of those compounds that occurred at an arbitrary level of 100 ppb or greater (Table 3-22 in Section 3).

Pellizzari's methods provided for the analysis of volatile and semivolatile compounds to ppb levels. The procedure was quantitative for volatile compounds with solubilities of less than 2 percent in water and a boiling point of less than 220 °C (428 °F), and for semi-polar compounds with solubilities equal to 10 percent and boiling points equal to 150 °C (302 °F). The technique was not quantitative for highly water soluble compounds (e.g., acetonitrile, formaldehyde, etc.). The procedure for semivolatile compounds gave quantitative recoveries for organic acids,

neutral compounds, and bases for compounds with boiling points greater than 60 °C (140 °F) and less than 270 °C (518 °F). Compounds with zwitterions (dipolar ions) were not recovered and analyzed, nor were compounds with boiling points greater than 275 °C (527 °F).

Of the compounds identified, phenols, dimethyl phenol isomer, cresole isomers, acetone, benzene, and toluene are of specific concern. All are suspected carcinogens that have been identified as high priority EPA point source effluent toxic pollutants. The cresole and phenols are of particular concern, since they have toxic as well as carcinogenic properties and may occur in high concentrations.

Analyses for trace elements should be designed in accordance with possible sources that can be defined. The elements fluorine and arsenic are of special significance in large areas of the Piceance Basin. Fluoride is present in high concentrations in the deep aquifers; thus any surface water changes resulting from mine inflow water reaching the surface through leakage from well reinjection systems, holding reservoirs, etc., will be immediately apparent as an increase in fluoride levels.

Arsenic is expected to volatilize in the oil shale retort and become enriched in the shale oil. It must be removed from the crude shale oil before hydro-treating, but it may become an air emission during the refining process (60). A number of inorganic trace elements known to be associated with oil shale at varying levels are listed in Table 3-19, Section 3.

Chemical and physical parameters. It is convenient to think of water quality parameters as belonging to one of two broad categories: (a) specific constituents, and (b) indicator parameters.

The first category is made up of those constituents that in themselves are potential pollutants and are directly measurable in waters. This group is represented by substances identified as components of raw or retorted oil shale, overburden, groundwaters, industrial or urban wastes, etc. that may be subject to mobilization and release to surface waters. Examples of parameters in this group include (a) dissolved, suspended, and settleable residues, both inorganic and organic, (b) radioactive isotopes, (c) specific cations and anions, (d) pesticides, and (e) oil and grease.

The second category includes those parameters that in themselves are not pollutants, but whose measurement either provides a measure of pollution or environmental disturbance or are required for the interpretation of other water quality data. Examples of parameters in this group include dissolved oxygen, pH, specific conductance, hardness, alkalinity, turbidity, temperature, and volume of flow (discharge).

To identify and set priorities for those parameters most appropriate for monitoring, potential pollutants were evaluated for their projected impacts on ambient water quality, and on beneficial water uses in particular. Also included were those indicator parameters whose ambient levels are a function or product of pollution or environmental disturbance, or whose measurements are required to interpret water quality data.

The following criteria were used to categorize and assign priorities to the chemical and physical parameters. These criteria relate a given parameter to projected water quality in the Colorado River System and to specific beneficial water uses. All recommended limits except those for radioactive substances are based on National Academy of Sciences *Drinking Water Standards* (72). Radioactivity criteria are based on EPA *Drinking Water Regulations* (73).

Criteria for priority A parameters:

1. The pollutant has (a) been reported in surface waters of the Colorado River Basin at levels equaling or exceeding acceptable limits for beneficial water uses and (b) is likely to have altered ambient levels in surface waters as a result of activities associated with the development and operation of an oil shale in-

dustry, to the point where further impairment of beneficial water uses will result; or

2. The pollutant is (a) one for which water quality criteria must be established for particular receiving waters based on tolerance levels of important, sensitive species in those waters, and (b) one that is likely to have as a result of oil shale development and operation activities, altered ambient levels in receiving waters to the point where the biota may be adversely impacted; or
3. The pollutant is one whose measurement is essential for interpreting other water quality data.

Criteria for priority B parameters:

1. The pollutant has been reported at levels in the Colorado River Basin that are generally within acceptable limits with respect to beneficial water uses, but its ambient levels in surface water could be altered by activities associated with the development and operation of the oil shale industry, to the point where impairment of beneficial water uses could result; or
2. The pollutant is (a) one of recognized significance in the aquatic environment, but one for which no water quality criteria have been established with respect to ambient levels and beneficial water uses, and (b) it is one whose ambient levels in surface waters could be altered by activities associated with the development and operation of an oil shale industry, to the point where impairment of beneficial water uses could result.

Criteria for priority C parameters:

1. The pollutant is one for which no water quality criteria are established and whose significance in terms of beneficial use criteria is largely unknown; but its ambient levels in surface waters could be altered by activities associated with the development and operation of an oil shale industry, with unknown consequences for beneficial water uses; or
2. The pollutant is one for which adequate surface water quality data are unavailable to characterize ambient levels in the Colorado River Basin, but it has been identified as a potential pollutant subject to release to surface waters by activities associated with the development and operation of an oil shale industry.

Physical and chemical parameters recommended for monitoring are summarized by category in Tables 5-6 through 5-8. The form of each recommended parameter is based on the available knowledge of activities and fates of pollutants in the aquatic environments.

TABLE 5-6. PRIORITY A CHEMICAL AND PHYSICAL PARAMETERS RECOMMENDED FOR MONITORING IN SURFACE WATERS[a]

Parameters	Form in which constituent is reported	Units
Aluminum	Aluminum (Al), dissolved	μg/l
	Aluminum (Al), total recoverable[b]	μg/l
Ammonia	Nitrogen ammonia (NH_3 - N)	mg/l
Bicarbonates	Bicarbonate ion (HCO_3)	mg/l
Boron, dissolved	Boron (B), dissolved	μg/l
Chlorides, dissolved	Chloride ion (Cl), dissolved	mg/l
Conductivity	Specific conductance	μmhos/cm at 25°C

TABLE 5-6. (continued)

Parameters	Form in which constituent is reported	Units
Copper	Copper ion (Cu), dissolved	μg/l
	Copper (Cu), total recoverable[b]	μg/l
Cyanides	Cyanide (CN), total recoverable	mg/l
Fluorides	Fluoride (F), dissolved	mg/l
Hardness	Hardness, total as $CaCo_3$	mg/l
Iron	Iron ion (Fe), dissolved	μg/l
	Iron (Fe), total recoverable[b]	μg/l
Lead	Lead ion (Pb), dissolved	μg/l
	Lead (Pb), total recoverable[b]	μg/l
Magnesium	Magnesium ion (Mg), dissolved	mg/l
	Magnesium (Mg), total recoverable	mg/l
Manganese	Manganese ion (Mn), dissolved	μg/l
	Manganese (Mn), total recoverable	μg/l
Mercury, total	Mercury (Hg), total recoverable[b]	μg/l
Molybdenum, dissolved	Molybdenum ion (Mo), dissolved	μg/l
Nickel, dissolved	Nickel ion (Ni), dissolved	μg/l
Nitrogen, nitrate	Nitrate nitrogen (NO_3-N)	mg/l
Oil and grease	Visible oil	Severity
	Emulsified oils	mg/l
Oxygen	Dissolved oxygen	mg/l
Oxygen demand, chemical	Chemical oxygen demand (COD)	mg/l
Pesticides	Organochlorine pesticides[b,c]	μg/l
Phenols	Phenolic compounds	μg/l
Potassium, dissolved	Potassium ion (K), dissolved	mg/l
Sodium, dissolved	Sodium ion (Na), dissolved	mg/l
Silica	Silica, dissolved (SiO_2)	mg/l
	Silica, total (SiO_2)	mg/l
Solids, dissolved	Total dissolved (filterable) residue	mg/l
	Fixed dissolved (filterable) residue	mg/l
Solids, suspended	Total suspended (nonfilterable) residue	mg/l
	Fixed suspended (nonfilterable) residue	mg/l
Sulfates, dissolved	Sulfate ion (SO_4), dissolved	mg/l
Temperature	Temperature	°C
Turbidity	Turbidity	NTU[d]
Water volume	Discharge	m^3/sec
Zinc	Zinc ion (Zn), dissolved	μg/l
	Zinc (Zn), total recoverable	μg/l

[a] Modified from Reference 65.
[b] To be measured in streambed sediments also (μg/kg).
[c] Applies to consent decree protocol pesticides.
[d] Nephelometric turbidity units.

Priority A parameters require intensive monitoring because: (1) very slight changes in their ambient levels would render water unacceptable for specified designated beneficial water uses, (2) changes in ambient levels would be indicative of potentially deleterious changes in water quality characteristics, (3) and data are required for the interpretation of other water quality data.

Priority B parameters require routine monitoring of a lower intensity than do those in the priority A category because slight changes in ambient levels can be

tolerated without exceeding established limits for designated beneficial water uses. The measurement of parameters in this category should be in addition to those in the priority A category, but at reduced frequencies.

Priority C parameters require periodic monitoring in addition to those in the A and B categories to characterize water quality with respect to ambient levels of particular constituents and designated beneficial water uses.

Biological Parameters—

Biological monitoring has long been recognized as an effective tool for evaluating the stability and environmental quality of ecosystems. Biological in-

TABLE 5-7. PRIORITY B CHEMICAL AND PHYSICAL PARAMETERS RECOMMENDED FOR MONITORING IN SURFACE WATERS[a]

Parameters	Form in which constituent is reported	Units
Acidity, total	Acidity, total as $CaCO_3$	mg/l
Alkalinity, total	Alkalinity, total as $CaCO_3$	mg/l
Alpha, gross	Total alpha activity	pCi/l
Arsenic	Arsenic ion (As), dissolved	μg/l
	Arsenic (As), total recoverable	μg/l
Barium, dissolved	Barium ion (Ba), dissolved	μg/l
Beryllium, dissolved	Beryllium ion (Be), dissolved	μg/l
Beta, gross	Total beta activity	pCi/l
Cadmium	Cadmium ion (Cd), dissolved	μg/l
	Cadmium (Cd), total recoverable[b]	μg/l
Calcium	Calcium ion (Ca), dissolved	mg/l
	Calcium (Ca), total recoverable	mg/l
Carbonates	Carbonate ion (CO_3)	mg/l
Carbon dioxide	Carbon dioxide (CO_2), dissolved	μg/l
Chromium	Chromium ion (Cr)[c], dissolved	μg/l
	Chromium (Cr), total recoverable[b]	μg/l
Cobalt, dissolved	Cobalt ion (Co), dissolved	μg/l
Lithium, dissolved	Lithium ion (Li), dissolved	μg/l
Nitrogen, nitrite	Nitrite nitrogen (NO_2 - N)	mg/l
Nitrogen, total	Total nitrogen (N)	mg/l
Oxygen demand, biochemical	Biochemical oxygen demand (BOD)	mg/l
Pesticides	Organophosphate pesticides [(b, d)]	μg/l
Phosphorus, total	Total phosphorus (P-Total)	mg/l
Phthalate esters	Total phthalate esters	μg/l
pH	pH	Standard units
Polychlorinated biphenyls	Total polychlorinated biphenyls	μg/l
Radium 226, 228	Radium 226, 228, dissolved	pCi/l
	Radium 226, 228, total	pCi/l
Sediments, streambed	Streambed sediments	—
Selenium	Selenium ion (Se), dissolved	μg/l
	Selenium (Se), total recoverable	μg/l
Silver	Silver ion (Ag), dissolved	μg/l
	Silver (Ag), total recoverable	μg/l
Strontium 89, 90	Strontium 89, 90, dissolved	pCi/l
	Strontium 89, 90, total	pCi/l

TABLE 5-7. (continued)

Parameters	Form in which constituent is reported	Units
Tin	Tin (Sn), total	μg/l
Titanium	Titanium (Ti), total	μg/l
Tungsten	Tungsten ion (W), dissolved	μg/l
	Tungsten (W), total	μg/l
Tritium	Tritium in water molecules	Hydrogen[3] units
	Tritium, dissolved	pCi/l
	Tritium, total	pCi/l
Vanadium, total	Vanadium (V), total recoverable	μg/l

[a] Modified from Reference 65.
[b] To be measured in streambed sediments; also μg/kg.
[c] Both trivalent and trivalent plus hexavalent forms should be measured.
[d] Applies only to specific organophosphate pesticides.

vestigations are of special significance in water quality monitoring programs because they offer a means for identifying areas affected by pollution and for assessing the degree of stress for a relatively small investment. In terms of time and money invested, biological monitoring in many situations provides one of the most efficient approaches in evaluating the nature and extent of pollution-related disturbances in aquatic ecosystems. Aquatic organisms act as natural monitors of water quality in that they respond in a measurable and predictable manner to stress induced by most types of pollution. Since the composition and structure of aquatic plant and animal communities are the result of all biological, chemical, and physical interactions within the system, communities reflect the summation of all internal and external influences affecting the system including antagonistic and synergistic actions.

Macrobenthic invertebrates are particularly useful natural monitors of environmental quality in lakes and streams because of their sensitivity to changes in environmental conditions, their stationary nature, and the relative ease with which they are sampled. Since macroinvertebrates as a group are relatively immobile, they cannot seek relief from unfavorable conditions, even intermittent pollution input, or other disturbances. This characteristic results in colonization by the more tolerant or opportunistic forms, which, in the absence of competition and predation from more sensitive forms, may completely dominate the community.

Since aquatic organisms serve as continuous monitors of the environment, they sometimes provide information that is not obtained by direct measurements of water quality. Pollutants such as heavy metals and many organic compounds tend to accumulate in the biota in far greater levels than are found in the water column as a result of uptake and concentration both through the food chain and directly from the water. Thus, an examination of tissue may reveal the presence of potentially hazardous substances in the biota that were not detectable in the water. Resident fish species whose entire life cycle is spent in short stream reach or other restricted habitats are especially useful for this purpose.

Biological monitoring should be incorporated into any monitoring program designed to assess the impact of development and operation of an oil shale industry on the freshwater ecosystem and water quality. Subtle changes in water quality characteristics may be indicated by changes in the aquatic biota before they are detected by physical/chemical monitoring procedures. Biological monitoring should not be viewed as an alternative to physical/chemical monitoring, but rather as a complementary tool for improving the efficacy of monitoring programs.

TABLE 5-8. PRIORITY C CHEMICAL AND PHYSICAL PARAMETERS RECOMMENDED FOR MONITORING IN SURFACE WATERS[a]

Parameters	Form in which constituent is reported	Units
Acetone	Acetone compounds	μg/l
Antimony	Antimony ion (Sb), dissolved	mg/l
	Antimony (Sb), total	mg/l
Benzene	Benzene compounds	μg/l
Bismuth	Bismuth ion (Bi), dissolved	μg/l
	Bismuth (Bi), total	μg/l
Bromine	Bromine (Br)	mg/l
	Bromide ion (Br), dissolved	mg/l
Carbon	Organic carbon, dissolved	mg/l
	Organic carbon, total	mg/l
Cerium	Cerium ion (Ce), dissolved	μg/l
	Cerium (Ce), total	μg/l
Cerium 144	Cerium 144, total	pCi/l
Cesium	Cesium ion (Cs), dissolved	μg/l
	Cesium (Cs), total	μg/l
Cesium 137	Cesium 137, dissolved	pCi/l
	Cesium 137, total	pCi/l
Chlorine	Residual chlorine (Cl), total	mg/l
Color	True color (platinum cobalt units)	PCU
Cresole	Cresole compounds	μg/l
Detergent builders linear alkylate sulfonates	LAS, total	mg/l
Dysprosium	Dysprosium (Dy), total	μg/l
Erbium	Erbium (Er), total	μg/l
Europium	Europium (Eu), total	μg/l
Gadolinium	Gadolinium (Gd), dissolved	μg/l
Gallium	Gallium ion (Ga), dissolved	μg/l
	Gallium (Ga), total	μg/l
Germanium	Germanium ion (Ge), dissolved	μg/l
	Germanium (Ge), total	μg/l
Gold	Gold (Au), Total	μg/l
Hafnium	Hafnium (Ha), total	μg/l
Holmium	Holmium (Ho), total	μg/l
Iodine	Iodine ion (I), dissolved	mg/l
Iridium	Iridium (Ir), total	μg/l
Lanthanum	Lanthanum ion (La), dissolved	μg/l
	Lanthanum (La), total	μg/l
Lutetium	Lutetium (Lu), total	μg/l
Neodymium	Neodymium (Nd), total	μg/l
Niobium	Niobium (Nb), total	μg/l
Nitrogen, Kjeldahl	Kjeldahl nitrogen, total	mg/l
Nitrogen, organic	Organic nitrogen, dissolved as N	mg/l
	Organic nitrogen, total as N	mg/l
Oils and grease	Hexane extractable substances[b]	mg/kg
Osmium	Osmium (Os), total	μg/l
Palladium	Palladium (Pd), total	μg/l
Pesticides	Miscellaneous pesticides[c]	μg/l

TABLE 5-8. (continued)

Parameters	Form in which constituent is reported	Units
Phosphorus	Phosphorus, total dissolved	μg/l
Platinum	Platinum (Pt), total	μg/l
Plutonium 238, 239	Plutonium 238, 239, dissolved	pCi/l
Praseodymium	Praseodymium (Pr), total	μg/l
Rhenium	Rhenium (Re), total	μg/l
Rhodium	Rhodium (Rh), total	μg/l
Rubidium	Rubidium ion (Rb), dissolved	μg/l
	Rubidium (Rb), total	μg/l
Ruthenium	Ruthenium (Ru), total	μg/l
Ruthenium 106	Ruthenium 106, total	pCi/l
Samarium	Samarium (Sm), total	μg/l
Scandium	Scandium ion (Sc), dissolved	μg/l
	Scandium (Sc), total	μg/l
Strontium	Strontium ion (Sr), dissolved	μg/l
Tantalum	Tantalum (Ta), total	μg/l
Technetium	Technetium (Tc), total	μg/l
Tellurium	Tellurium (Te), total	μg/l
Terbium	Terbium (Tb), total	μg/l
Thallium	Thallium ion (Tl), dissolved	μg/l
	Thallium (Tl), total	μg/l
Thorium	Thorium (Th), total	μg/l
Toluene	Toluene compounds	μg/l
Uranium	Uranium ion (U), dissolved	μg/l
	Uranium (U), total	μg/l
Ytterbium	Ytterbium ion (Yb), dissolved	μg/l
	Ytterbium (Yb), total	μg/l
Yttrium	Yttrium ion (Y), dissolved	μg/l
	Yttrium (Y), total	μg/l
Zirconium	Zirconium ion (Zr), dissolved	μg/l
	Zirconium (Zr), total	μg/l

[a] Modified from Reference 65.
[b] To be measured in streambed sediments only.
[c] Applies only to specific pesticides.

Selecting and setting priorities for biological parameters were accomplished by considering both the components of the aquatic community most responsive to stress, and the measurement technique most appropriate for directly or indirectly measuring such response. The following criteria were used to categorize and assign priorities to the biological parameters.

Criteria for priority A parameters:

1. The variable exhibits a predictable and measurable response in the aquatic community to the type of stress conditions anticipated as a result of expected pollutants and habitat alteration associated with oil shale development activities, and
2. The variable is one for which currently available analytical and measurement techniques are adequate to provide useful information.

Criteria for priority B parameters:

1. The component is a member of the aquatic community associated with

specific habitats that may be affected by particular conditions induced by development of an oil shale industry and associated activities.

Priority A biological parameters are recommended for routine monitoring in any basic water quality monitoring program designed to assess the impact of oil shale and associated development on aquatic ecosystems. However, all priority A parameters need not be monitored at the same frequencies.

Sampling to determine bioaccumulation of toxic and hazardous substances in fish and macroinvertebrate tissue should be conducted annually at key mainstem stations. Because uptake may vary considerably between species and age classes, attempts should be made to obtain the same species and size classes of fish and similar macroinvertebrate communities during each sampling. Fish and macroinvertebrates selected for analyses should be representative of resident species in the area.

Since the costs of such analyses are high, it is recommended that three or four whole fish be homogenized and analyses made on composite samples. Similarly, tissue analyses of macroinvertebrates should be conducted on homogenized composites of several samples.

Annual collection of fish should be adequate for the analyses indicated in Table 5-9. In addition, several specimens of two or three common representative resident nongame species (dace, darters, etc.) should be collected and preserved for future analyses. It is hoped that techniques for identifying tumor development or other evidence of carcinogenics will be developed in the near future. These samples would provide a reference collection for these types of examinations and other analyses.

Macroinvertebrate collection for community analyses should be made three times yearly (spring, late summer, late fall) using standardized collection techniques appropriate for each locale. To assure adequate characterization of bottom fauna communities, a minimum of 1,000 organisms should be obtained at each station during each collection period.

Periphyton samples should be collected two or three times yearly using standardized techniques, including artificial substrates and natural rock scrapings. Analyses should include dry and ash-free determination for biomass estimates, species identification and counts and chlorophyll analyses.

Priority B biological parameters need not be routinely monitored unless a specific problem is encountered or suspected in a particular habitat. For example, phytoplankton and macrophytes would not normally be monitored in western streams, where primary productivity is attributable mainly to periphyton and aquatic vascular plants are typically scarce. However, in impoundments, measurement of both phytoplankton and aquatic macrophytes may be of considerable interest because of eutrophication and associated problems.

Fecal coliform and fecal streptococci bacteria are useful indicators of domestic or animal wastes entering waterways, but they would not normally be monitored in a routine program unless the potential for such contamination is suspected. For example, anticipated increases in human population densities in small towns, establishment of temporary dwellings in rural areas, etc. would be sufficient reason to initiate measurement of these parameters. In such instances probably seasonal sampling would be sufficient to establish baseline data. But frequency may have to be increased to monthly as the population increases.

Measurement of priority B parameters (Table 5-10) on fish would not normally be performed unless a specific problem (stunted fish, tainting of flesh, etc.) were detected. The intensity and duration of such investigations would need to be determined on the basis of the severity of the problem and initial test results.

Groundwater Monitoring Methodology

Monitoring of groundwater quality should be an extension of the environmental assessment and control technology evaluations performed as part of the original

TABLE 5-9. PRIORITY A BIOLOGICAL PARAMETERS RECOMMENDED FOR MONITORING IN SURFACE WATERS[a]

Community	Parameter	Analysis	Units
Macroinvertebrates	Counts and identification	N[b]/unit substrate area or unit sampling effort (time) or unit sample	N/m^2 N/min N/sample
	Biomass	Total wt./unit substrate area (ash-free) or unit sampling effort	g/m^2 g/min
	Community composition and diversity	n[c]/taxon S[d]/N	n/ith taxon S/N
	Toxic substances in tissue	Wt. substance/unit tissue wt.	$\mu g/g$
Periphyton	Counts and identification	N/unit substrate area Diatom species proportional count	N/cm^2 percent
	Biomass	Total wt./unit substrate area (ash-free)	mg/m^2
	Community composition and diversity	n/taxon	n/ith taxon
	Chlorophyll *a*	Wt./substrate area	$\mu g/cm^2$
Fish	Counts and identification	N/unit sampling effort	N/sample
	Biomass	Total wt./unit sampling effort (wet wt.)	g/sample
	Toxic substance in tissue Community composition	Wt. substance/unit wt. tissue Species list/sample	mg/g

[a] Modified from Reference 65.
[b] Total numbers.
[c] Number of individuals.
[d] Number of taxa.

TABLE 5-10. PRIORITY B BIOLOGICAL PARAMETERS RECOMMENDED FOR MONITORING IN SURFACE WATERS[a]

Community	Parameter	Analysis	Units
Phytoplankton	Counts and identification	N[b]/unit volume	N/ml
	Chlorophyll *a*	Total wt./unit volume	μg/liter
	Community composition and diversity	n[c]/taxon S[d]/N	n/ith taxon S/N
Fish	Flesh tainting	Taste test panel	Rating scale
	Growth rate	Age/length by species	yr/mm
	Condition factor	Length/weight	$X = \frac{10^5 \times \text{wt(gm)}}{\text{length (L)}^3}$
Macrophytes	Species identification and community association	Areal coverage and community	Map of species association
Bacteria	Fecal streptococci	N/unit volume	N/100 ml
	Fecal coliforms	N/unit volume	N/100 ml

[a] Modified from Reference 65.
[b] Total Numbers.
[c] Number of Individuals.
[d] Number of Taxa.

planning and design of an oil shale facility. As such, it should provide for:

1. Detection and delineation of groundwater pollution before the pollution reaches streams or points of groundwater use;
2. Detection of potential pollution from activities that by design are not supposed to contribute to groundwater;
3. Definition of any possible pollution to groundwater systems before the pollutants reach points of discharge into surface water;
4. Verification that injection well systems are functioning to prevent pollution to sources of usable-quality groundwater or to surface water;
5. A data bank that can be used in the future assessment and revision of technology control programs on environmental issues.

It should be emphasized that for a monitoring program to achieve the above objectives, the focus must be on identifying the pollution sources, specific pollutants, and their respective mobilities in the subsurface environment. It should also be recognized that the drilling and sampling of observation wells will be needed to field verify the conclusions drawn from indirect monitoring activities, to provide for compliance activities, to determine long-term trends in water quality and changes in water levels, and to ascertain the effectiveness of operational programs such as subsurface waste injection and grouting programs for abandoned *in situ* oil shale chambers.

A groundwater monitoring methodology should fulfill the following requirements when properly applied in an oil shale area (74):

Identification of potential pollutants

Definition of hydrogeology and groundwater use

Study of existing groundwater quality

Evaluation of infiltration potential of wastes at the land surface

Evaluation of mobility and attenuation of pollutants in the unsaturated and saturated zones

Priority ranking of sources and causes of pollution, based on:

a. Mass of waste, persistence, toxicity, and concentration
b. Potential mobility
c. Known or anticipated harm to water users

Selection and implementation of the monitoring program

Monitoring guidance for solid wastes in oil shale areas is presented in the following subsection on solid waste monitoring. The reader is encouraged to examine this section, because a similar approach can be taken for developing monitoring for liquid-holding reservoirs, storage ponds, and other installations that could result in infiltration of pollutants into the subsurface (75).

Near-Surface Aquifers—

As mentioned, monitoring wells will be needed to supply verification data. Guidelines for monitoring methodology published by EPA (74,76) describe how the wells should be located, but because the subject is most important to groundwater quality monitoring with respect to oil shale, some key recommendations are presented here.

Because of the longer time scale involved in groundwater movements (weeks or months may be required to move relatively short distances), the location of monitoring sites is much more critical than for surface waters if a pollutant is to be detected before a significant buildup occurs in the system. Site selection must be based on a general knowledge of the area hydrology as well as on an analysis of the possible pollution sources. Haphazard location of monitoring wells is certain to result in excessive costs and inadequate coverage. Monitoring wells to be effective must be placed down the groundwater hydraulic gradient of possible pollution

sources. Within local valleys, wells completed in alluvium should be placed downstream of sources. Determining the number of wells required is not as simple as determining the number of stream gauging stations. Because of its small lateral dimensions, a stream may be considered well mixed, so that only a single sampling point is needed. Water in an alluvial aquifer is far from well mixed, and samples may be necessary at more than one point along a line perpendicular to the direction of flow. The further downstream the wells are placed from a suspected source, the fewer wells are required. However, greater downstream distances imply longer time intervals before pollution can be detected. As a general guideline, one shallow monitoring well should be placed within 30.5 m (100 ft) down-gradient of each reinjection well. Monitoring wells will also be placed a short distance downstream from each reservoir, raw shale pile, and spent shale pile. These locations should be as near as possible to the center of the groundwater drainage pattern, and they should be no farther downstream than the intersection with the next larger tributary branch. For wide sources, more than one well should be planned. Well construction should be such as to allow sampling from different depths within the saturated interval.

The preceding discussion relates to horizontal variations of water quality in a shallow aquifer. Many of the same factors that cause horizontal variations act to cause vertical variations in the water quality of an aquifer. Where significant vertical variations have been determined or may be strongly suspected as being likely to occur, monitoring wells should be constructed so that samples can be withdrawn from different parts of the vertical section. This should mean that wells will be constructed at different depths in an aquifer. Some would produce from the upper part while others produce from the lower part. Of course, such well completion would depend on the thickness of the saturated zone of an aquifer.

Sample collection from monitoring wells should be performed by pumping to produce a sample that is representative of the aquifer water in the vicinity of the well. Whenever possible the amount of water pumped (or removed if sampling is by a method other than pumping) from the well prior to actual sample collection should be about three times the volume of water estimated to be standing in the well prior to start of pumping.

Selection of chemical parameters to monitor should be based on hydrological and geochemical considerations as well as the nature of the potential pollution. The same general considerations apply as for surface water. Sediment, of course, will not be a factor in groundwater.

Deep Aquifers—

Determinations of water quality in deep aquifers of the Green River Formation should be made in the vicinity of dewatering activities related to underground oil shale mines and *in situ* retorting, as well as in the areas of influence of injection wells. Monitoring of dewatering activities should be performed routinely. In most cases, the necessity of drilling special monitor wells can be greatly reduced by monitoring for water quality and water-level fluctuations in existing dewatering wells and in wells that have been drilled for future dewatering (to take care of dewatering needs as mining operations expand).

In mine dewatering, the sampling should emphasize the determination of salinity and total dissolved solids. Once the sampling program is established, samples should be collected about once monthly, or perhaps quarterly, depending on the continuity of the dewatering activities. Considerable water should be removed from inactive dewatering wells and wells that serve only for monitoring just before samples are collected. Continuous water level records should be obtained from key nonpumping wells so that relationships among changes in hydraulic gradients, pumping depths, and water quality can be established.

Monitoring of *in situ* retorting operations (especially the modified *in situ* operations) will be similar in some respects to monitoring of deep mines. However, the

situation will be more complex from certain standpoints. For example:

The subsurface leaching of spent shale in the retort chambers must be addressed;

Rates and pathways of movement of dissolved pollutants in aquifer zones affected by the retorting must be considered;

Changes in hydraulic characteristics of the subsurface must be factored into the monitoring program;

Impacts of related possible occurrences (such as subsidence) should be addressed.

Establishment of a monitoring program should consider these issues in view of the existing hydrogeologic framework. It appears that monitoring designs will be on a case-by-case basis until more experience is obtained. However, considerable guidance on the inorganic and organic constituents to be analyzed can be gained from the laboratory studies concerning leaching of retorted shales. This matter is discussed in considerable depth later in this section under the subsection on monitoring of solid wastes.

Monitoring of groundwater quality in the Green River Formation is very difficult because groundwater flow (direction and rate of movement) is controlled by fracture and fault systems. These systems produce a physical setting of heterogeneous porosity. As a consequence, attempts to apply conventional concepts of monitor-well siting, well construction, and sampling procedures are likely to be less than completely successful. Most conventional concepts were developed for application to sand aquifers, which have hydraulic conditions approaching homogeneity and which have, as a result, a groundwater flow that is perpendicular to the equipotential lines of measured head in the aquifers. Because this matter appears to be of major significance to monitoring the environmental impacts of development of the Green River Formation, the following discussion (76) is included to aid the reader in understanding the situation and to provide suggestions for appropriate monitoring approaches. Because the conditions in the Piceance Creek Basin are thought to be generally typical of the entire Green River Formation, this area is used as the setting for the discussion.

Groundwater flow in the Piceance Creek Basin occurs in several complex systems of fractures and faults (77). The evaluation of a fractured-rock flow system is generally much more complicated than assessment of a granular, porous media type of aquifer system. In fractured-rock systems, even defining the direction of flow may not be straightforward. Generally, the direction of flow and the flow gradient in groundwater systems are identified by measuring the head (or water level) in a set of wells and estimating lines of equal head. Flow, then, is perpendicular to these equipotential lines (Figure 5-2). However, flow in fractured rock is along fractures, and these flow paths can provide a flow direction that is nearly perpendicular to that which may be estimated from simple observation of head levels (Figure 5-3). Using this illustration (Figure 5-3), placing a well at Point B to monitor the effects of an injection well or other waste source at Point A would clearly fail to produce data that address the defined information requirements. The need for detailed hydrogeologic evaluation is thus an integral part of the monitoring design methodology.

The aquifer systems in the Piceance Basin include a series of horizontal fracture sets very irregularly interconnected by vertical fractures and faults. The system has commonly been portrayed as including two aquifers separated by the rich oil shale beds of the Mahogany Zone. In actuality, the irregular spacing of both vertical and horizontal fractures, the appreciable variability of hydraulic properties among these fracture sets and the varying degrees to which halite and nahcolite minerals have been leached from different zones create numerous distinct aquifer units. Where wells are located and where they are perforated (open to water-bearing zones) have a significant influence on the data collected. This is true for data on both aquifer characteristics and groundwater quality.

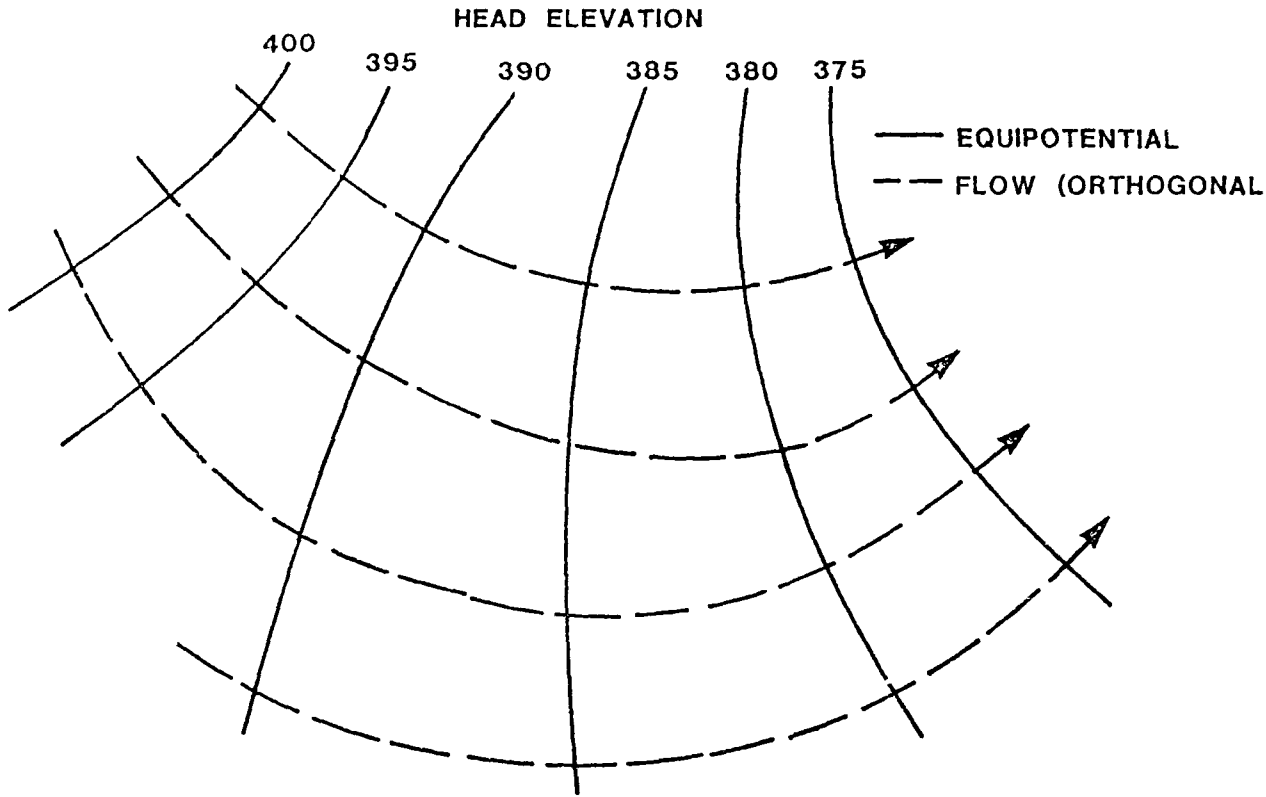

Figure 5-2. Groundwater flow net in homogenous aquifer. (Source: Reference 76)

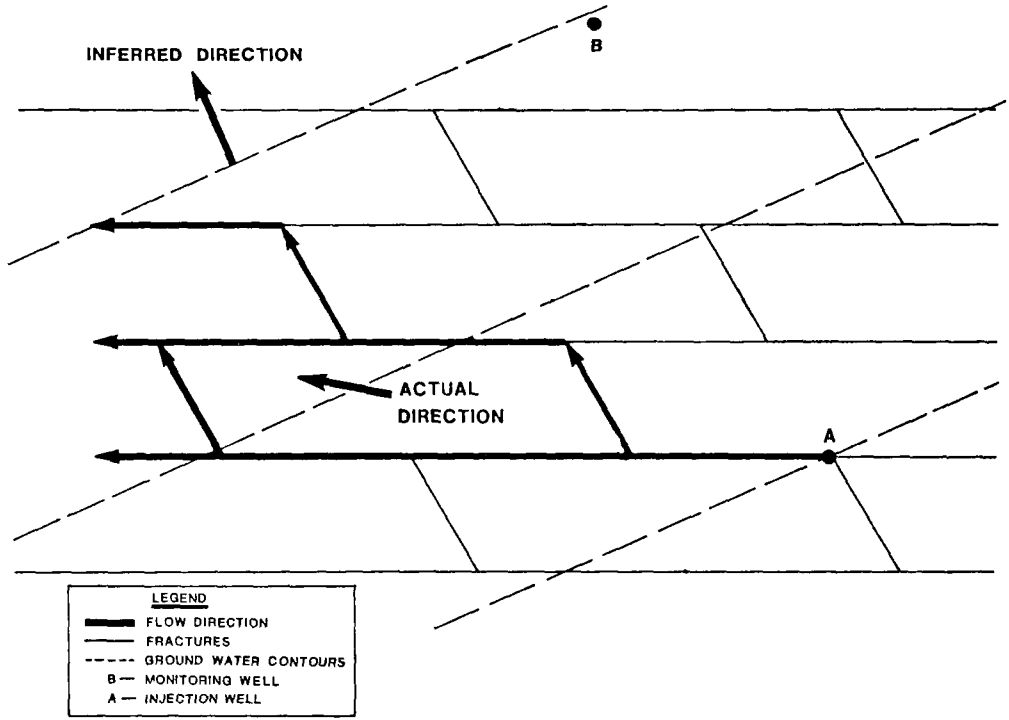

Figure 5-3. Idealized two-dimensional pattern showing relation between true direction of groundwater flow and direction inferred by drawing orthogonal lines to regional water level contours.
(Source: Reference 78)

An example is two wells that are located close together and that are perforated over exactly the same interval. The perforated interval contains two fractured strata of equal hydraulic conductivity (Figure 5-4). One strata contains abundant saline minerals, and the other has few. One well intersects a fracture in the upper strata but none in the lower (saline) strata, whereas the other intersects a fracture only in the lower strata. Water sampled from these two wells provides drastically different water quality data in spite of their proximity and construction similarity.

This situation may be further complicated by varying permeabilities of different strata. Some fine-grained, high-organic-content strata are resistant to fracturing and may form effective aquitards. This situation can result in different head levels between layers and mixing of highly different quality waters in interconnections such as well bores. As an example of how well completion (and recompletion) can affect water quality data, consider the data reported in Table 5-11 for Tract C-b (79).

These wells had initially encountered and been open to a highly saline water zone that apparently had a higher hydrostatic head than the less saline overlying aquifer zones. Thus, water collected from these overlying zones was affected by the interconnection. Recompletions were undertaken to isolate these different water quality zones.

Also, the intervals of completion and perforation may affect water level data. For example, on Tract C-b, an apparent mound of water in the center of the tract may be due to data from a well (SG-6) completed over a small segment of the aquifer zone. If this interval has a high head, then this well will show a greater head level than other wells in the area that are perforated over a wider zone and thus exhibit a more average head.

Injection Wells—

Indications are that injection wells will be used to a considerable extent for disposal of wastewaters, especially the water from dewatering operations. Since these wells most likely will be covered by permits from State-level regulatory agencies, some monitoring requirements will be specified in the permits. However, the adequacy of such specified monitoring should be evaluated in terms of the overall monitoring needs in an area of development. For information on monitoring of injection wells, the EPA report, Monitoring Disposal-Well Systems, (81) is recommended. The following summarizes the contents of that report.

A prerequisite to the monitoring of injection wells is a knowledge of the hydrogeologic framework of the area. An estimate of the characteristics of the subsurface environment can be made before drilling a well, based on projections of data from outcrops, previously drilled wells, and possibly surface geophysical studies. A much more accurate knowledge of the local subsurface environment is obtained when a well is drilled and tested. Data obtained from a well are based on rock and fluid samples, geophysical logs, and pumping or injection tests.

When the characteristics of the subsurface environment have been estimated or determined, the response to wastewater injection can be predicted with reasonable accuracy. Such predictions are essential to monitoring because they provide a baseline of expected performance, including rate of pressure buildup and rate and direction of travel of injected wastewater.

The principal means of injection well monitoring is by monitoring of the well itself. The wells provide more protection than is commonly realized because the well is, in most cases, the most likely source of escape for injected wastewater. Periodic inspection and testing of injection well facilities complements continuous monitoring of well performance and should prove helpful in detecting deterioration of these facilities before failure.

Monitoring wells can be used for several purposes; they may be constructed in the injection aquifer, in or just above the confining beds, or in any aquifer that could be impacted by the injection operation. Local geology and hydrology, the

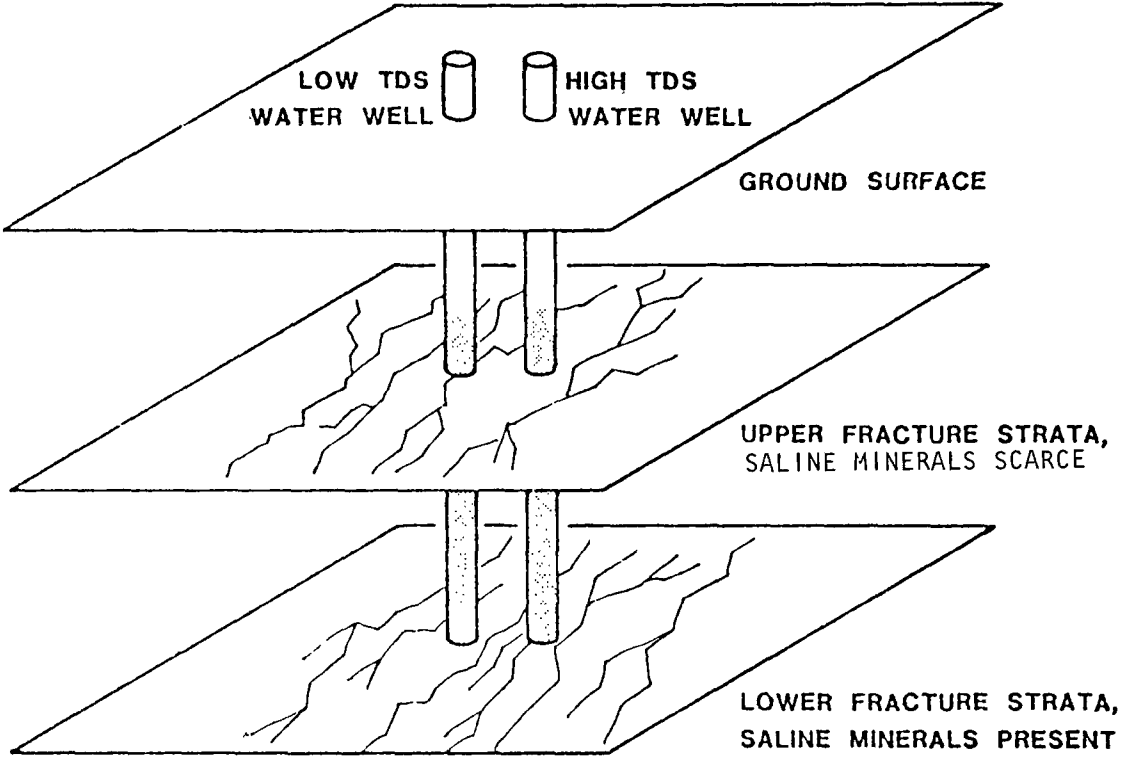

Figure 5-4. Fractured rock aquifer system yielding water of varying quality, depending on location and perforation of wells. (Source: Reference 80)

TABLE 5-11. EFFECTS OF WELL RECOMPLETION ON WATER QUALITY

Original well designation	TDS before recompletion ppm	TDS after recompletion ppm	New well designation
SG-11, string 1	39.000	16,000	SG-11, string 1R
SG-10	42,000	2,800	SG-10R
SG-17, string 1	28,000	4,300	SG-17, string 1R

waste being injected, and economics are all factors in determining the need for and location of monitor wells. The nature of the waste being injected will also determine the depth of monitoring needed and what analyses should be conducted on collected samples.

Other types of monitoring include surface geophysics, sampling of springs, streams, and lakes, and monitoring to record any seismic events that might be related to operation of the injection well.

Quality Control and Assurance—

Quality control procedures are implemented as part of a monitoring program to insure the reliability of the data collected. Since monitoring data are used as the basis for various decisions (e.g., determining compliance with regulations or need to implement environmental control measures), quality control procedures for both field and laboratory segments of the monitoring programs are essential. In addition, quality assurance proceedings are implemented to provide documentation of the quality control efforts.

Quality control activities included as part of the field monitoring and sample collection include the following:

1. Instrument calibration (e.g., use of proper standards, proper number of standards, and appropriate frequency of recalibration);
2. Use of appropriate sample collection procedures (collection procedures for the sampling of wells are presented earlier in this section):
   a. Use of appropriate bottle type (e.g., clear glass, dark glass, sterile bottles, PVC)
   b. Measurement of conductivity, pH, etc., during pumping of wells for sampling to obtain representative samples
   c. Use of proper field processing and preservation method (e.g., filtration, addition of chemical preservatives, and cooling)
   d. Use of proper packing and shipping procedures when sending samples to an analytical laboratory
3. Proper training of personnel involved in field activities, including actual data collection activities and quality control and quality assurance procedures such as the use of replicate and spiked samples.

Standard Water Analyses

The following is a list of surface water, groundwater, and process water quality parameters for whose measurement EPA-recommended methods are emphasized (82):

pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD); total suspended solids (TSS), hardness, acidity, alkalinity, CO_2, dissolved oxygen (DO), silica, phenols, carbon, and nitrogen as ammonia, ammonium, and organic nitrogen.

Cations: arsenic, aluminum, boron, barium, beryllium, cadmium, calcium, copper, chromium, iron, lithium, mercury, magnesium, manganese, lead, nickel, potassium, selenium, silver, sodium, strontium, vanadium, zinc.

Anions: chloride, cyanide, fluoride, iodide, sulfate, sulfide, bicarbonate, carbonate, phosphate.

Analytical Instrumentation—

Figure 5-5 shows the elements that several instruments can measure. See Quinby-Hunt (83) for an additional comparison of instrumental analyses of metals in water.

Presently, atomic absorption spectroscopy is the most accurate and cost-effective analytical tool available for quantitative analysis of most elements. Consequently, it is the most commonly used technique for elemental analysis and is the EPA-approved method for analysis of metals in water. However, it has one very important disadvantage: it can only be used to test for one element at a time. A number of techniques provide data on several elements simultaneously and are more rapid than AAS if data on a variety of elements in many samples are needed. Some multielemental techniques are x-ray emission, spark-source mass spectrometry, neutron activation analysis, and inductively coupled plasma emission spectrometry. As part of an evaluation of these multielement analysis techniques applied to environmental analytical problems, the latter three techniques were used to analyze effluent samples from pulp mills. The samples were characteristic of effluent samples having high organic carbon and high alkali content (similar to the Omega-9 retort water samples used in an interlaboratory comparison study discussed later in this section). The pulp mill effluent sample analysis emphasized comparison of the three techniques with AA analysis when applied to the 13 EPA consent-decree elements (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thalium, and zinc). No single multielement technique was applicable for all of the consent-decree elements at the 1-mg/l (8.34×10^{-9} lb/gal) level. Spark-source mass spectrometry (SSMS), however, was applicable at this level to all consent-decree elements except mercury. Mercury was apparently best determined by cold-vapor AA at levels of less than 0.1 mg/l (8.34×10^{-10} lb/gal). In general, the SSMS results agree reasonably well with the other techniques, considering the attendant problems of sample inhomogeneity and variations in both sensitivity and sample handling from one technique to the other (84).

Inductively coupled plasmas suffer from numerous chemical interferences. Low pressure plasmas have been employed in an attempt to reduce these interferences; however, they have poor reproducibility, produce varying degrees of ionization through the plasma, and are susceptible to interferences (82). The technique is highly sensitive, and practical application to total metal determinations requires careful analytical work. Over 25 elements per water sample can be analyzed (see Figure 5-5) at about a third of the cost for flame AAS. Quantitative data for samples of complex matrices were in good agreement with flame AA spectrophotometric results for each element investigated (85).

A discussion of instrumental analysis of oil-shale-type waters is contained in Fox *et al.* (86). The water was the Omega-9 water, from the 1976 Rock Springs Site 9 true *in situ* oil shale combustion experiment, conducted by the Laramie Energy Technology Center. "The chemical composition of this sample is specific only to itself and is not necessarily representative of *in situ* oil shale waters in general. Nevertheless, the analytical problems encountered in the analysis of this sample are typical of these waters" (86). Approximately 63 parts of groundwater were mixed with one part of combustion plus dehydration water. The chemistry of this specific water is dominated by an alkaline pH and the presence of high levels of organic and inorganic carbon, nitrogen, and sulfur as well as sodium and chloride. The high levels of organic and inorganic carbon, nitrogen and sulfur are typical of oil shale

PERIOD	GROUP Ia	GROUP IIa	GROUP IIIa	GROUP IVa	GROUP Va	GROUP VIa	GROUP VIIa	GROUP VIII			GROUP Ib	GROUP IIb	GROUP IIIb	GROUP IVb	GROUP Vb	GROUP VIb	GROUP VIIb	GROUP O
1 1s	1 H																1 H	2 He
2 2s 2p	● 3 □ Li	■ 4 □ ● Be											● 5 □ B ■	6 C	7 N	8 O	9 F	10 Ne
3 3s 3p	● 11 □ ● Na	■ 12 □ ● Mg											● 13 ▲ □ Al ■	● 14 ▲ □ Si	15 □ P ▲	16 ▲ S □	17 ○ Cl ▲	18 Ar
4 4s 3d 4p	● 19 K □ ▲	● 20 Ca □ ▲ ■	21 Sc ■	22 Ti ■ ▲	● 23 V □ ▲ ■	● 24 Cr □ ▲ ■	● 25 ○ Mn □ ▲	● 26 ○ Fe □ ▲ ■	● 27 ○ Co □ ▲ ■	● 28 ○ Ni □ ▲ ■	△ 29 ● Cu □ ▲ ■	● 30 ○ Zn □ ▲ ■	31 Ga ▲ □	32 Ge ▲ □	△ 33 ○ ● As □ ▲ ■	△ 34 ○ ● Se □ ▲ ■	35 ○ Br ▲	36 Kr
5 5s 4d 5p	37 Rb □ ▲	● 38 ● Sr □ ▲	39 ▲ Y □ ■	40 Zr □ ▲	41 Nb □ ▲	● 42 ▲ ● Mo □ ■	43 Tc	44 Ru □	45 Rh □ ▲	46 Pd □	● 47 Ag □ ▲	● 48 Cd □ ▲ ■ △	49 In □ ▲ ■	50 Sn □ ▲	○ 51 Sb □ ▲ ■	52 Te □ ▲	53 I ▲	54 Xe
6 6s (4f) 5d 6p	55 ● Cs □ ▲	● 56 ● Ba □ ▲ ■	57* La □ ▲	72 ● Hf □	73 Ta □ ▲	74 W □ ▲	75 Re □	76 Os □	77 Ir	78 Pt □ ▲	79 Au □ ▲	80 Hg □ ▲ △	81 Tl □ ▲	● 82 Pb □ ▲ ■ △	83 Bi □ ▲	84 Po	85 At	86 Rn
7 7s (5f) 6d	87 Fr	88 Ra	89** Ac															

*LANTHANIDE SERIES	58 Ce □ ▲	59 Pr □	60 Nd □	61 Pm	62 ○ Sm □ ▲	63 Eu □	64 Gd □ ▲	65 Tb □	66 Dy □ ▲	67 Ho □	68 Er □	69 Tm □ ▲	70 Yb □	71 Lu □ ▲
**ACTINIDE SERIES	90 Th □ ▲ ■	91 Pa	92 ○ U □ ▲ ■	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

X-RAY ▲
AA □
OPTICAL EMISSION ■
IZAA △
NAA ○
ICAP-ES ●

Figure 5-5. Elements measurable by various instruments.

process waters, whereas the high levels of sodium and chloride are atypical of the waters and probably originated from groundwater intrusion. The neutron activation results for three out of four laboratories were consistently accurate. The x-ray fluorescence (XRF) and neutron activation analysis (NAA) (excluding one laboratory's results) were the most consistent and accurate of the instrumental techniques evaluated. Spark-source mass spectrometry (SSMS) detected more elements than any other techniques evaluated and consistently had the lowest detection limit. However, it had a high coefficient of variation (63 percent). The single element techniques, AAS and proton-electron spin spectrometerry (PES) produced consistent and accurate results. Atomic absorption spectroscopy was most frequently used to measure As, Ca, Fe, Mg, K, Se, Na, and Zn.

Intercomparison studies of instrumental techniques and aqueous samples are complicated by the problems of long-term sample stability and low elemental concentrations. Extensive sample preparation is often required. The preparation procedures can introduce uncertainties into the results in addition to the usual instrumental uncertainties. Some of these problems are discussed later in this section. The elements measured with the best accuracy (CV F20 percent) in the Omega-9 study were Na, U, Br, Cl, F, W, V, and Zn. The elements measured poorly (CV F50 percent) were Al, La, Li, Hg, Sn, Ti, P, Si, Cd, Co, and Se. The elements most frequently detected were As, Ca, Fe, Mg, Se, Na, and Zn. A range was reported for Al, La, Li, Hg, Sn, and Ti. These variations are probably due to matrix interferences or sample handling and preparation methods. Since all of these elements except La are environmentally significant, work should be directed at discovering the source of the variability and correcting it. Those elements that were looked for but not detected by more than one method were Be, C, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Ru, Rh, Pd, In, Os, Ir, Pt, Au, Tl, Bi (86). Most of these elements occur at low levels in oil shale and, although processing may change solubilities, should exist at very low levels in the process water or would be relatively insoluble at pH 8. In addition, except for Bi and Be, none of these elements has previously been of interest environmentally, and thus analytical techniques have not been refined to detect low levels of them in complex aqueous matrices. Pb, Be, and Bi were either below the detection limit of all techniques used or were detected only by one participating lab. These elements are environmentally significant, and more sensitive techniques should be developed to detect them in this type of matrix. The instrumental methods are relatively free of interferences, with the exception of the high sodium concentration. Spark-source mass spectrometry consistently produced the lowest detection limits but had the poorest precision of all instrumental methods evaluated. Both XRF and NAA produced precise and accurate results. Atomic Absorption (AA) was successfully used to measure the elements Ca, Mg, Fe, Na, Si, As, K, Se, and Zn (86).

Analytical Problems and Interferences—

The Omega-9 study demonstrated that standard analytical methods cannot be used to determine most water quality parameters in complex waters such as oil shale process waters. Methods specific to each type of water need to be developed and published. Instrumental methods generally produce more accurate results, as these encounter fewer interferences than chemical methods. However, significant variation and error can result from differences in sample preparation and the fact that most of these techniques produce precision data for a subset of the total set of elements reported. Extensive experimental work is required to develop analytical methods for the routine measurement of cyanide, COD, phenols, orthophosphate, solids, and sulfide in this type of water. Existing methods for the measurement of sulfate, inorganic carbon, ammonia, and some sulfur species may not be adequate and may require additional laboratory testing (86).

Cyanide, if present, occurred at low levels in the samples. The primary sulfur species identified to date are thiosulfate, sulfate, tetrathionate, and thiocyanate.

From an analytical standpoint, sulfur species may interfere with other chemical measurements, cause the precipitation of elemental sulfur on acidification, and result in sample instabilities from bacterial growth. Environmentally, some of these species are significant from a toxicity standpoint, and others may interefere with wastewater treatment processes. Little work has been done on the organic nitrogen and carbon species present in the Omega-9 water. However, the primary inorganic carbon and nitrogen species are, respectively, HCO_3^- and $CO_3^=$ and NH_4^+. The high levels of these inorganic species result in low values for the measured TDS (see *Solids* discussion) and present a difficult waste treatment problem.

Many of the analytical techniques investigated in the Omega-9 study were inadequate for the analysis of complex matrices such as oil shale process waters. Each method should be evaluated on a case-by-case basis. Although many of the wet chemical techniques evaluated gave reproducible results, the accuracy of measurement is poor because of interferences. This is true for cyanides, phenols, phosphorus, sulfide, sulfate, COD, solids, and $CO_3^=$.

The primary interferences for wet chemical measurements are high concentrations of sulfur, carbon and nitrogen species, the presence of strong color and emulsified oil and grease, and a diversity of organic compounds. Carbon, nitrogen, and sulfur species combine with many of the reagents used, producing erroneous results. The presence of color and oil and grease interfere with some colorimetric and electrode measurements. This type of interference affects both the precision and accuracy of measurement of F^-, conductivity, pH, alkalinity, $CO_3^=$, HCO_3^-, $PO_4^=$, phenols, and Cl^-. The precision obtained for many of the water quality parameters using the same method in different laboratories is poor and generally outside of quoted precisions (82,87). This is true for COD, phenol, inorganic and organic carbon, conductivity, ammonia, and sulfate, probably because of differences in pretreatment selected by the individual laboratories to mitigate suspect interferences, and because of the presence of color, oil, and grease, which interfere with colorimetric and electrode methods. The determination of HCO_3^-, $CO_3^=$, NH_4^+, HS^-, and other species depend on equilibrium calculations. The ionic strength is so high that the usual assumption of infinite dilution is not valid. Laboratory measurements of appropriate equilibrium constants need to be made so these species can be accurately determined. A number of analytical problems are discussed below (86).

Chlorine—Typically, instrumental methods measure total chlorine and chemical methods measure the chloride ion. The mercuric nitrate method is recommended in *Standard Methods* (55) and by EPA (82) for the analysis of chloride in waters. However, in the presence of other constituents that react with mercury, the method gives high results.

Organic Carbon—The data indicate that there is an analytical problem associated with the measurement of organic carbon in Omega-9 water. The low values for the CO_2 purge method could be due to the loss of volatile organics during the N_2 purge. This problem needs to be investigated experimentally.

Solids—Total, total dissolved, and fixed solids were measured with good precision. However, the significance of these measurements for waters similar to Omega-9 is questionable. TDS, as defined in *Standard Methods* (87), is the residue remaining after a sample has been filtered and dried at 103° to 150°C (217° to 302°F). This parameter is intended to be a good indicator of total dissolved salts, as these are not significantly lost on heating. However, this parameter is a poor indicator of the dissolved salts in waters similar to dissolved salts in waters similar to Omega-9. The species $CO_3^=$, HCO_3^-, NH_3, and NH_4^+ constitute over 65 percent by weight of the dissolved salts present in Omega-9. On heating to 103° to 150°C (217° to 302°F), these species are lost from solution through the formation of volatile salts or by stripping out dissolved gases. Therefore, the TDS determination gives a low, nonrepresentative value for the dissolved salts present. The same considera-

tions apply to total solids (86).

Alkalinity, Bicarbonate, and Carbonate—Conventionally, HCO_3^- and $CO_3^=$ are determined from alkalinity and pH measurements. However, this method is not valid for oil shale process waters because of the presence of buffering components other than the carbonate system (ammonia, borate, silicate, organic bases) and the high ionic strength of the water. The presence of these species results in an overestimation of the $CO_3^=$. This method is discussed by Stumm and Morgan (86).

Sample Quality Control—

The treatment of the sample from the time it is collected through analysis is of primary importance in determining the analytical result. Sample preservation and storage is important for these waters, because bacteria may grow in them and affect the organic contents as well as turbidity, etc. An additional concern with aqueous samples is the loss of constituents by adsorption onto container walls or precipitation reactions. These effects are usually minimized by acidifying the sample to a pH of less than 2 with concentrated HNO_3, although this step might itself cause chemical reactions to occur. Filtration and sample preservation at 4 °C (39 °F) has minimized some of these problems.

Alternative Test Procedures—

The EPA has provided a mechanism for establishing the equivalency of alternative procedures to those promulgated as standard procedures. The specifications for the comparability data necessary to demonstrate equivalence are summarized in the following paragraphs and as outlined below:

Nationwide Use Approval of Alternative Test Procedures:

Five industrial (discharge) sources identified by Standard Industrial Classification (SIC) Code or five drinking water sources.

Six samples from each source.

Four replicate analyses each by proposed and approved methods.

Total tests:

5 (sources) × 6 (samples) × 4 (replicates) × 2 (methods) = 240 tests.

Limited Use (State or Regional) Approval of Alternative Test Procedure:

Five sources.

Three samples from each source.

Four replicate analyses each by proposed and approved methods.

Total tests:

5 (sources) × 3 (samples) × 4(replicates) × 2 (methods) = 120 tests.

Use by Single Permit Holder or Drinking Water System:

One source.

Three samples from source.

Four replicate analyses each by proposed and approved methods.

Total tests:

1 (source) × 3 (samples) × 4 (replicates) × 2 (methods) = 24 tests.

Statistical Protocol

1. Calculate basic statistics of mean and standard deviation.
2. Test for outliers.
3. Apply Cochran's test for equality among within-sample standard deviation.
4. Apply F-test for equality of pooled within-sample variances.
5. Apply T-test for equality of method means.

Background—On December 1, 1976, the Guidelines Establishing Test Procedures for the Analysis of Pollutants (88) was amended to allow applications for

approval of alternative test procedures for nationwide use. Such applications were required to include comparability data between the proposed alternative test procedure and an approved procedure. This system is intended to test the equivalency of two methods using very specific comparability data. Application information and EPA contacts are listed in this Federal Register reference.

Specifications for Comparability Data—For applications requesting approval of an alternative test procedure for use by a single permit holder, comparability data should obviously be generated for samples from all the types of discharges covered under the permit. A similar requirement for applications requesting nationwide use is impractical considering the vast number of discharge types usually implied. However, it does seem reasonable to require comparability data on samples from the five (5) types of discharges that are likely to have the greatest impact on the NPDES Permit Program. Therefore, of the discharge types identified by primary 1972 SIC code or point source subcategory that might require use of the alternative test procedure, comparability data should be required on samples from the five involving the most permits or the largest amount of total discharge. EPA should be able to specify these discharge types for each application, or possibly for each parameter. In addition, samples from other types of discharges might be required at the discretion of EPA.

Methods and Materials Standardization—

Reliable chemical characterizations have been difficult to obtain because of the lack of adequate standards and limitations of many available analytical methods, including very low or very high levels of most constituents and chemical interferences. These problems have been identified by many researchers faced with making chemical measurements. They were first nationally acknowledged when the ASTM Committee D-19 (Water), formed Subcommittee D-19.33 (Water Associated with Synthetic Fuel Production) to address analytical problems specific to alternate fossil energy process waters. Eight samples of three different fossil energy-related waters are now available for laboratories wishing to participate in interlaboratory studies. Parameters currently tested are phenol, arsenic, and total organic carbon. Participants must use ASTM procedures; additional results from other procedures are welcomed for comparison. The Subcommittee Chairman is Larry Jackson at the Laramie Energy Technology Center.

The National Bureau of Standards (NBS) has a Surrogate Standards Program for oil shale materials. The Bureau has conducted several interlaboratory studies with a standardized shale oil. By May 1980 NBS will have issued reports of the results and descriptions of the methods used. The shale oil material, certified for 6 polynuclear aromatic compounds and phenols, should also be available then. Dr. Harry Hertz at NBS, Washington, D.C., is in charge of this program.

Analysis of Organic Pollutants in Surface Water and Groundwater

Introduction—

Until adequate information is available to determine what harmful organic compounds are released to surface water and groundwater from oil shale processing activities, monitoring must be construed as survey analysis to determine, insofar as is feasible, the identities and amounts of all compounds released. Currently available analytical techniques can provide identifications and concentration estimates for organic compounds that will pass through a gas chromatograph. The remaining sample components, which have been estimated to constitute 50 to 80 percent (by weight) of the total organic carbon content of a water sample, are largely uncharacterized, and much work is needed to develop techniques for analysis of compounds that cannot be characterized by gas chromatography.

For gas compounds that will pass through a chromatograph, the most powerful analytical technique currently available is the combination of gas chromatography and mass spectrometry (GC/MS). This technique can provide qualitative informa-

tion with only a few nanograms (10^{-9}g) of a sample component. The usefulness of this technique for organic water pollutant analysis has been amply demonstrated by many laboratories during the past few years, but some aspects of current analytical procedures need improvement. These aspects include development of quality control guidelines, standard reference materials, internal reference compounds, sample preservation procedures, recovery information, and improved separation techniques.

Quality control guidelines must begin with sampling procedures and cover all analytical techniques through sample component concentration calculations. Standard reference materials are needed for trace-level organics in matrices similar to those that will be analyzed, because the sample matrix cannot be completely destroyed to release organic pollutants. Internal reference compounds are needed to permit accurate concentration calculations after organic pollutants are identified. Adequate sample preservation techniques are necessary to insure that identified contaminants were really sample components and not the result of sample composition changes. (Current expressed desires for sample archives depend on adequate sample preservation.) Recovery information is necessary to inform the analyst of what percentage of a given organic pollutant can be observed with the analytical extraction, separation, and detection procedures used. Improved separation procedures might permit development of materials for reversible sorption and desorption of specific classes of organic compounds (89).

Identification and measurement of specific organic components of wastes and effluents from oil shale processing is necessary to determine the nature of organic pollution generated, to develop adequate treatment facilities and pollution prevention procedures, and to select appropriate monitoring techniques.

Two fundamentally different approaches to pollutant analysis exist. The analyst can look for selected compounds, or he can attempt to detect and measure all compounds present in a sample. In the first approach, specialized analytical procedures to isolate, concentrate, and detect previously selected compounds are used. This approach, however, assumes that the environmentally hazardous organic compounds have been identified. Unfortunately, inadequate present information makes it impossible to know which organic compounds should receive special attention as water pollutants from oil shale processing and should, therefore, be monitored in surface and groundwater.

To obtain adequate information upon which future monitoring requirements can be based, the second approach, survey analysis, must be used in an attempt to learn as much as possible about sample composition. Traditional and relatively crude measurements of organic pollution—such as biochemical oxygen demand, chemical oxygen demand, and total organic carbon—are not adequate, although they should not be classified as useless. Such tests do not provide individual pollutant information that is necessary to select and develop effective environmental monitoring techniques. Although many analytical problems remain to be solved, significant progress has been made during the past decade in the development of organic pollutant survey techniques.

The following discussion is intended as an overview of currently available techniques and of problem areas that require further attention.

Sampling—

The need for proper water sampling techniques cannot be overemphasized. Data from expensive, time-consuming analyses of organic sample components will be useless if collected samples are not representative of the sampled water or if samples are contaminated or degraded during collection, shipping, storage, or handling. Routine survey analysis to identify and measure all compounds that are amenable to analysis by gas chromatography and GC/MS in one sample currently costs between $2,000 and $3,500. When sample components are particularly difficult to identify, almost infinite amounts of time and, therefore, money can be ex-

pended on one sample. Because analysts routinely attempt to identify components at concentrations of greater than 1 mg/l (1 ppb), a relatively small amount of contamination is sufficient to mask sample components and distort analytical data.

Sampling techniques must be correlated with the type of water to be sampled, the analytical method to be used, and the sample volume required to provide sufficient material to be detected with the particular analytical method used. Usually, water samples are either grab samples or composite samples. A single grab sample, which is a relatively small water volume (frequently about 4 l or 1 gal) taken at one time, is usually not as representative as a composite sample that is collected over a longer time period or intermittently (a series of grab samples).

General procedures for both grab and composite sampling include collection of water samples in clean glass containers (washed with a diluted mineral acid, rinsed with deionized/distilled water, and heated at 450 °C (842 °F) for 2 hours to remove organic material) sealed with Teflon-lined caps. (Organic compounds can be leached from plastic containers, and adhesives in regular screw caps can dissolve and contaminate the sample.) To minimize the possibility of photodecomposition, prevent loss of volatile components, and minimize composition changes, samples should be stored in dark-colored bottles in a cold (F4 °C or 39 °F), dark place. Time required for shipment from field sites to analytical laboratories should be minimized.

Samples to be analyzed with the purge and trap technique for low-boiling organics require special attention to ensure that sample bottles contain no headspace, which permits equilibrium of volatile organics between vapor and dissolved phases. Narrow mouth glass vials with greater than 50 ml (1.7 oz) capacity should be filled to overflowing (to eliminate headspace) and sealed with screw caps lined with Teflon-faced rubber septa (placed with the Teflon side toward the water sample).

Too little is known about the effects of storage conditions and time. Sample composition can change through decomposition, vaporization, adsorption onto sample container walls, microbial action, and chemical reactions. Adsorption effects are especially significant for components of dilute solutions. To detect contaminants introduced during shipping, storage, and handling, containers filled with organic-free water can be transported to the sampling site and subsequently treated as if they were samples (i.e., subjected to the same handling and analysis procedures).

Sampling aqueous media by sorption of organic components using activated carbon, macroreticular resins (such as Tenax GC and XAD-2) and other accumulator materials provides a time-integrated and representative sample, but problems may be encountered when sorbed materials must be desorbed for analysis (90-97). Little information is currently available, however, about appropriate water flow rates, sorbent capacity for different compound types, and optimum techniques to recover sorbed materials. More than one accumulator material probably is necessary to collect the wide variety of organic compounds found in surface and groundwater, and more work is needed to determine appropriate sorbents and optimum techniques for reversible sorption and desorption of specific classes of organic compounds.

A recently developed automatic sampler can collect up to 14 samples on accumulator columns (variable sizes) that are returned to the laboratory for desorption and analysis of nonpurgeable organic compounds (98). The water flow rate is adjustable, and sample volume and collection time span can be programmed. Two or more accumulator columns can be used to collect a sample in series. The sampler also can collect up to 26 samples for later analysis of purgeable volatile compounds that can be removed by bubbling an inert gas through the sample. The sampler is refrigerated and can be operated in a laboratory or at a remote site and can function unattended for up to 7 days.

Extraction —

For subsequent analytical procedures, organic contaminants must be removed from the water sample and concentrated to permit detection and identification. The variety of chemical and physical properties of organic water pollutants preclude their removal and concentration with a single technique. Sample contamination and loss of sample components are the analyst's constant concerns.

Volatile Compounds—Organic compounds having low boiling points (below about 150 °C or 302 °F) can be removed from water samples by purging with a pure stream of an inert gas such as helium or nitrogen (99). Volatile organic sample components dissolve in the inert gas and are carried with it into a cartridge containing a sorbent (such as Tenax-GC or XAD-2), which traps the organic compounds but allows the gas to pass through. This technique is useful for compounds that would be lost or obscured by the solvent used in liquid/liquid extraction procedures. For quantitative recovery, the analyst must be concerned with how much of a given compound will be retained by the sorbent volume used, how long purging should be continued, what sample temperature must be maintained during purging, and how long the component can be retained on the sorbent during preanalysis storage. Trapped compounds are usually thermally desorbed by flushing with inert gas into a gas chromatograph or GC/MS for analysis.

A modified version of this method was used to measure volatile organic compounds in a comprehensive EPA study of public water supplies in the United States (100).

Semivolatile Compounds—Many compounds that cannot be removed by inert gas purging can be removed by partitioning into an organic solvent. In this procedure, an aliquot of the water sample is shaken with a nonwater-soluble organic solvent in a separatory funnel. Organic compounds that are more soluble in the solvent than in water will be partitioned into the solvent. Partitioning, however, is not complete, and extraction efficiency varies with individual compounds. To separate components into basic, neutral, and acidic fractions, analysts frequently perform three extractions—one after each of three sample pH adjustments (55). To concentrate extracts for analysis, the organic solvent layer is removed from the separatory funnel and placed in a Kuderna-Danish evaporator (a device that is specially designed to minimize loss of organic components during solvent evaporation) and heated to reduce the extract volume. (Many of the volatile compounds that can be removed by inert gas purging are lost during the solvent evaporation step in this procedure.)

Relatively large volumes of solvent (such as 600 ml solvent/l or 76.8 oz/gal of water sample) are used in the extraction procedure. When this volume is reduced to permit detection of extracted sample components, semivolatile impurities in the solvent also are concentrated for later detection along with sample components. Solvent blanks are obtained by evaporating the same volume of solvent as that used in the extraction to the final sample extract volume and analyzing this solvent residue by means of the same analytical techniques used for the sample extract. Compounds observed in the solvent residue are assumed to be solvent impurities or procedural contaminants, either of which should also appear in sample extracts. An impurity in methylene chloride, a commonly used solvent, has been shown to react with residual free chlorine contained in some chlorinated samples. This reaction produced many chlorinated hydrocarbons in significant concentrations relative to other detected compounds (private communication with O. J. Logsdon, U.S. Environmental Protection Agency, Denver, Colo.).

The volume of water to be extracted depends on the desired level of detection of sample components. The analyst knows the detection limit of the analytical method and can calculate how much sample must be used to provide sufficient material to detect organic compounds at a given concentration. Because contaminant extraction efficiency is less than 100 percent, complete recovery is not feasible and should

not be expected. Much effort has been expended to determine the best solvent concentrations and to calculate recovery rates for particular organic compounds, but much more information is needed (101,102).

Continuous Extractors—Sample foaming and emulsion formation frequently hinder, if not prevent, sample extraction with separatory funnel shakeouts. For samples presenting these problems, a promising apparatus for continuous liquid/liquid extraction is commercially available (Aldrich Chemical Co., Milwaukee, Wisc., Cat. No. Z10,157-5; and Ace Glass Co., Vineland, N.J., Part No. 6841-10). It involves a Soxhlet-type cyclic distillation, agitated liquid/liquid contact, and return of solvent containing dissolved organic sample components to a solvent reservoir. Continuous extractors are available for use with solvents that are either heavier or lighter than water. This method has the advantage of requiring relatively small solvent volumes, but it requires long extraction periods (such as 24 hours per fraction) compared to separatory funnel procedures requiring only about 30 min per fraction.

Bioassay Fractionation—To determine whether biological effects of complex mixtures are caused by the whole substance or by low concentrations of active compounds, the mixture is subdivided into fractions, which are then individually tested for biological effects (103). Fractions exhibiting high biological activity can be subfractionated and tested again. Each active fraction can be analyzed chemically to identify individual components.

Comparison of relative toxicities (to the zooplankton *Daphnia pulex*) of untreated oil shale process water fractions indicated that the ether-soluble weak acid fraction was approximately 20 times more toxic than the ether-soluble strong acid fraction and approximately 30 times more toxic than the water-soluble strong acid fraction (104). The weak acid fraction contains phenols, which are toxic but considered to be relatively easy to remove through appropriate effluent treatment.

Separation and Identification—

Gas Chromatography—In most cases, detection of organic water pollutants requires that sample components be separated through chromatographic techniques. The static atmosphere over a water sample in a closed container can be sampled directly and analyzed with gas chromatography (105). Although rapid, this qualitative detection procedure is limited by the solute gas/liquid partition equilibrium and by the limited volume of headspace gas that can be conveniently sampled and analyzed. Compounds that are volatile but too water soluble for extraction, sorption, or inert gas sparging may be analyzed by direct aqueous injection into a gas chromatograph or a combined GC/MS system (106). Because of the relatively high minimum detection limits of this method (approximately 1 to 50 ppm), more sensitive methods usually are required for water pollutant analysis. A common procedure for analyzing smaller concentrations of organics is injection of an aliquot of a concentrated sample extract; the injection volume depends on component concentrations, column capacity, and detector sensitivity.

Volatile and semivolatile compounds travel through a GC column at different rates, depending on their affinities for the column packing material. Compound retention times can be modified by varying packing materials, column temperatures, carrier gas flow rates, and column sizes. Various detectors may be used to observe eluting sample components. For comprehensive survey analyses, the most commonly used detectors are flame ionization detectors and mass spectrometers. (Other GC detectors permit observation of compounds containing specific atoms such as sulfur, phosphorous, nitrogen and halogens.)

A common identification method involves comparison of the GC retention time of the sample component with that of a standard sample, when both are analyzed with identical chromatographic conditions and more than one column packing material. This method is not feasible, however, when samples contain more than a

few components. Because several compounds may co-elute, more definitive information is needed and can be obtained by MS or by spectroscopic techniques (such as infrared and nuclear magnetic resonance). The best identification technique currently available for survey analysis is GC/MS, because it is sensitive and compound-specific, and computerized systems provide automated analysis and identification. This technique is discussed in more detail in a later section. Spectroscopic techniques frequently require more sample than is usually available, although GC-Fourier transform infrared (FTIR) has been shown to be feasible, and a commercial system is now available. Although this technique currently lacks the sensitivity available with GC/MS systems, it can be used for some samples and holds great promise for the future. With present GC-FTIR systems, identifiable infrared spectra can be obtained from 0.2 mg (3.09×10^{-6} grains) of an organic compound (107). The use of GC-FTIR for analysis of components of water from an *in situ* coal gasification process has been reported (55). When sufficient sample is available, this technique can provide information that will permit identification of compounds that could not be identified unequivocally using GC/MS techniques, or it can provide information supporting tentative identifications from mass spectral data.

Liquid Chromatography—Some compounds that are extractable or sorbable are not amenable to gas chromatographic analysis. Although derivitization techniques can be used to convert some of these compounds into volatile derivatives that are gas chromatographable, the exact nature of the reactions in complex mixtures is frequently uncertain. The most promising technique for these compounds appears to be liquid chromatography (LC), which can be used to separate organic compounds that are thermally labile (and decompose in GC injection ports) or too polar or insufficiently volatile to pass through a GC. Recent advances in LC technology have made this technique useful for environmental sample analysis. Because GC and LC are suitable for different compound classes, these techniques complement each other.

The need for more sensitive and compound-specific LC detectors has limited the use of LC for environmental pollutant identification. Presently, the most promising approaches to selectivity include multiwavelength, ultraviolet-visible absorption, fluorescence detection, and electrochemical detection (108). Ultraviolet (UV) absorption detectors are sensitive to UV-absorbing compounds but are of limited value for providing the molecular structure of an unknown compound. Fluorescence emission detectors are useful for certain classes of compounds (such as many polynuclear aromatic hydrocarbons and heterocyclic analogues). A combination absorbance-fluorescence detector can be used (109). Tentative compound identifications can be based on fluorescence emission spectra and chromatographic retention data, but further information is required for specific compound identification. Progress has been made in development of LC/MS and LC/IR interfaces (110,111). Both systems will provide specific information needed for identification of compounds eluting from an LC.

The usefulness of UV and fluorescence detectors can be extended by making fluorescent or UV-absorbing derivatives of compounds either before or after chromatographic separation (pre-column or post-column derivatization) (112). Other chemical modification techniques can be used to make LC effluents amenable to detection by chemiluminescence, AAS, and polarography (113-115).

Eluting compounds or groups of compounds can be collected from an LC and analyzed by solid probe mass spectrometry, or (if amenable to GC) by GC/MS. Organic sample components that interfere with GC/MS analysis of water extracts can be reduced or eliminated by selective LC fractionation (116). A promising technique combines LC and MS. A commercially available LC-MS system permits continuous introduction of LC effluent into the MS by using an endless steel conveyor band as the interface (110).

Mass Spectrometers as Chromatographic Detectors—As an organic compound enters an electron impact mass spectrometer, it is bombarded with electrons and broken up into fragments; charged fragments are detected and recorded. A plot of detected charged fragments versus relative abundances is the compound's mass spectrum, which provides composition information about the compound. Environmental samples may contain hundreds of organic compounds at concentrations greater than 1 mg/l (8.34×10^{-9} lbs/gal); these will pass through a GC column and are detectable with a mass spectrometer. A computer-controlled mass spectrometer connected to the GC or LC permits continuous repetitive acquisition and storage of mass spectra of sample components eluting from the chromatographic column. Appropriate software permits the analyst to plot spectrum number (time) versus summed ion intensities (or selected-ion intensity summations) for each mass spectrum; this provides a chart similar to a gas or liquid chromatogram. Using this total ion current profile (sometimes called a reconstructed gas chromatogram), the analyst (or, with appropriate software, the computer) can select mass spectra of interest and plot them for examination. Subtraction of ions produced by extraneous organic molecules (from traces of air, water, vacuum pump oil, column packing materials, and sample components not completely separated from the component of interest) leaves a sample component mass spectrum that can be plotted for visual inspection and retained for future use.

A mass spectrum provides a chemical fingerprint that is characteristic of an organic compound and can be interpreted to obtain the compound structure. Spectra interpretation, which requires experience and knowledge of organic ion decomposition mechanisms, can be rapid (seconds or minutes) or can require several hours. Indexed compilations of mass spectra can be searched manually to compare the spectrum of a sample component with that of a known compound spectrum. In the past few years, a computerized mass spectral search system (MSSS) has been developed and is commercially available as part of the National Institute of Health-EPA Chemical Information System (117). The data base now contains approximately 32,000 mass spectra of different compounds. A four-volume collection (118) of 25,560 of these spectra was published in late 1978 or early 1979. A supplement of 6,053 spectra that were recently added to the file will be published in 1979.

The computer matching program provides an indication of how well the stored mass spectrum matches the unknown mass spectrum, but a reasonably good match should be considered only suggestive of a probable identification. Because some compounds are not uniquely characterized by their mass spectra, identifications based on comparison of integer mass spectra are not unequivocal and should be considered as tentative. Confirmatory information can be obtained by comparison of the GC retention time and mass spectrum of the sample component with analogous data obtained using a standard pure compound analyzed under the same conditions used for the sample. Standards are not always readily available, and the confirmation process is expensive and laborious for samples containing a hundred or more observable components. Understandably, many reported identifications have not been confirmed. Despite these obvious drawbacks, GC/MS is currently the most powerful and widely used technique for identification of specific organic compounds as environmental pollutants. Literature reviews of environmental applications of mass spectrometry from 1969 through 1976 cited 922 reports concerning organic compound analyses (119-121).

Electron impact (EI) mass spectra may not contain one important piece of information—compound molecular weight. A chemical-ionization (CI) mass spectrometer coupled to a GC frequently provides this information, however. The main difference between chemical ionization MS and electron impact MS is the method of ionization of the sample component; but the resulting spectra are quite different. In some cases, CI/MS can distinguish isomers that produce similar EI spectra but different CI spectra.

In CI/MS, a reagent gas is present in large amounts relative to the sample component. (A reagent gas to sample ratio of approximately 1000:1 is common.) Reagent gas ions are formed by electron bombardment of the reagent gas, and these ions react with sample molecules to form ions that are characteristic of both sample and reagent gases. The characteristics of the CI mass spectrum depend on the nature of the reagent gas and the type of ion/molecule reaction that ionizes the sample. The most commonly used reagent gases are methane and isobutane. Different structural information can be obtained with different reagent gases, and the use of more than one reagent gas provides complementary structural information (122). The reagent gas can be the GC carrier gas or can be added to column effluent before it enters the mass spectrometer. Molecular weight information can be obtained from sample quantities comparable to those used in EI/MS. Because relatively little fragmentation occurs in CI/MS, much of the structural information available from EI/MS cannot be obtained from CI spectra. Few collections of CI mass spectra are currently available for comparison of sample component spectra with known compound spectra, but CI/MS systems are commercially available and are widely used. Some mass spectrometers can be operated in either EI or CI modes.

Some confusion may result from references to analysis by high resolution GC/MS and by GC/high resolution MS. The former involves the use of GC columns that are usually relatively long (approximately 20 to 50 m or 65 to 164 ft) and relatively small in diameter (approximately 0.25 mm or 10^{-3} in. I.D.). Although these capillary columns have relatively small sample capacity, they have the advantage of increased capability to separate organic compounds. High resolution mass spectrometry, on the other hand, refers to the use of a mass spectrometer that will provide mass-to-charge ratios accurate enough to permit calculation of an empirical formula for that fragment. All possible combinations of specified atoms that would produce the detected ion can be calculated using available computer software. Low resolution mass spectra provide only nominal mass-to-charge ratios that do not differentiate between many possible combinations of atoms.

Relatively few laboratories have high resolution mass spectrometers, which are more expensive and difficult to operate and maintain than low resolution instruments. A further limitation of high resolution spectrometers is that sensitivity must be sacrificed to obtain higher accuracy.

Quantitation —

Determination of the amount of an organic compound present as a water pollutant requires relating a detector response to a quantity of that particular compound. This is usually accomplished by using an internal standard that is added to the sample and subjected to the same analytical procedures as the sample. The concentration of the unknown sample component is calculated after measuring the detector responses for the sample component and a known amount of the internal standard. This calculation is valid only if the internal standard closely resembles the sample component in chemical and physical properties.

In environmental samples containing hundreds of organic compounds, the many different compound classes present will produce different detector responses relative to the amount of compound present. The impossibility of using an internal standard for each sample component has led to the use of calculated response factors (55). Using solutions of standard compounds, the analyst can calculate the relative detector response for sample components and internal standards. This technique, however, is laborious and time consuming, because the analyst needs a standard sample for each sample component and information about the detector response to varying concentrations of each compound. For these reasons, quantitative calculations in survey analyses usually are only approximations. When only a few compounds are being analyzed, quantitative data can be more accurately determined than is feasible when the analyst is attempting to identify and measure every organic pollutant present.

Internal standards need to be compounds that will not be found in environmental samples. For this reason, isotopically labeled compounds are useful internal standards.

When an analyst knows the percentage of a particular compound that is recovered with the analytical procedures used, the amount that was present in the original sample can be calculated from the detected quantity. Because the recovered amount varies significantly, correction factors are important for accurate concentration calculations. For example, with the inert gas purging technique, one investigator reported approximately 10 percent recovery of acetonitrile and more than 80 percent recovery of benzene and toluene (55).

More work is needed to improve present quantitation techniques for organic water pollutant analysis.

Consent Decree Compounds—

The technique currently being used to detect organic Consent Decree priority pollutants in industrial effluents illustrates the use of computerized GC/MS systems to detect specified pollutants in water and wastewater samples (123). This technique is based on the appearance of a significant, sufficiently unique ion that is characteristic of a particular compound at the appropriate GC retention time in a reconstructed gas chromatogram. These two pieces of information indicate the presence of a compound in an extract even when the compound's full mass spectrum is distorted or obscured by interfering compounds.

Using standard samples of each compound to be detected, the analyst must determine the compound's GC retention time with the particular column to be used for analysis. The compound's mass spectrum must be inspected to select ions sufficiently unique (when used with GC retention time) to be characteristic of the compound. When feasible, the use of more than one characteristic ion and the relative intensity of each provides more definitive information.

Concentrations of detected compounds are calculated by using relative response factors calculated by GC/MS analysis of one or more standard solutions containing standards of the organic Consent Decree compounds.

SOLID WASTE

Monitoring Methodology

The handling and disposal of solid wastes are expected to create some of the major environmental problems associated with commercial development of oil shale. The solid wastes include spent oil shale, raw oil shale, spent catalysts from upgrading processes, construction debris, garbage, and sewage and water treatment plant sludges. Studies to date (124,125) have concluded that the main environmental problems pertaining to solid wastes will consist of the surface erosion of spent shale piles and the leaching of soluble salts and organic compounds from the spent shale piles. In addition to spent shale, the spent shale piles will normally include raw shale fines, spent catalysts, sludges, and process wastewaters. Raw shale, such as that removed from underground in preparation for modified *in situ* operations, will most likely be stored separately on the surface to await crushing and retorting.

Spent shale piles will be subject to surface erosion during periods of runoff. During these periods, soluble substances such as organic salts can be dissolved from the spent shale and become part of the runoff water along with suspended materials. (The quality of surface runoff from spent shale piles is discussed in Section 3.) About 10 kg/kkg (20 lb/ton) of salt is water soluble in freshly retorted shales, and additional soluble substances will be available in the spent shale piles from the process wastewaters and spent catalysts that will be disposed therein. If spent shale piles were to erode at a rate equal to that of natural erosion in the Piceance Creek Basin, the average annual rate of suspended sediment would be about 6,725 kg/ha

(3 tons/acre) (124). It can be anticipated that with the best control measures, some disposal piles will erode at rates greater than this average. The latter condition could result from the high erodibility of some fine-grained spent shales such as TOSCO II, unsuccessful attempts at revegetation, or instability of slopes and impounding structures.

Monitoring Surface Waters for Impacts of Oil Shale Solid Waste Disposal—

Surface water monitoring should include sampling for chemical analysis and quantification of streamflow throughout the region subject to oil shale development. The monitoring results should provide an assessment of water quality in the Colorado River, and they should also provide sufficient detail to evaluate properly the effects of the individual oil shale operations within the watershed. To date, much of streamflow monitoring has been performed by the USGS, which maintains 50 streamflow stations in the oil shale area on the Colorado River and its major tributaries. An additional 21 stations are monitored within the Piceance Creek Basin by the USGS, with assistance from industrial concerns. Streamflows at another nine gauging stations are measured continuously by oil shale companies in the Parachute Creek watershed. Sampling for chemical analysis and sediment loading is performed regularly at all of the stations by the USGS and the oil shale companies. Crawford *et al.* (124) concluded that, given maintenance of the present surface water gauging stations, it appears that adequate background data will be available for determining the effects of direct discharges of most oil shale development activities on surface water.

The present monitoring of solid waste disposal with respect to surface water considerations seems drastically lacking in provisions for regular inspection of spent shale piles and catchment structures to determine the probability of mass movements in the disposal piles or sudden failure of the catchment structures. Since no large disposal piles have thus far been constructed, knowledge about their stability or how to inspect for their stability seems inadequate. A monitoring program should, however, be developed based on the best opinions available and should be updated as research results and operational experiences become available.

Monitoring Groundwater for Impacts of Oil Shale Solid Waste Disposal—

Monitoring for impacts on groundwater quality of solid waste disposal in the oil shale industry is much more difficult than measuring the direct effects of such disposal on surface waters. However, an evaluation of the total, long-term effects on surface water must include the contributions of groundwaters that have been altered by the leaching of substances from oil shale solid wastes. Consequently, water quality monitoring must address the issue of possible groundwater changes.

A large number of test holes and water wells have been drilled in the oil shale region of Colorado, Utah, and Wyoming. These have provided very useful data about the geology, hydrology, and quality of the area's groundwater. Some of the wells are being measured for water-level changes on a routine basis, and some are being sampled regularly for water quality considerations. The evaluations of these results will be necessary in understanding the ranges of natural changes in hydrology and water quality. With these evaluations, long-term changes resulting from impacts of the oil shale industry can also be assessed. The measurements will, however, have limited usefulness in the close-up, short-term evaluation of impacts from solid waste disposal, particularly with respect to the leaching of the disposed materials.

For the reasons discussed above, a study was initiated by EPA to develop a preferred groundwater-quality monitoring program for the proposed oil shale developments in Federal Prototype Lease Tracts U-a and U-b in northeast Utah. The study followed methodology described in the preceding section concerning groundwater monitoring methods. The oil shale developments that were proposed

for the tracts consisted of underground mining of the shale and surface retorting by TOSCO II and Paraho processes. Since the solid wastes, including spent shale, were to have been disposed of on the surface in a spent shale pile, the development represents an environmental situation that is similar to most oil shale developments that (1) will use surface retorting facilities and dispose of spent shale and other wastes above ground, or (2) will store on the land surface the raw shale that is removed from underground to make way for modified *in situ* operations.

Briefly stated, the methodology used includes the following operations:

Identification of potential pollution sources and their significant pollutants

Priority ranking of the pollutant sources

Assessment of existing or proposed monitoring programs

Identification of alternative approaches for addressing perceived monitoring deficiencies

Selection of recommended monitoring approaches

Included under the broad topic of the monitoring plan are recommendations for developing background data bases on pollutant source characteristics, the hydrogeologic framework of the study area, existing water quality, and infiltration information, as well as recommendations for monitoring pollutant mobility. Hence, needs for baseline characterization are identified and evaluated in addition to direct operational monitoring needs.

Efforts to identify the potential pollution sources in the solid waste category and their respective pollutants resulted in the data summarized in Table 5-12. Shown are eight potential causes of water pollution. Data on the pollutants and their possible concentrations (such as in leachates) will be used in the next step concerning priority ranking of the sources and in efforts to design the recommended monitoring program.

TABLE 5-12. SUMMARY OF SOLID WASTE POLLUTANTS AND POLLUTANT SOURCES[a]

Pollution source or cause	Disposal methods	Potential pollutants	Possible concentration
Surface disturbance	Some stockpiles, revegetation use	Salts-$CaSO_4$	Uncertain
Construction debris	Landfill	Nitrates Sulfides Trace Metals	Uncertain
Raw oil shale	Stockpiled or placed on spent shale pile	—See discussion of spent shale—	
Spent oil shale	Spent shale pile	Major inorganics:	(mg/l)
		TDS	140,000
		Sodium	35,000
		Calcium	3,000
		Magnesium	4,700
		Potassium	600
		Sulfates	90,000
		Chlorides	3,000
		Fluoride	17
		Trace elements:	(mg/l)
		Mercury	0.005
		Lead	0.004
		Cadmium	0.006
		Arsenic	0.2

TABLE 5-12. (continued)

Pollution source or cause	Disposal methods	Potential pollutants	Possible concentration
		Copper	0.2
		Zinc	3
		Selenium	2
		Iron	2
		Boron	10
		Organics:	
		Oil and grease	Unknown
		Phenols	Unknown
		TOC	3 to 5 percent by weight
		Benzene extracts	2,500 ppm possibly
		Carcinogens (PCM, PAH)	Unknown
Sulfur byproducts	Sale or disposal in spent shale pile	Sulfur compounds	50 percent elemental S
Oil upgrading catalysts:	Spent shale pile (landfill) or recycle		Unknown (solubility characteristics of spent catalysts are unknown)
HDN (naphtha, hydrotreater)		Nickel, arsenic	
Miscellaneous catalysts		Iron, copper, nickel, zinc oxides and sulfides, cobalt molybdate	
Spent filters (carbon and diatomaceous earth		Adsorbed	Unknown (nature and solubility of these organics are uncertain)
Miscellaneous Landfill (garbage, etc.)	Landfilled or put in spent shale pile	Nutrients Sulfides Organics	Uncertain
Sewage sludge	Soil amendment for revegetation	Organics Nutrients	Uncertain
Water treatment plant sludges	Spent shale disposal pile	TDS	Uncertain

[a] Source: Reference 126.

The priority ranking of pollutant sources and pollutants (Table 5-13) is based on a sequence of data compilation and evaluation steps. These steps include (a) identification of the potential pollution sources mentioned above, methods of waste disposal, and potential pollutants associated with the various waste sources, and (b) an assessment of the potential for infiltration and subsequent mobility of these pollutants in the subsurface. The three basic criteria used to develop the ranking of pollutant sources are:

Mass of waste, persistence, toxicity, and concentration

Potential mobility

Known or anticipated harm to water use

With respect to the potential sources of pollutants in the solid waste category, and indeed for all sources on the oil shale tracts, the principal source of ground-

TABLE 5-13. PRELIMINARY PRIORITY RANKING OF POLLUTANT SOURCES AND POLLUTANTS FOR OIL SHALE TRACTS U-a and U-b[a]

Source priority ranking	Potential pollution source	Potential pollutant ranking		
		Highest	Intermediate	Lowest
Highest	Spent shale	TDS, Na, SO_4, As, B, Se, F, organics (PAH, carcinogens[b])	Ca, Mg, Zn, Cd, Hg, organics (phenols, etc.)	Pb, Cu, Fe
	High TDS wastewater	TDS	—	—
	Sour water	Ammonia, phenols	Organics	—
	Retort water	As, Cl, S, organics, (POM carboxylic acids, phenols)	TDS, organics (amines, etc.)	Carbonates, PO_4, NO_3
	Spent catalysts	As, Mo	Zn, Ni	Fe, Cu, Co
Intermediate	Stormwater runoff	TDS, organics, As, Se	Na, Ca, SO_4, HCO_3, organics	Zn, Cd, Hg
	Water treatment plant sludges	TDS	Major macroinorganics	Trace metals
	Miscellaneous landfill materials	Organics	—	—
	Sulfur byproducts	Sulfides, sulfates	—	—
	Oily waste waters	Organics	Trace metals	—
	Spent filters	Organics, As	Trace metals	—
Lowest	Sewage sludge	Organics	Nutrients	—
	Mine water	TDS, oil and grease	Trace metals, organics	Macroinorganics
	Sanitary waste water	Organics	Nutrients	Macroinorganics
	Surface disturbance	Calcium salts, TDS	Macroinorganics	—

[a] Source: Reference 126.
[b] Suspected carcinogens such as benz(a)anthracene, benzo(a)pyrene, 7, 12-dimethylbenz(a)anthracene,dibenz(a,j)acridine, and 3-methylcholanthrene.

water contamination was determined to be spent shale. Particular contaminants in spent shale include an extremely high salt concentration (possibly as high as 140,000 mg/l or 1.17 lbs/gal TDS) and a high loading of organics. The mobility of salts will be limited mainly by precipitation reactions, which could remove calcium and magnesium carbonates, and gypsum. Some sorption of organics may occur. Mobility of organics will be enhanced by the high TDS, and leaching of both types of contaminants (organics and inorganics) will occur together. Organic concentrations may be diminished by precipitation at higher pH values, by surface reactions, by auto-oxidation, and by microbial decomposition. Trace metal mobility will be affected by pH, complexing with organics, sorption on organics, precipitation as sulfides, etc. Microorganism levels probably will be limited by the high TDS.

The spent shale pile will contain a fabricated vadose (water unsaturated) region overlying the indigenous vadose zone. Movement of water and pollutants in the fabricated vadose zone may be reduced by the presence of indurated layers formed by the precipitation of calcite and gypsum. However, estimated leachate values of exchange sodium percentage, sodium adsorption ratio, and total dissolved solids are such that the hydraulic conductivity will remain high.

Attenuation of pollutant movement in underlying geologic formations may result mainly from precipitation of salts, because sorptive effects will be limited (except possibly to organics).

The above discussion suggests that pollutants in spent shale leachate may be attenuated by a variety of physical/chemical processes. However, because of the initially high concentrations of the major inorganic constituents, the overall salinity level will remain high in leachate. In fact, if leachate were somehow to penetrate shallow alluvial aquifers or other freshwater aquifers, serious quality impairment would occur.

Monitoring Spent Shale Disposal—

In the following discussion, considerations that should be included in a recommended groundwater quality monitoring program for a spent shale disposal situation are presented. The monitoring steps addressed are pollutant source characterization, water use, hydrogeologic framework and existing water quality, infiltration potential, and pollutant mobility.

Pollutant Source Characterization—During the development and operation of the oil shale facilities, on-site inspection of disposal procedures is recommended on a regular basis. Observations should be made of the following activities:

1. Preparation of disposal area before disposal (removal of soils, storage of removed materials, etc.)
2. Procedures for transport, spreading, contouring, and compaction of spent shale
3. Placement of other solid and liquid wastes in or on the spent shale pile
4. Surface sealing of spent shale pile
5. Construction of revegetation trenches
6. Irrigation or imposed leaching activities

The frequency of these on-site surveys will vary according to the intensity of activities. For example, during project initiation, weekly or biweekly surveys should be made. As operations reach a steady state (during each development phase), survey frequency can be extended to perhaps monthly or even quarterly observations. As revegetation activities are initiated, more frequent (again perhaps weekly) observation is required.

Knowledge of the chemical characteristics of liquid wastes to be disposed into the spent shale pile and of the soluble components of solid wastes is essential to the monitoring program. Development of the monitoring program should include analyses of liquid wastes and solid waste saturated extracts for the chemical

characteristics outlined in Table 5-14. Waste products to be included are (in decreasing order of priority):

1. Processed shale (saturated extract)
2. High TDS wastewater
3. Sour water
4. Spent catalysts (saturated extract)
5. Water treatment plant sludges (saturated extract)
6. Sulfur by-products (saturated extract)
7. Oily wastewaters
8. Spent filters (saturated extract)
9. Mine water

TABLE 5-14. OUTLINE OF PRELIMINARY CHEMICAL ANALYSIS PROGRAM FOR MONITORING PROCESSED SHALE DISPOSAL AREA[a]

Priority for analysis category	Analysis category	Priority for monitoring constituents		
		Highest	Intermediate	Lowest
Highest	General parameters	pH, e.c., Eh	TDS	—
	Major inorganics	Na, SO_4, Cl, F	Ca, Mg, K HCO_3 CO_3 Sulfides NH_3	NO_3
	Trace elements	As, Se, Mo, B	Zn, Cd, Hg Ni	Pb, Cu, Fe
	Organics	DOC		DOC fractionation, phenolics, specific compounds (BaP)
Intermediate	Radiological	Gross A activity Gross B activity	Ra-226, 228	U, Th
Lowest	Bacteriological	TPC	TC	FC

[a] Source: Reference 126.

Water Use—Data should be obtained from the State and Federal agencies that are concerned with water resources and economic development.

The Hydrogeologic Framework and Existing Water Quality—The hydrogeologic framework and existing water quality in the vicinity of a disposal site should be adequately described to measure the changes in water quality that might occur as a result of the oil shale activities. Recommended approaches for a more or less typical situation are presented in the following paragraphs.

Characterization of Alluvium. Recommended activities for monitoring program development are as follows:

1. Test drilling and geophysical surveys to define the characteristics and boundary condition for the alluvial system (i.e., thickness, subsurface extent)
2. Sampling of water quality of alluvial aquifer
3. Pump testing of saturated zones identified to determine hydraulic characterisitics

Formation Fracturing. Fracturing in the bedrock formations that are in contact with the spent shale may create pathways for the movement of pollutants from the disposal area to surface waters or to deep aquifers. Identification of the density and character of this fracturing is thus the key to evaluating pollutant mobility and development of the monitoring program. As the materials in the alluvial channels and canyon slopes are cleared for construction of the processed shale pile, visual surveys should be made of the surface of the bedrock formation. Fracturing should be mapped, and the maps used for locating monitoring sites for following mobility in the processed shale disposal area.

Testing Green River Formation. Testing recommended for the aquifers in the Green River Formation includes:

1. Evaluation of water quality sampling procedures at existing and proposed wells to establish suitable sampling methods and sampling frequency
2. Evaluation of existing pumping test data and performance of additional pump testing at existing wells
3. Installation, pump testing, and water quality sampling of new wells where hydrologic assessments indicate they are needed

Infiltration Potential—Infiltration potential is to be evaluated to examine the water-balance for the processed shale pile and to provide a basis for monitoring pollutant mobility in the processed shale disposal area. The two areas where infiltration should be assessed are the surface of the disposal pile itself and the surface of the underlying formation (i.e., in fractures). For these assessments, it is recommended that double-ring infiltrometers be used as follows:

1. At various stages of the construction of the processed shale pile including:
   a. As shale is spread before compaction
   b. After compaction
   c. After surface is sealed
   d. During revegetation (i.e., in revegetation trenches)
2. At the surface of cleared areas where the underlying formation is exposed

In conjunction with these infiltration tests, monitoring of subsurface mobility should also be employed as presented in the following discussions. Such monitoring offers the opportunity to provide the infiltration assessments, provide estimates of subsurface hydraulic conductivity, test various monitoring equipment (e.g., moisture blocks, suction cup lysimeters, and neutron probes), and (via sample collection) provide an analysis of leachate formation and composition.

Pollutant Mobility—Pollutant mobility monitoring needs in the processed shale disposal area include monitoring (a) in the processed shale pile itself, (b) in alluvium that may be present in the disposal area, and (c) in the bedrock formations.

Monitoring in the Processed Shale Pile. Monitoring in the processed shale disposal pile includes the sensing of changes in moisture content (thus potentially inferring movement of water and solute materials) and the collection and characterization of these solute materials. The monitoring program should be initiated with the infiltration evaluations presented above. Infiltration test sites should be instrumented as follows:

1. Water content (or "soil"-water pressure) sensing:
   a. Access well for neutron moisture logging
   b. Soil moisture blocks (at various depths)
2. Suction cup lysimeters for water quality sampling (tensiometers should be used to appropriate suction levels)

As indicated above, a sequence of infiltration tests during the various stages of pile construction is recommended. The initial testing of spent shale before and after

compaction forms the basis of initial monitoring of the shale pile. The test sites should be maintained as long as possible during pile construction. As benches are formed in the disposal pile, permanent monitoring sites should be established on them with access (neutron logging) tubes, tensiometers, or other sensors demonstrated to be applicable during infiltration testing.

Monitoring installations in completed segments of the processed shale pile would include (1) selected infiltration test sites as described above; (2) selected sites associated with revegetation trenches such as those depicted in Figure 5-6. These trench sites are appropriate because water harvesting efforts make these the most likely initial locations of infiltrating water. Access tubes for neutron logging, tensiometers, suction cup lysimeters, or other monitoring devices shown to be suitable during the infiltration testing would extend below the trenches into the processed shale pile itself. Should appreciable pollutant movement be indicated by monitoring within the processed shale pile, monitoring in the natural hydrogeologic realm would be indicated.

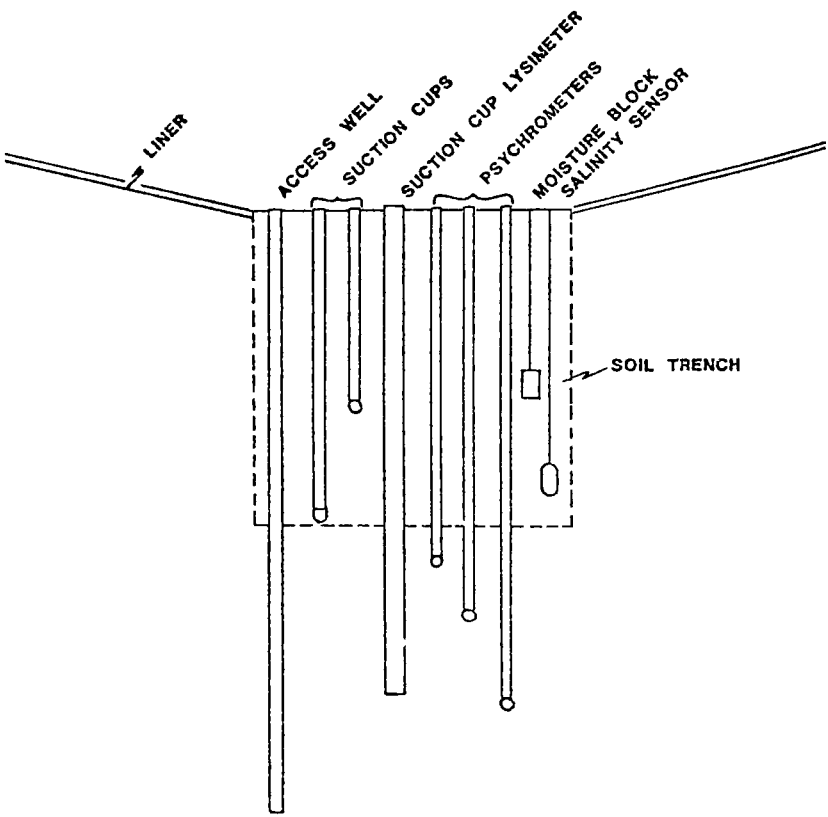

Figure 5-6. Possible monitoring facilities: soil trenches. (Source: Reference 126)

Along with the revegetation trenches, an intensive sampling program should also be conducted in the vicinity of the toe of the completed spent shale pile. Lower reaches of the pile may become saturated as a result of leaching for salinity control, or because of subsurface movement of water from trenches. Leachate produced by saturated conditions may flow out of the pile into downstream alluvium, or downward into underlying formations. A possible array of monitoring facilities in the toe of a spent shale pile is illustrated in Figure 5-7.

Monitoring in the Alluvium. Monitoring wells should be drilled in the alluvium in locations where pollution from the spent shale pile is most likely to occur, such as near the toe of the pile. Recommended procedures for constructing these monitoring wells include drilling a 20- to 30-cm (8- to 12-in.) hole to the base of the alluvium. A 10- to 15-cm (4- to 6-in.) diameter PVC casing should be installed to the bottom of the hole. The casing should be perforated opposite the interval from a few meters (several feet) below the static water level to the bottom. Clean pea gravel of known composition should be used to gravel pack the well. The upper few meters (several feet) should be filled with cement to form an annular seal. The wells should be logged by a geologist during drilling and developed by airlifting and/or pumping upon completion. A locking cap should be installed along with a suitable barrier to prevent destruction.

Water samples should be retrieved by installation of suitable submersible pumps for the reasons previously discussed. After well development, a submersible pump should be installed and field tests performed during continuous pumping for several hours or days. Temperature, electrical conductivity, and pH of the discharged water could be measured. After completion of this phase, a determination should be made as to the length of pumping necessary before collection of a water sample. At least two or three well volumes should be pumped before sample collection. This procedure will allow collection of water samples typical of the alluvium near the monitor well.

Sample collection should include field measurement of pH, specific conductance and Eh. Water samples should be filtered and preserved at the time of collection (127).

Appropriate sampling frequencies should be developed during the initial sampling program. Initially, depth to water and field measurement of pH, specific conductance, and Eh (or DO) should be monitored on a monthly basis. More detailed chemical analyses (Table 5-14) should be performed on a quarterly basis unless appreciable water quality changes are noted during the monthly sampling. Sampling frequency should be reevaluated after each sampling year.

Analytical Methods for Leachates from Oil Shale—

Paul Mills and Ann Alford

This discussion will consider the generation of a leachate material for use in testing for organic and inorganic parameters. When the leachate is generated, the methods described in the preceding subsections on standard water analyses and analysis of organic pollutants can be used (i.e., the leachate can be treated as a water sample). At present, there is no standard method for extracting a leachate from a solid material. EPA has proposed one under Section 3001 of the Solid Waste Disposal Act as amended by the Resource Conservation and Recovery Act of 1976 (128). This acetic acid extraction procedure is used to determine whether a waste is to be classified as "hazardous" or not. EPA is also considering a "rain leach" test to be applied to the materials classified as hazardous; the test simulates rainfall leaching, and would be used to determine if a waste can be put in a monofill, or should be placed in a hazardous waste disposal site.

Relevant Parameters—

To critically evaluate laboratory leachate generation methods, it is first necessary

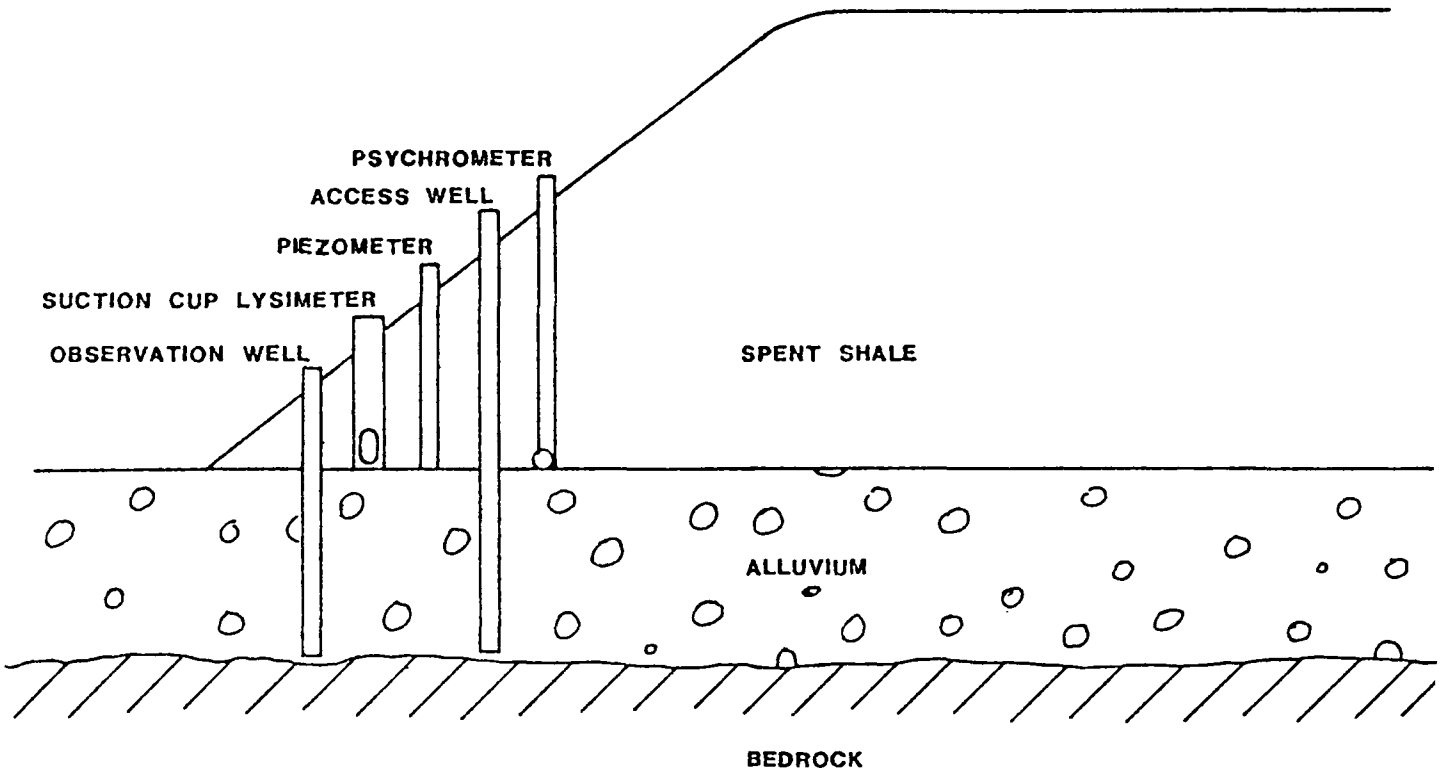

Figure 5-7. Possible monitoring facilities at the toe of the spent shale pile. (Source: Reference 126)

to consider leaching under natural conditions. Leachate is liquid that has contacted solid material and has extracted and/or suspended constituents from it. The character of the leachate depends on both the composition of the material and on environmental factors, including pH, the redox potential, the chemical composition of the leachate, and temperature. Factors that primarily affect leachate transport include the flow rate of the eluant and the surface area, porosity, and permeability of the material leached. Factors that could affect the leaching of salts are shale texture, retorting process, soluble salt concentration of the shale, degree of compaction, seasonal precipitation patterns and surface infiltration, amounts and types of vegetative cover, aspect, slope, and elevation of the surface of the disposal pile, and degree of cementation in the disposal pile (129).

An ideal leaching test should control all these parameters and be quick and inexpensive. A principal concern of any test procedure is that of reproducibility; also related to this is the comparability of test results from different wastes. Existing laboratory tests fall into two main categories: Batch (shake) tests and column tests. Shake tests consist of placing a sample of the material to be leached in a container with a suitable eluant, agitating the mixture for a specific period of time, and analyzing the resulting leachate. Shake tests are quick, simple, require minimal equipment, are inexpensive, and reproducible. But the conditions chosen for the shake test variables may be difficult to relate to environmental conditions, and the results may be difficult to interpret. Column tests, in which the waste is packed in a column and the leaching solution passed through, simulates the waste/leachate migration found in disposal piles. The column test is good for predicting release patterns over time. However, the column tests are limited by: problems from channeling, nonuniform packing, unnatural clogging and biological effects, edge effects, longtime requirements, and difficulty in obtaining reproducible results. Several factors affecting the parameter's concentration in the leaching tests are discussed below.

Leachate Composition—The use of distilled water or other mild leaching solutions allows the waste to create its own leaching environment, whereas a synthetic leachate or strong chemical solution essentially controls the leaching environment.

Solid/Liquid Ratio—With a high solid/liquid ratio, many elutions will be necessary to collect sufficient leachate for analysis of the leachable fraction of the component. But a low solid/liquid ratio can produce low concentrations of the parameters of interest and difficult analytical problems.

Time per Elution—Though the time per elution is arbitrary, the test should be long enough to allow rapidly equilibrating species to approach equilibrium, yet short enough to minimize biological growth, secondary effects, and consistent saturation of the species of interest. The time should also be convenient to personnel if possible.

Temperature—Generally, leaching tests have been conducted at room temperature, and the effects of temperature on the leaching pattern of the waste within the range of average laboratory temperatures may not be great enough to justify specially controlled temperature conditions. Temperature should be measured and reported, however.

Agitation Technique—An agitation technique for shake tests is needed that promotes mixing without causing waste particle or container abrasion. Methods such as reciprocal shaking, wrist action shaking, or circular shaking are suitable provided they produce well mixed systems and are slow enough to avoid promoting abrasion.

Surface Area Contact Between Waste and Leachate—For some wastes, the amount of surface area in contact with the leaching solution can be important in controlling parameter concentrations in the leachate. The surface area of a waste may be controlled initially during sample preparation before the test by grinding, cutting, etc., or by the agitation technique.

Interpretation of Tests—

Caution must be exercised in data interpretation, since test data cannot always be transposed directly to practice. It may be possible to correlate test conditions with concentrations by running extensive verification tests correlating the behavior of a waste in the test with the behavior of the same waste in a carefully monitored disposal pile. Correlation coefficients could then be developed for parameters and conditions similar to those in the verification study, and the tests results could be used to estimate concentrations. A short leaching test cannot completely duplicate the long-term leaching characteristics of a waste. The short test might completely miss a parameter having exponential release, or it might over-estimate the release of a parameter showing a concentration maximum. These patterns could be seen in a long-term study, but they are difficult to determine in a short test. Shake tests are designed to yield equilibria rather than kinetic data. Leachate generation under natural conditions, by contrast, is a highly dynamic process rather than a static one. Furthermore, the specific character of leachate, in terms of both quality and quantity, will be site-specific. A recent publication summarizes a number of leachate studies (130) and includes a discussion of leaching mechanisms and leachate compositions.

Inorganic Analysis—

Leachate samples will present numerous difficulties in flame atomic absorption analysis for heavy metals such as Cr, Ni, Fe, Pb, Cu, and Zn because of the presence of complex matrices (as discussed for water samples in the preceding subsection on standard water analyses). Detailed specific interferences for heavy metals are given in References 131 and 132. Nonspecific interferences such as acids or salts hinder the evaporation of the solution or the solvent and generally result in a depression of the absorbance during metal determinations. Spectral or line interference can often be avoided by judicious choice of an analyte resonance line and by using a narrow band-width as close as possible to the width of the selected line emitted by the hollow cathode tube. Element-specific interference effects are expected to cause complications in leachate analyses. Alkali and alkaline earth elements such as Na and K are subject to a wide range of interferences, but this can be corrected by the addition of a more easily ionized element such as Cs at a concentration level considerably higher than that of the analyte atome. Ca and Mg are interfered with by a number of common cations and anions, such as $SO_4^=$, PO_4^-, $CO_3^=$, HCO_3^-, Na^+, K^+, and Al^{+++}. An inorganic releasing agent, lanthanum, has been found effective in suppressing interferences and in preventing formation of oxides in the flame.

The COD/TOC ratio can be used to determine the reliability of either the COD or TOC measurements. If the results of the analysis of a given leachate sample yield a ratio of COD/TOC greater than the theoretical maximum value of 4.0, either the COD or the TOC value is in question.

Organic Analysis—

Spent shale composition depends on the type of retorting process used and retort conditions, with some spent shale containing up to 5 percent organic carbon. The organic portion contains PAH's, some of which have carcinogenic and mutagenic properties. The identity and solubility of specific organic components of spent shale leachate should be determined. Techniques used to analyze organic compounds in water are also used to analyze organic compounds in spent shale leachates.

Researchers at the Denver Research Institute (133) have reported that some potentially harmful organic compounds may be leached from spent shale by water. Benzene extractions of several spent shale samples showed that 0.24 percent (average) of the spent shale was benzene-soluble organic material, and wet shale (15 to 20 percent moisture) yielded more benzene soluble material than dry shale.

When spent shale that had been extracted with water was extracted with benzene, that spent shale benzene extract contained 0.13 percent soluble organic material, indicating that 0.11 percent of the soluble organic material in the original sample had dissolved in water. The benzene extract of this water extract contained only about 20 percent (by weight) as much material as the shale benzene extract, but some components were identified as azarenes and PAH such as benzo(a)pyrene and 7,12-dimethylbenzanthracene.

A variety of analytical techniques were used in this study, but techniques to detect PAH were emphasized. Leachate components were isolated from thin layer chromatography plates after two-dimensional development with two solvent systems and fluorescence detection. Fluorescence spots scraped from the TLC plates were analyzed using mass spectrometry and liquid chromatography. Analysis with nuclear magnetic resonance and infrared spectroscopy indicated low aromaticity and surprisingly high alkane content of the extract mixture.

Analysis by gas chromatography (15.24-m or 50-ft Corasil SCOT column) showed that the spent shale extract contained volatile (eluting in the 65° to 100°C or 149° to 212°F temperature range) and semivolatile (eluting in the 100° to 300°C or 212° to 572°F temperature range) components that appeared to be C_{10} to C_{25} hydrocarbons and some higher molecular weight compounds. Planned future analysis by combined GC/MS should help identify specific extractable components. Preliminary results indicated that LC (with ultraviolet and fluorescence detection) and gel permeation chromatography are useful techniques to separate extracts into fractions for further characterization by mass spectrometry or combined GC/MS.

This work indicates the valuable information that can be obtained using available analytical techniques. Spent shale leachates should be analyzed with techniques designed to permit identification and measurement of as many organic components as possible (133).

Solid Inorganics—Paul Mills

For a summary of existing trace element composition data for shale and its products and an evaluation of these data and related studies, refer to the EPA publication, *Trace Elements Associated with Oil Shale and Its Processing* (134). Although some uncertainties and data gaps exist at present, a number of general conclusions have been deduced from the available trace element data and studies.

For many elements, wide ranges of concentrations have been reported for oil shale and its products. These ranges reflect natural geographic and vertical profile variations in the shale, differences in retorting methods, and uncertainties associated with various sampling and analytical techniques.

Compared to average rocks, oil shale contains much higher levels of Se and As, moderately higher levels of Mo, Hg, Sb, and B, and lower levels of Co, Ni, Cr, Zr, and Mn. Other elements are present in concentrations typical of common rocks.

Most elements are not converted to volatile or oil soluble substances during retorting and are consequently retained by processed shale. However, up to 30 percent of Hg, 15 percent of As, and 8 percent of Se in raw shale can be found in shale oil, retort gases, and retort waters.

Most metals contained in retorted shale are not readily water soluble. However, elements that form anionic species (Ca, Na, Mg, B, F, Mo, Se) can be leached from retorted shales by percolating water.

Trace Elements in Oil Shale—

In recent years, considerable data on the minor element composition of oil shales have accumulated. For many of the selected elements, reported levels vary by one order of magnitude, and for a few elements, by two orders of magnitude. The

ranges reflect at least three factors: (a) natural variations in oil shale samples in a vertical profile, depending on mineral and organic matter composition, (b) natural geographic variations, and (c) variations in measurements as a result of different sampling, preparation, and analytical techniques. In most cases, it is difficult to distinguish the relative importance of these three factors. For example, variations between laboratories for shale from the same area are often as great as geographic variations determined by the same laboratory with the same sampling method and sample preparation (135).

Samples of overburden and spoils can be collected and prepared by many methods, which vary with available resources, time, and purposes. In selecting a method, care must be exercised that the chemical properties of the samples are not altered during sampling and before analysis. No simple answers exist to the problem of collecting or to the question of sampling frequency. Good judgment and experience are required.

The types of analyses performed on solid samples are highly dependent on the types of material samples. For solid piles or streams, the nature of the analytical method rarely affects the sampling methods used, but the handling and preservation methods are affected.

Sampling methods for solids use two general techniques—grab sampling and grab-and-composite sampling. Grab sampling is the general sampling technique used where low precision is required. Grab-and-composite sampling is the more precise technique. In most cases, the difference between the two is only a matter of degree, since the sample collecting methods are identical. In the second method, grab samples are collected periodically over the duration of the test and then composited to form a single sample. The following sampling methods, although they pertain mostly to coal, are readily adaptable to other solid streams:

ASTM Method D 2013-72: Sample Handling

ASTM Method D 2234-74: Gross Sampling Collection

ASTM Method E 300-73: Sample Handling and Collection

Caution should be exercised in transporting and processing samples for laboratory analyses. Polyethylene plastic bags are recommended for transporting samples from the field. Canvas (unless lined) and ordinary paper bags are not recommended because these materials may absorb soluble salts from wet samples, and the glue in the paper bag may interfere with accurate analysis for boron. Galvanized equipment should be avoided if zinc is to be analyzed. Samples to be analyzed for nitrate-nitrogen cannot be stored moist under warm conditions. Moist or wet samples should be immediately frozen or spread to dry on waxed paper or similar water-proof material, ground to 2-mm (3.94×10^{-2} in.) size, and stored in closed, water-resistant containers until analyzed. Knowledge of potential sources of contamination and chemical transformations that may occur in samples is required. The principles of sampling are discussed in (136).

Sampling by drilling methods that involves a circulating fluid may potentially affect the composition of soluble constituents in the sample, either by leaching out salts or by impregnating the sample with contaminants from the circulating fluid. This problem is particularly acute in sampling overburden and spoils in the western United States. The drilling method affects the chemical composition of overburden samples (137). Drilling fluids that used saline water or sodium bentonite, or both, as the drilling mud, increased salinity and adsorbed sodium in samples, whereas drilling with air or using water of relatively low salinity did not appreciably change the sample composition. The use of an organic polymer developed for drilling fluid use did not appreciably change sample composition.

Sample Preparation—

The first step in the preparation of solid samples is to ensure homogeneity. This is accomplished by mixing (quartering and riffling) the sample and grinding it to

less than 200 mesh. Drying with concurrent gravimetric determination of moisture content is often required. The drying temperature must be selected to avoid loss of volatile components. For very high moisture contents, drying may be necessary to allow mixing, grinding, and sieving.

Elemental analysis by some techniques requires conversion of the element to the liquid phase. For major constituents in coal ash, this is accomplished by a $LiBO_2$ fusion and HNO_3 acid dissolution (138). For minor or trace elements, $LiBO_2$ fusion may result in a loss of volatile elements because of the high temperature required (138,139). The use of acid dissolution, although time consuming, alleviates this problem. Several acid digestion techniques have been reported (69,140-142). Each of these is appropriate for a limited number of elements.

Duplication of effort can be eliminated with the use of a perchloric acid digestion (PAD) technique applicable to a large number of elements. A PAD technique has been developed by the National Bureau of Standards (143). This technique includes a slow digestion with nitric acid followed by an acid mixture (HCl, HNO_3, HF), then perchloric acid. Solid samples with low organic content may be digested directly. Samples with high organic content, such as coal, must be ashed before digestion. Ashing without loss of volatile elements can be accomplished with a low temperature oxygen plasma asher.

Sample Analysis—

Once the samples have been treated and dissolved in appropriate reagents, instrumental and chemical methods can be used to measure their constituents. Such instruments as AA, XRF, NAA, and ion electrodes may be used, similar to the discussion for standard water parameters in the preceding subsection on standard water analyses. Additional descriptions of the use of these techniques for solid samples are found in Fruchter *et al.* (144) and Fox *et al.* (145).

Organics in Solid Samples—Ann Alford

Techniques used to analyze organic compounds in surface water and groundwater are also used to analyze organic compounds in solid samples, such as sediments, soils, and solid wastes. Special requirements to be considered for solid samples are sampling techniques and extraction of organic components from the solid sample.

Sampling—

The main objective in sampling is to obtain and preserve homogeneous, representative samples with minimum contamination. To obtain representative samples of carbonaceous spent shale, the quartering and riffling technique can be used (124). To obtain homogeneous soil samples, large soil particles can be ground and sieved until a uniform particle is obtained (124). Oil shale can be crushed to an approximate size of 2 to 3 mm (.08 to .12 in.) (146). When volatile components are to be analyzed, however, grinding and crushing should not be used.

Sediments can be collected by inserting a sediment corer and using a clean spatula to dig around the corer until the spatula can be inserted beneath the corer (147). The sediment sample should be transferred to a clean glass sample bottle with a screw cap lined with aluminum foil. The samples should be frozen, transported in ice, and stored at temperatures below 0 °C (32 °F).

Extraction—

Soxhlet Extraction—The most commonly used technique for removing organic components from solid samples is solvent extraction in a Soxhlet apparatus, after the sample holder (thimble) and apparatus have been extracted (with the same solvent that is to be used for the sample) to remove any organic contaminants. Spent shale samples have been extracted with double distilled benzene with the Soxhlet apparatus surrounded with black shields to prevent sample component composi-

tion changes induced by fluorescent light (124). Benzene/methanol mixtures are also common solvents for sediment extraction, but no one solvent or mixture is universally recommended and accepted (146,148).

Headspace Sampling Followed by Soxhlet Extraction—After addition of pure water and an internal standard, sediments can be sampled for volatile components with dynamic headspace sampling with a stream of purified nitrogen and trapping of volatile organic components on Tenax-GC (147,149,150). While the sample is agitated with a magnetic stirrer, headspace sampling is performed at room temperature for 2 hrs and at 70 °C (158 °F) for 2 additional hrs. The residual solids are then extracted in a Soxhlet apparatus with methanol followed by methylene chloride (149). The methanol extraction step is necessary to change from an aqueous to an organic solvent. To remove organics remaining in the water from the headspace sampling step, liquid/liquid extraction techniques are used.

Compounds not usually considered to be volatile (such as pyrene, naphthalene, and substituted naphthalenes) can be removed from the sample by headspace sampling. This technique is especially suited for the series of one to three condensed ring aromatic hydrocarbons (147). Compounds more volatile than phenanthrene are substantially removed, and 20 percent of the total amount of phenanthrene in a standard solution was removed during headspace sampling (144).

Headspace Sampling Followed by Liquid Chromatography—An alternative technique employs dynamic headspace sampling for volatile components followed by coupled-column LC for nonvolatile components (147,150). This technique requires minimal sample handling, and organic-free water is the only solvent needed for sample preparation.

After headspace sampling, water remaining in the sample container is pumped through a liquid chromatograph pre-column packed with Bondapak C18. This pre-column is then attached to a gradient elution liquid chromatograph, and sorbed compounds are eluted with methanol/water, beginning with 30 percent methanol and increasing to 100 percent methanol in 40 min. Components can be observed with ultraviolet and fluorescent detectors, and fractions can be collected for subsequent analysis by spectroscopic and mass spectrometric techniques.

Because the liquid chromatographic technique becomes more effective as the headspace sampling technique becomes less efficient, the two procedures complement each other very well. These procedures were used to detect petroleum-derived hydrocarbons in sediment taken from the site of an oil spill that had occurred 10 years before samples were collected (150).

Sonication—Ultrasonic energy has been used to extract organic residues from soil, and the method is reported to be rapid, reliable, and sensitive (151). Comparison of extraction efficiency with 30-sec ultrasonification and 8-hr Soxhlet extraction showed only small differences in recoveries of organochlorine insecticides added to soil (151). With sonication, recoveries of eight insecticides exceeded 95 percent when 10 to 100 g (154 to 1,540 grains) of each compound was added to 50 g (770 grains) of oven-dried soil. Soxhlet extraction of soil after sonication extraction produced only negligible amounts (F 1 percent) of standards that had been added to the soils. Extraction of organochlorine compounds was affected by the solvent, soil sample moisture content, and soil type. With one clay soil, best recovery was achieved when the soil sample was saturated with moisture; but soil moisture did not seem to be a critical factor for good recovery. No evidence of breakdown or structure alteration during extraction was observed in the four organochlorine insecticides (heptachlor, heptachlor epoxide, dieldrin, and aldrin) tested. Acetone was recommended as the extracting solvent to be used.

To remove organic compounds (hydrocarbons, phthalates, polycyclic aromatic hydrocarbons, fatty alcohols, sterols and stanols) from an estuarine tidal mud, solids from centrifuged mud were extracted with a heptane and isopropanol mixture (1:4) and sonication (152).

To determine the best technique for extraction of petroleum-derived compounds in estuarine and marine sediments, benzene extraction with a Soxhlet apparatus, sonication, and reciprocal shaking were performed (153). The largest amount of extracted material was recovered with the reciprocal shaker. Comparison of benzene, hexane, and chloroform as extracting solvent showed that the largest quantity of material was recovered with benzene.

Steam Distillation—An apparatus for steam distillation of pesticides and industrial chemicals from sediments and tissue is commercially available (151). Because solvent extraction techniques remove lipids, waxes, and related natural products along with pesticides and industrial chemicals, chromatographic separation procedures may be necessary to remove interfering compounds before extracts can be analyzed. The distillate extract, however, can usually be analyzed by GC without further cleanup procedures. A sediment sample blended in water is placed in a distilling flask. When the mixture is boiled, steam distillate condenses on inner walls of the cooling jacket. Condensate passes through a solvent (such as isooctane or toluene) that traps organic compounds. Analysis of Hudson River sediments contaminated with polychlorinated biphenyls (PCB) showed that 78 percent of the PCB were steam-distilled within 60 min (154).

Sulfur Removal from Extracts—Some sediment extracts contain substantial amounts of elemental sulfur, which interferes with analysis. Sulfur can be removed, however, by percolation of the sample extract through active copper powder (155).

Conclusion—

Before analytical techniques are selected for survey analyses and monitoring of the environmental effects of oil shale processing, more work is needed to determine optimum sampling and extraction procedures for solid samples.

HEALTH TESTING APPROACH AND METHODS

David Coffin

The prime purpose of testing as applied to the oil shale industry is to determine potential health hazards to persons employed in the industry and to persons handling products, as well as persons in the general population who come in contact with airborne or waterborne effluents from the industry or from combustion of fuels in power sources. It is prudent that in the *de novo* approach to such a problem all points be covered where human contact with a product or effluent and the like is possible. Additionally, it is axiomatic that whole animal testing should be carried out by the specific route by which human contact would occur. For example, mine dust and fumes from products should be tested by inhalation exposure, oily products by skin bioassay, and contamination of water by ingestion either directly or through the food chain route. If a product might exist as both a liquid and a fume, skin bioassay and inhalation exposure should be employed.

A second order of testing is concerned with characterization of the biological and chemical profiles of products and emissions to gain an identification of the toxic chemical to obtain a better understanding of the relationship of the technological process to the biological effects. A possible extension of the latter (which will only come with time and a coordinated approach along with prime safety testing) is that some of the short term tests may become predictive of direct health parameters, thus gaining a saving of time and funds in the general health testing of synfuels. This is one of the objectives of the Interagency Matrix Approach mentioned under Health Effects. An example of the value of such short-term testing already exists in the Matrix Approach where combined Ames testing and chemical fractionation is elucidating the presence of reactive organics not found in analogous petroleum products which may well explain basic differences in toxicity between the synthetic fuels and petroleum. By such means it is also possible to follow the effects of

TABLE 5-15. HEALTH TESTING IN PROGRESS IN THE OIL SHALE INDUSTRY

Technology step	Potential toxicant	Possible route of contact	Prime health testing	Second order testing
Mining and rock crushing	Shale rock dust	Inhalation	Inhalation exposure of animals	
Retorting	Retorted shale dust	Inhalation Skin contact	Inhalation exposure of animals	Ames testing and other mutagenic tests, *in vitro* toxicity testing
	Gaseous emissions	Inhalation	Skin carcinogenic bioassay in animals	
	Retort waste water emissions	Ingestion	Ingestion in animals	
Retort product	Raw shale crude (retort tar)	Skin contact	Skin carcinogenic bioassay in animals Toxicity by skin contact	Ames testing, other mutagenic tests on fractions; Short-term carcinogenic testing
Refinery feed stock	Upgraded retort product (shale crude)	Skin contact	Skin carcinogenic bioassay in animals Toxicity by skin contact	Ames testing, other mutagenic testing on fractions Short-term carcinogenic testing
Refinery	Various airborne effluents	Inhalation	Extrapolation from other data on basis of chemistry	Ames tests and as above
Refined products	Diesel fuel, jet fuels, gasoline fuel oil, residual oil, etc.	Skin contact, inhalation of fumes; Ingestion via food chain	Skin carcinogenic bioassay Toxicity by skin contact Inhalation exposure of animals Food chain testing	Ames testing and as above
Combustion products	Gaseous and particulate emissions	Inhalation	Gases - extrapolation from other data on basis of chemistry	Ames tests and as above on particulate emissions

hydrotreating, influence of boiling point and secondary treatment of products in the reduction of mutagenicity. If such mutagenicity can be shown to be directly related to carcinogenicity in a given class of materials, then it is possible that such a test could eventually successfully supplant a more time consuming, expensive whole skin bioassay for example.

We may expect that a high order of health safety measures will be built into the developing oil shale industry. This will be accomplished by the use of closed systems for retorting or refinery streams wherever possible and by the application of stringent control measures for effluents. Thus, in most instances, carcinogenic or otherwise toxic material will be handled in a manner so as to minimize human contact.

Because of the possibility of equipment malfunction, a no-risk situation can never be absolutely assured. Thus, it is important to have an understanding of the toxic potential of internal refinery streams and the like so that appropriate measures may be taken in the case of emergency. While it is known from the experience with petroleum that carcinogenicity is generally a function of boiling point, this information may not be directly relatable to synthetic fuels where carcinogenic compounds not found in petroleum, and with possibly different boiling point distribution, are known to exist.

While effluents from retorts or refinery are predictably well controlled, even minimal amounts gaining entrance to air or water might be a significant contribution to ambient concentrations of certain toxicants if an industry of the magnitude of certain current predictions develops.

Application of tests to various industrial technological steps is summarized in Table 5-15.

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SECTION 6
ENVIRONMENTAL GUIDELINES

This section presents suggested interim environmental goals applicable to an oil shale industry. The basis for past air and water permit decisions is discussed. These goals/guidelines should be considered as a starting point for detailed discussions on specific project environmental control requirements. Variations depending upon project location, process technology, and size of project are expected.

This section also contains a summary of EPA policies and procedures related to an oil shale project. This discussion is meant to provide oil shale developers and the public with an understanding of the logic and process which EPA uses in the evaluation of an oil shale project. Finally, this section presents the oil shale industry position on environmental impacts and regulatory policies.

CRITERIA FOR ENVIRONMENTAL GOALS

The existing legislative and regulatory framework for the oil shale industry is described in Section 1. Section 2 describes a regulatory approach to defining environmental standards that should be met by any oil shale facility and by an oil shale industry. The environmental goal applicable to the oil shale industry should be the minimization of environmental impacts. Minimization must be defined in terms of potential environmental harm, economics, energy penalty, and intermedia tradeoffs. A "no significant degradation" policy has been quantified for a few air pollutants (SO_2 and particulate), and it has been qualitatively stated for water quality. Protection of minimum stream flows for aquatic life, provision of adequate water quality for applicable water use, protection of health- and welfare-related air quality aspects, minimization of detrimental land disturbance in order to preserve adequate wildlife habitat, and protection of valuable socioeconomic, cultural, historical, and aesthetic values are environmental criteria that constitute the basis for defining specific environmental standards.

SUGGESTED INTERIM ENVIRONMENTAL GOALS

The source standards and ambient standards discussed in Section 1 apply to individual oil shale facilities and to an oil shale industry. The ambient standards will have the more direct impact on the industry (rather than on any individual facility) because the Piceance Basin and the Uinta Basin (and Colorado River Basin) have finite carrying capacities for air pollutants and water pollutants/water use. Attempts to define the size of an oil shale industry that could fit into these finite carrying capacities have been limited by inadequacy of data and comprehensive predictive techniques. Facility siting is an obvious major factor in determining the ultimate size of an oil shale industry.

The framework for appropriate environmental guidelines consists of existing legislative requirements, environmental standards, and source regulations. Decisions made as to what constitutes Best Available Control Technology (BACT) and best practical technology (BPT) in permits issued for oil shale and related facilities also provide precedent criteria for requirements to be applied to future oil shale projects.

The goals discussed below should be considered starting points for detailed discussions on specific project environmental control requirements.

Air

Air emissions result from the construction, mining, retorting, and upgrading phases of an oil shale facility. Control requirements for certain pollutants are included in Prevention of Significant Deterioration (PSD) regulations, which dictate that these emissions be controlled by the use of BACT. Controlled emissions are then used as input to computer air quality diffusion techniques in order to predict the estimated maximum ambient air quality concentrations that may occur as the result of operation of the facility. These predicted concentrations are then compared with applicable PSD increments, State ambient air quality standards, and the National Ambient Air Quality Standards. If BACT is provided and all ambient standards are met, a permit may be issued.

A future regulatory constraint with which an oil shale industry will have to comply is the protection of visibility in nearby Class I areas. The Flat Tops Wilderness Area is the closest Class I area to oil shale country at the present time. The National Park Service is considering requesting Class I status for Dinosaur and Colorado National Monuments. Also, there are wilderness study areas located on the edges of Piceance Basin, which, if they were designated as wilderness and also redesignated to a Class I status, would receive visibility and PSD increment protection under Section 165 of the Act. Final regulations regarding visibility are expected in late 1980. Although it is premature to estimate the exact constraints these regulations may impose, it is reasonable to assume that SO_2 and NO_X, which transform to SO_4 and NO_3, and primary fine particulates will have to be minimized, since they are the key contributors to visibility degradation.

In order to provide guidance for future oil shale developers, PSD requirements for four permitted facilities are summarized below. Additional guidance may be extracted from air NSPS for "similar" facilities as listed in Appendix D.

1. Colony development operation (46,000 BP) (1)

   Construction

   - Paved access roads
   - Routine application of dust suppressant to all disturbed areas
   - Gravel or oil service roads

   Mining and solids handling

   - Wet suppression techniques used in mine
   - Primary crushing
   - Baghouse collectors on crushing, conveying and transfer points; 99.7 percent collection efficiency
   - Traveling stacker with water spray
   - Underfeed reclaim
   - Covered conveyors

   Retorting/upgrading (TOSCO II)

   - Particulate scrubbers on preheat system (99.8 percent control at 762 mm or 30 in. W P water), elutriators (99.8 percent control at 1,016 mm or 40 in. W P), and processed shale moisturizer (99.0 percent control at 508 mm or 20 in. minimum W P)
   - Incineration of hydrocarbons in preheat system to less than 100 ppm weight carbon
   - Treatment of raw process sour gas to less than 228.84 mg H_2S per scmd (0.10 grain H_2S per scfd) of fuel gas (457.68 mg per scmd or 0.20 grain per scfd total S)
   - A combined 99.6 percent SO_2 removal efficiency on acid gas via a three stage Claus plus tail gas cleanup
   - 20 percent opacity

Fuel gas combustion limits for particulate and nitrogen oxides of 2.29 and 17.17 kg per million Cal (0.02 and 0.15 pound per million BTU), respectively

Product/waste handling

Application of chemical dust suppressant on processed shale pile

Rapid revegetation of processed shale pile

Double seals on floating roof storage tanks containing "high" vapor pressure liquid

Routine maintenance on pumps, valves, compressors and seals

2. Union Oil Company (9000 BPD module) (2)

Construction

Chip and seal construction roads

Routine application of dust suppressant to parking lot and high volume roads

Mining and solids handling

Routine wetting/dust suppression techniques during mining

Primary and secondary crushing underground

Baghouse collectors on crushing, conveying, and some fugitive handling emissions; 99.5 percent collection efficiency

Baghouse collectors on "finish feed" screening; collection efficiency 99.8 percent

Underfeed reclaim

Covered conveyors

Retorting (Union B)

Treatment of raw process sour gas via the Stretford process to a concentration of 137.30 mg H_2S per scmd (0.06 grain H_2S per scfd) of fuel gas (1098.41 mg scmd or 0.48 grain per scfd total S)

Stretford efficiencies of 99.77 percent for H_2S and 97.9 percent overall sulfur

20 percent opacity

Fuel gas NO_X combustion limits of 34.35 kg per million Cal (0.30 pound per million BTU) for recycle heater and 22.90 kg per million Cal (0.20 pound per million) for steam boilers

Product/waste handling

Vapor recovery on tank truck loading

Routine maintenance on pumps, compressors, valves, flanges

Application of chemical dust suppressant on processed shale pile

Rapid vegetation of processed shale

3. C-b shale oil venture

Construction

Routine application of chemical dust suppressants to disturbed areas

Mining and solids handling

20 percent opacity on mine vent

Use of low sulfur fuel oil in ANFO

Retorting (modified *in situ*)

Treatment of retort off-gas via a Stretford unit to 99.0 percent overall sulfur recovery and a H_2S concentration in off-gas of less than 15 ppm

Fuel oil combustion limits for steam generation of 11.45 and 91.60 kg per

million Cal (0.10 and 0.80 pound per million BTU) for particulate and SO_2, respectively

Product/waste handling

Rapid revegetation of run-of-mine shale

4. Rio Blanco Oil Shale, Inc. (1000 BP) (3)

Construction

Routine application of chemical dust suppressants to disturbed areas

Mining and solids handling

20 percent opacity on mine vent

Retorting (modified *in situ*)

Treatment of retort off-gas via an SO_2 scrubber to a 90.0 percent overall sulfur recovery and no greater than 250 ppm SO_2 in the off-gas

Fuel oil combustion limits of 11.45 and 91.60 kg per million Cal (0.10 and 0.80 pound per million BTU) for particulate and SO_2, respectively

Product/waste handling

Rapid revegetation of run-of-mine shale

In addition to the control technology requirements listed above, the PSD permits have included requirements for stack and ambient monitoring. Primary emphasis for "first generation" plants will continue to be on source characterization.

Water

A no-discharge-of-pollutant concept is a desirable goal for oil shale facilities. To accomplish this goal, maximum recycle/reuse strategies will have to be employed. Treatment of internal streams for reuse and treatment of streams discharged to surface water or groundwater will be necessary. Consumptive use of water should be minimized, since this practice provides the double benefit of minimizing water quality degradation (due to concentration effect) and conserving water for other users in a water short area. Primary sources of potential wastewater streams may be categorized into three principal sources: (1) mine dewater; (2) process water; (3) leachate. Treatment of any potential discharge must comply with best available technology economically achievable (BATEA) and best management practices (BMPs) as defined by the NPDES permitting authority. Water quality criteria and applicable stream standards must also be met. These standards are discussed in more detail in Appendix D. Also, Colorado and Utah have adopted antidegradation policy statements in their water quality planning processes.

In order to provide guidance for future oil shale developers, NPDES permit requirements for three permitted *in situ* facilities are summarized below. See also Appendix D.

1. Rio Blanco Oil Shale, Inc. (CO-0034045) (4)

This permit is for the pump testing and mine dewatering phase only. No discharge of process water is allowed under this permit.

Parameter	Limit
Flow	N/A
Total suspended solids	30 mg/l 30 day average 45 mg/l 7 day average
Total dissolved solids	3000 mg/l daily max
Fluoride	3.0 mg/l daily max
Boron	5.0 mg/l daily max
Oil and grease	10 mg/l grab sample
pH	6.0 to 9.0

This permit has been proposed (5) for revision to extend through December 31, 1980. Limits are as shown below.

30 day		Daily max
Flow	N/A	N/A
TSS	30 mg/l	45 mg/l
TDS	1200	1800
Fluoride	2.0	3.0
Boron	1.0	1.5
NH_3 as N	N/A	N/A
Phenol	N/A	N/A
Oil and grease	N/A	10
pH	6.0 to 9.0	N/A

2. C-b shale oil venture (CO-003961) (6)

This permit is for the pump testing and mine dewatering phase only. The permit allows discharge of treated mine water and runoff; no discharge of process water is allowed. Limits are shown below.

Parameter	30 day average	Daily max
Flow —		
10% of Piceance Creek	**10% of Piceance Creek**	**10% of Piceance Creek**
TSS	30 mg/l	45 mg/l
TDS	1200 mg/l	1800 mg/l
F	—	9.0 mg/l
B	—	3.5 mg/l
NH_3 as N	—	1.3 mg/l
Cl	—	0.02 mg/l
Phenol	—	0.2 mg/l
Al-dissolved	—	1.1 mg/l
Fe	3.5 mg/l	7.0 mg/l
Cd	—	—
Cu	—	0.24 mg/l
Hg	—	0.00005 mg/l
Ag	—	0.00025 mg/l
Zn	—	—
Oil and grease	—	10 mg/l
pH	—	6.0 - 9.0

Note: All parameters are total unless noted as dissolved.

3. Occidental Oil Shale Inc. (CO-0029947) (7)

Process water is collected in a sump and sent to a steam boiler for steam generation. Boiler blowdown goes back to the mine. Therefore, no discharge of process water occurs. Excess mine water may be discharged onto waste shale and is limited as shown below.

	30 day average	Daily max
TSS	30 mg/l	45 mg/l
Fe	3.5 mg/l	7.0
Oil and grease	—	10.0
pH	—	6.0 to 9.0

Since no permits for oil shale processing have been issued, other than a no-discharge-of-process-water concept, little guidance from past decisions is available. Qualitative guidance to help define BAT and BMP is presented below. This "crystal ball" guidance should be considered as a starting point for detailed discussions on specific projects.

No discharge of retort water

No discharge of oily process water

Reinjection of mine water into similar quality aquifers

Diversion of surface runoff from process areas

Collection of runoff from disturbed areas in sedimentation ponds

Collection and containment of processed shale pile leachate and runoff

No discharge of TDS wherever practicable unless total discharge is less than 0.9 tonne (1 ton) per day of salt

Treatment of process water prior to disposal on processed shale pile whenever practicable

In addition to the effluent limits established in the permits issued to date, source monitoring requirements have been defined. These have included routine (i.e. monthly grab samples) samples for the permitted parameters, plus characterization of a suite of parameters at high and low flows during the year.

Solid Waste

The types of solid waste to be handled from an oil shale project include processed shale, raw shale fines, spent catalysts, and sludge. The largest volume material is processed shale. Unlike for air and water, no Federal permits have been required of oil shale developers for solid waste disposal. Regulations required by the Resource Conservation and Recovery Act promulgated in February, May, and October of 1980 defined hazardous waste characteristics and safe treatment, storage, and disposal practices for hazardous wastes. Spent catalysts and sludge are likely to be found hazardous but processed shale is likely to be treated as a solid waste. Requirements at 40 CFR 257 govern solid waste disposal. Requirements at 40 CFR 260 will include characterization of wastes, groundwater monitoring, and disposal practices defined as Best Engineering Judgment on a case-by-case basis by the permit writer.

In lieu of definitive past permit requirements, the "crystal ball" concepts and practices listed below may be used as a starting point for detailed discussions on specific projects if a solid/hazardous waste permit is found to be necessary.

Isolation and containment of hazardous wastes such as spent catalysts

Record keeping and reporting of all hazardous wastes

Provision of an impermeable layer at the bottom of the processed shale pile in order to prevent potential leachate from entering the groundwater system

Provision of an interface of soil-like material (about 30 cm or one foot) on top of processed shale to provide the establishment of vegetation

Facilities that treat, store, or dispose of hazardous wastes should not be located in the 100-year flood plain, in wetlands, in critical wildlife habitat, or in recharge areas for sole source aquifers

Because there is no experience with disposal and management of massive amounts of processed shale (about 18 million tonnes or 20 million tons per year for a 50,000 BPD surface retorting operation), proper disposal techniques and proper monitoring of compactive efforts, pile moisture profile, and pile movement must be developed and experienced with the first generation projects. Thus experience will, in return, provide information for development of better disposal practices for second generation projects and for the development of subsequent regulations specific to the industry.

EPA Policies and Procedures

Oil shale developers have requested further guidance from EPA in a number of policy/procedural areas. This section responds in a summary fashion to those requests. Topics addressed include:

PSD increment consumption
NAAQS policies
Air modelling responsibilities
Wilderness areas
PSD monitoring
Permit basis, i.e. BACT, BMP/costs
Permit lifetimes
Consolidated permits
Consolidated hearings
Completed permit application
Permit enforcement procedure
Regulation certainty
Stream classifications
Salinity
TSCA applicability to shale oil
Program delegations

Additional information and clarification may be obtained via discussions with appropriate Regional and Headquarters EPA officials. The following discussions assume the reader's familiarity with the issue.

PSD Increment Consumption—

The nearest Class I area to oil shale country is Flat Tops Wilderness Area. It is managed by the United States Forestry Service (USFS). Potential oil shale project distances from the nearest point of Flat Tops are as follows: Colony (60 km or 36 mi), C-b (60 km or 36 mi), C-a (85 km or 51 mi), Union (55 km or 33 mi), Superior (65 km or 39 mi), Chevron (65 or 90 km, 39 or 54 mi), Exxon (70 km or 42 mi), U-a, U-b (.150 km or .90 mi), Geokinetics (.175 km or .105 mi), TOSCO-Sand Wash (.175 km or .105 mi), and Paraho (.150 km or .90 mi). It is commonly believed that the PSD Class I increments constitute the limiting constraint to the size of an oil shale industry. PSD Class II increments will determine how large an individual facility may be and how closely spaced separate oil shale projects may be located. Accurate estimates of the ultimate size of the industry or its spacing cannot be developed until accurate emissions data, better knowledge of air dispersion patterns in an area of relatively complex terrain, and a refined analytical tool to better estimate impacts are developed. Based upon preliminary screening studies, however, Class I increments may limit the industry to a size of 200,000 to 400,000 BPD (private communication from Joseph, EPA Region VIII, to T. Thoem, EPA Region VIII, April 1976; memo from T. Thoem, EPA Region VIII, to EPA File 3-1-7-1-9, April 1979). This estimate has caused concern for several potential developers who feel that there may be no increment left when they are ready to develop.

The Environmental Protection Agency has a policy of processing PSD permit applications on a "first come, first served" basis. The time point is determined by the date at which an application is determined by EPA to be "complete." The Agency has sought comment on other allocation systems for the consumption of PSD increments, but no other systems stand out as being more equitable or attractive at the present time. EPA believes strongly that it should not place value judgements on types of oil shale projects to receive priority treatment. When the

States take over the PSD program, they may wish to prescribe value judgements based upon State priorities and objectives.

When the PSD Class I increment is consumed, four options are available. First, all future permits may be denied (8,9). Second, future applicants may provide offsets for their project emissions by improving control of existing facilities. Third, the project proponent has the opportunity to demonstrate to the Federal Land Manager that air quality related values (including visibility) will not be adversely impacted, notwithstanding violations of the Class I increments. If the Federal Land Manager concurs and so certifies to the PSD permitting authority, the permit may (not shall) be issued. A fourth option would necessitate a Congressional redesignation of the Class I area to Class II.

By linearly adding cumulative impacts from each source, EPA is tracking increment consumption. This approach will continue even though it would physically require the winds to blow from different directions at the same time, until the increment is consumed. The Agency also will continue working on modification to a flat terrain regional model (10) which has been developed. This may be applied to assess cumulative impacts. The ultimate need is the development of a regional complex terrain model.

National Ambient Air Quality Standards Policies—

Federal lease tracts C-a and C-b received a one-year lease suspension in part because of measured concentrations of particulate, hydrocarbons, and ozone which exceeded the NAAQS. Correspondence between EPA and DOI (private communications from Kleppe, Department of Interior, to Train, U.S. Environmental Protection Agency, June 1976; from Train, EPA, to Kleppe, DOI, July 1976; from Farrand, DOI, to Quarles, EPA, February 1977; from Costle, EPA, to Farrand, DOI, March 1977; from Green, EPA, to Rutledge, Area Oil Shale Supervisor, July 1977), existing regulations (40 CFR 51.18), interpretative rulings (12/21/76), and guidance from EPA Headquarters to the Regions (private communication from Tuerk, EPA, to Regional Administrators) have established EPA policy on this issue. The policy is summarized as follows. Concentrations of particulate matter attributable to native soil undisturbed by man may be disregarded. The hydrocarbon "standard" is not an enforceable standard; rather, it is a guide to show achievement of the ozone standard. The ozone standard has been revised from its previous level of 160 mg/m^3 to 240 mg/m^3 (6.99×10^{-5} $grains/ft^3$ to 1.05×10^{-4} $grains/ft^3$). No valid concentrations above about 170 mg/m^3 (7.43×10^{-5} $grains/ft^3$) have been recorded. Further, much of the contribution to the elevated concentrations must be considered naturally caused, and hence subject to 40 CFR 51.18 discounting.

Air Modelling Responsibilities—

The project proponent must demonstrate that emissions from the proposed project will not violate any applicable ambient standards. EPA has published guidance on acceptable air quality models (11,12). It is necessary for a project proponent to demonstrate the equivalency of a proposed substitute model. Opportunity must be made for a public hearing. EPA feels at this time that the development, application and validation of other than guideline models is the responsibility of the project proponent for single source site specific impacts (within 50 km or 30 mi). The Agency is trying to develop multi-agency interest in the development of an "oil shale country" regional complex terrain model.

Wilderness Areas—

Several areas in and near oil shale country have been designated for further study for possible wilderness classification. These areas, if so designated by the BLM or USFS, do not receive automatic Class I designation. Redesignation may occur only via Congressional or State action.

The National Park Service has made a preliminary finding that Colorado National Monument and Dinosaur National Monument deserve redesignation to Class I status (13). Congressional or State action is necessary for this to occur.

PSD Monitoring—

As provided at 40 CFR 52.21 (n), ambient monitoring may be required by EPA for the source to establish baseline air quality (up to 1 year preceding permit application) and to determine the impact of the operation of the source. The *Alabama Power vs EPA* decision has expanded the number of pollutants for which monitoring may be required. EPA revised regulations implementing the Alabama Power decision are due to be promulgated by June 2, 1980.

It has been the past practice of EPA Region VIII to allow potential oil shale developers the opportunity to demonstrate that air quality data collected near their proposed site are transferable and representative. The extensive air quality monitoring performed at Federal lease tracts C-a, C-b, and U-a, U-b have characterized the air quality in oil shale country for several pollutants. Concentrations of SO_2, NO_X, H_2S, and CO have been detected at the minimum detection limits of the instrument. In the absence of a major new source of these pollutants becoming operational prior to another developer's PSD application, those data should be representative of the area. EPA has recommended that no nonmethane hydrocarbon monitoring be performed (9). Therefore, the parameters to be considered for a baseline monitoring program would include ozone, visibility, fine particulates (including chemical characterization for SO_4 and NO_3), and certain trace elements which are regulated by the Act and which may be emitted by an oil shale facility, e.g. mercury.

Meteorological data should be obtained at the project site. Both low level and upper air data should be collected. The methodology used, the duration, and the frequency must be dictated by how the data will be used. If data will be collected for model development/refinement, short term intensive upper air data may be collected under representative conditions. If data are being collected to characterize general annual wind patterns, tower data may be suitable. If low level drainage must be defined for modelling purposes, surface winds may be representative.

PSD permits issued to date have required a minimum amount of operational ambient monitoring. Emphasis had been placed upon extensive source monitoring in order to characterize all potential emission streams. As we gain more confidence in estimated emissions data and as (if) the industry grows, a shift will probably occur toward less source monitoring and more ambient monitoring. All monitoring must observe proper quality assurance procedures which have been defined by EPA (14).

Permit Basis—

The logic behind the evaluation of any permit application for a prospective oil shale developer is and will be as follows. First, the proposed pollution control equipment must represent best control technology as defined by EPA. Second, controlled residuals must not cause or exacerbate ambient standards.

The concept of BACT for air emissions control has been defined (8,9) as the maximum degree of reduction determined on a case-by-case basis taking into account energy, environmental, and economic impacts and other costs. Standards of Performance for water effluent control must reflect the greatest degree of effluent reduction achievable through application of the best available demonstrated control technology processes, operating methods, or other alternatives including wherever practicable a standard permitting no discharge of pollutants. In establishing performance standards, EPA shall consider the cost of achieving the effluent reduction, any nonwater quality environmental impact, and energy requirements. Although disposal standard practices have not yet been defined for solid waste disposal, it appears that the concept of Best Engineering Judgment will be used. Factors associated with BACT and BAT will presumably help define BEJ.

Because industry wide performance standards do not exist for oil shale, all permit evaluations for BACT and BAT will be on a case-by-case basis. After application of BACT and BAT, the permit writer will assess the residuals impact on ambient air and water. If it is predicted that applicable PSD increments or stream standards will be violated, better control than prescribed by BACT or BAT must be employed. This may be accomplished by reevaluating the economic and energy costs associated with BACT or BAT. Since it appears that PSD Class I air quality increments may be a limiting constraint to the ultimate size of the industry, EPA Region VIII has encouraged potential oil shale developers to provide "better than BACT" controls in order to maximize the amount of oil production from the area.

Guidance on NPDES permitting strategy and procedures has recently been provided at 40 CFR 121-125 as published in Federal Registers of June 7, 1979, and June 14, 1979. It should be pointed out that critical definitions such as navigable waters appear in these revisions. In essence, navigable waters are defined as any flowing waters, wetlands, or impoundments. It should also be pointed out that the NPDES permit for new sources is now required prior to construction of the source. A final NPDES permit may not be issued until a final EIS, if necessary, has been issued. It has been past practice for EPA to encourage potential oil shale developers to apply for NPDES permits even if they anticipate no discharge. The developer will be in a more advantageous position in case of future enforcement actions.

Permit Lifetimes—

Concern has been expressed by oil shale developers over changing rules and regulatory uncertainty. PSD permits issued by either EPA or the State are issued for the life of the project. Situations which could affect the validity of a PSD permit include (1) failure to commence construction within 18 months of receipt of the permit; (2) violation of permit conditions; and (3) Congressional changes in the Clean Air Act. NPDES permits are restricted to 5-year time periods by Section 402(b)(1)(B) of the Clean Water Act. Application must be made by the project proponent for permit renewal at least 180 days prior to its expiration. Hazardous waste permits issued pursuant to RCRA are issued for an initial 10-year period with provisions to review permit conditions at 5-year intervals. UIC permits are treated the same as RCRA permits.

Factors considered by EPA in the renewal of permits include new information on health or environmental risks, changes in the national standards, and changes in the type or volume of waste.

Consolidated Permits—

Proposed regulations designed to consolidate various program and procedural requirements under the RCRA, UIC, NPDES, and PSD programs were published at 40 CFR 122, 123, and 124 on June 14, 1979. Promulgation occurred in May 1980. Draft consolidated permit application forms have been published. Final application forms for all parts are due to be available by April 1981. This application covers RCRA, UIC, and NPDES permit requirements. Consistent procedures among five regulatory programs—RCRA, UIC, NPDES, 404, and PSD—are proposed. In addition, the agency intends to move in the direction of issuing a single consolidated permit. EPA is encouraging the States to consider similar action.

The promulgated regulations include instructions for completing the general, RCRA, and NPDES portions of the application forms and include guidance on NPDES sampling and analytical methodology.

Consolidated Hearings—

The promulgated consolidated permit regulations provide the opportunity for joint EPA-State public hearings on any or all of the permits covered by the consolidated permit application. Special consideration may have to be afforded

NPDES permits since the Clean Water Act requires evidentiary hearings rather than the adjudicatory hearings specified for the other programs.

As a further mechanism of coordination, EPA and the Department of Interior have discussed possibilities of at least sequential, if not joint, public hearings on projects which need approval by both agencies. Further, the Colorado Joint Review Process has identified opportunities for joint public hearings on similar permits issued by the Federal and State agencies.

Completed Permit Application—

The requirements for type and detail of information to be included in permit applications is generally provided in the applicable statute and regulations. The proposed consolidated permit application forms provide additional detail. These forms are available for NPDES and RCRA permits at the present time and will be available for UIC by April 1981. For PSD applications, EPA accepts data presented on the applicable State new source permit application form in order to avoid preparation of duplicative applications. These data must be complemented by additional requirements unique to PSD (vs State new source review) as detailed at 40 CFR 52.21.

Upon receipt of a permit application, EPA (or delegated State agency) will review it for completeness and adequacy. If information gaps exist, the applicant will be notified of the deficiencies. Upon receipt of adequate information to begin review of the application on a substantive level, i.e. for BAT or BACT considerations, the application will be deemed complete and so noted. This starts the clock on the review timetable. EPA Region VIII has established the target of completing all permit application processing within six months of receipt of a completed application. The only statutory deadline which exists for any permit processing is a one year requirement for PSD permits.

Permit Enforcement Procedures—

The objective of EPA enforcement is to achieve the highest degree of compliance possible. This can be accomplished only to the extent that most of the regulated parties comply with environmental requirements with a minimum amount of prodding, surveillance, and formal enforcement actions.

Although the enforcement process differs slightly by media, the general flow of an enforcement action is as follows.

Violation of permit

Issuance by EPA of notice of violation

Opportunity for enforcement conference

Issuance by EPA of an enforcement order

Civil and/or criminal penalty sought by EPA

Issuance by Court of opinion

The above process may terminate at any point depending upon magnitude and frequency of violation, violator's attempts to comply with requirement, out-of-court settlement, and other factors.

Regulation Certainty—

Potential oil shale developers and industry in general have expressed concern about the changing environmental regulations. This issue has been partially discussed previously under the topic of permit lifetimes. Additional considerations are discussed below.

The 1970's brought about new and revised environmental legislation. Each piece of legislation dictated that implementing regulations be developed by EPA. Litigation on these regulations occurred on several major issues. The Court determinations resulted in the requisite changes, additions, and/or deletions in EPA's regula-

tions. Several pieces of legislation were instructive to EPA that the initial program was to be developed and implemented by EPA. In parallel, EPA was to develop guidance regulations in order to provide program delegation to the respective State. Because of the number of Federal Acts and associated regulations, and legal challenges to Federal and State regulation which occurred in the 1970's, it is little wonder that environmental regulatory certainty was unavailable.

It appears that the 1980's will bring a stabilization of legislative and regulatory activities in the environmental area. The basic framework now exists for essentially all media. Changes in this framework will probably consist of fine tuning rather than major overhauls. Changes in basic legislation and court determinations pursuant to legal challenges of implementing regulations are the two factors which affect regulatory/permit condition certainty. These factors are beyond EPA and State control.

Situations are limited in which a source that has received a permit will be required to provide retrofit technology. The situation is especially true for oil shale developers, since there are essentially no commercial projects which have been permitted and which are under construction. With the guidance on environmental goals provided in this document, plus more detailed technology-based guidance to be provided in a subsequent document in this oil shale series entitled Pollution Control Guidance Document, prospective oil shale developers should not be confronted with retrofit requirements. Information which demonstrates that health or environmental problems are occurring as a result of the operation of an oil facility may result in retrofit requirements.

Stream Classifications and Water Quality Standards—

The framework for the water quality requirements which must be met by oil shale developers is presented in Section 1 of this document. Water quality criteria (15) establish concentrations which have been found to be detrimental to human health, to aquatic life, or to other water users. States adopt appropriate criteria as water quality standards. States then designate all streams in the State according to existing or desired use. States must review their water quality standards and stream classifications at regular three-year intervals (16). These standards and stream classifications must be submitted to and approved by EPA. The status of Utah and Colorado standards and stream classifications is discussed in Section 1 and Appendix D.

Salinity—

The salinity of the Colorado River and its tributaries is the subject of countless studies, legislation, litigation, regulation, and policies. Details of the status of pertinent existing EPA and appropriate State salinity regulations are described in Appendix D. Agreements to reduce and control salinity levels in the Colorado River Basin have been reached by the Colorado River Basin Salinity Forum and its member States. Pertinent to oil shale developers, EPA Region VIII developed a document entitled *NPDES Permit Effluent Policy Incorporating Colorado River Salinity Standards*—dated November 22, 1976. This policy prescribed no discharge of cooling tower blowdown and no discharge of process effluents to surface water or groundwater when the average annual salinity of the discharge exceeds 879 mg/l (7.33×10^{-3} lbs/gal). Opportunity was provided to the prospective discharger to demonstrate that containment and/or treatment of the discharge of effluents greater than 879 mg/l (7.33×10^{-3} lbs/gal) was not economically and/or technically reasonable. Colorado, which now administers the NPDES, has superseded this policy with a requirement that there shall be no discharge of salts wherever practicable. A discharger must show that containment and/or treatment of the discharge of effluents greater than 879 mg/l (7.33×10^{-3} lbs/gal) was not economically and/or technically reasonable. A discharger must show that containment and/or treatment is not economically or technically achievable unless the discharge contains less than .9 tonne (one ton) per day of salt.

Region VIII EPA has and will continue to advocate improvement in salinity concentrations in the Basin. Portions of Region VIII's Energy and Water policies advocate maximum reuse and recycle in order to minimize the concentrating effect of consumptive use of high quality water. Wherever practicable, lower quality water should be treated for reuse in order to minimize consumptive use of high quality water. Measures, perhaps dictated by BMPs, should be taken to prevent nonpoint source discharges of saline water. Runoff from land disturbance and processing areas, in addition to leachate and runoff from processed shale piles, should be contained. Treatment to acceptable salinity levels may be necessary.

TSCA Applicability to Shale Oil—

Certain potential oil shale developers petitioned to have shale oil and its refined products listed on the Toxic Substances Inventory. This inventory of existing commercially-produced chemicals and compounds was published in June 1979. The list included shale oils designated as number 68308-34-9. If a material has been placed on this inventory, all manufacturers of this product are exempt from premarket notification and testing requirements. However, this does not exempt manufacturers, processors, or transporters of this product from any future control. If EPA finds that the manufacture, processing, distribution, use, or disposal of this chemical presents an unreasonable risk of injury to health or the environment, it may take one of several regulatory actions. The chemical could be (1) prohibited from being manufactured; (2) restricted as to type or amount of use; (3) require cautionary labeling, and/or (4) require certain record keeping and notification procedures.

Program Delegations—

It is the stated intent of all environmental legislation to delegate the implementation of permit and regulatory programs to the States. A summary of the present status of program delegation is provided in Section 1. Region VIII will operate the program until the States develop the necessary legal, regulatory, and staffing capability to administer the program. Upon delegation of the program, EPA's role converts to an oversight/audit responsibility and a technical assistance capability.

The ability of EPA to effect an individual action such as issuance of a permit for a particular project varies from program to program. The authority to veto individual permits issued by the State under the NPDES program if the permit is found faulty on either procedural or substantive grounds lies with EPA. This authority does not exist in the PSD program. The Agency may provide comments on a proposed permit, but if a permit is issued against EPA's recommendation, the only recourse is court relief.

INDUSTRY VIEW OF REGULATION

Editors' Note

The following discussion was prepared by the Rocky Mountain Oil and Gas Association, at the invitation of EPA, for inclusion in this document. It is included in the belief that readers of this document would be interested in the views of the emerging oil shale industry regarding environmental regulation. The publication of industry's views in this EPA document should not in any way be considered as EPA acceptance or endorsement of these views.

Industry Position

This chapter of the Environmental Perspective document has been prepared by members of the Environmental Subcommittee of the Rocky Mountain Oil and Gas Association Shale Committee at the invitation of EPA. The positions stated in this chapter represent broadly held views in the oil shale industry. In certain cases, individual company opinions may vary in some respects with the positions taken.

The oil shale industry commends and supports EPA's effort to compile this document which summarizes the current state of environmental knowledge about oil shale development. This document will provide in a single volume, a convenient and useful source of information on the environmental regulations, research priorities and policies related to oil shale.

As shown by this volume, much is already known about the environmental nature of oil shale and the impacts which will result from development of this resource. As a potential resource of interest to developers and the government for many decades, oil shale has been the subject of extensive and intensive environmental study. The results of these studies are publicly available in published reports of the industry and of government, and in the open files of the Department of Interior Prototype Oil Shale Leasing Program. As a result, the level of knowledge concerning the impacts from development of this resource is far greater than has ever been gathered for any other developing industry prior to construction of any commercial operations.

The development of oil shale on a commercial basis will result in some significant impacts within the oil shale region. The detailed evaluations of environmental concerns which have been conducted make industry confident that such impacts can and will be controlled within the limits of current regulatory standards. Further, the environmental concerns regarding oil shale are the same in nature or risk as those occurring in presently operating energy industries. As an industry which can and will operate within strict standards protecting public health, safety and welfare, the industry has confidence that adverse environmental impacts will be well within publicly acceptable levels.

Although much is known about the environmental impacts of oil shale, there are, on the other hand, environmental questions related to commercial sized operations which can only be answered finally by commercial field demonstration and experience. The information and experience gained from the initial operation of oil shale plants will provide data and information from which performance standards can be set and reasonable and appropriate rules developed. Industry expects to continue working in cooperation with EPA and other governmental units to assure that development of an oil shale industry progresses in an environmentally acceptable manner.

In developing an oil shale regulatory system, the industry believes certain general principles should apply which will provide effective and fair rules. Those principles include the following:

Regulation must provide a balance between environmental and economic costs. The oil shale industry should be treated on an equal footing with other comparable industries.

In establishing rules, maximum flexibility should be provided to deal with a variety of processes and projects which will operate under significantly different circumstances.

Flexibility should be encouraged to allow for innovative technology, particularly during the construction of first generation plants.

Permit and approval terms and conditions must be frozen during construction, startup and initial operating phases to provide the necessary stability for private investment decisions.

Regulatory decision making should be expeditious and within agreed upon time schedules.

EPA should clearly differentiate between industry's obligation to demonstrate operating compliance with established standards and government's obligation to carry out general research and information gathering programs.

These principles should apply to all areas of environmental control and regulation. The remainder of this chapter addresses specific areas of environmental interest.

Health Effects/Toxicology—

Oil shale products, by-products, and starting materials have been subjected to extensive chemical and biological testing. The data from all programs conducted so far, as well as from epidemiological studies of workers, indicate that occupational risks and environmental health situations are no different from those in presently existing fossil energy industries. No unique or unusual oil shale risks have been demonstrated.

The cancer incidence associated with the Scottish oil shale experience is not currently significant for two important reasons. First, industrial hygiene practice was nonexistent; and second, primitive refining methods in use at the time concentrated the polycyclic aromatic hydrocarbon (PAH) in the fractions of shale oil used. Under these conditions, the materials used were indeed carcinogenic to man. In view of modern petroleum industry practices, which deal with virtually identical compounds, the Scottish experience is only relevant from a historical standpoint. This conclusion is reinforced in examining the Estonian oil shale industry, in which the effectiveness of realistic industrial hygiene practices has been demonstrated by a low cancer incidence.

Recent experiments which purport to compare the carcinogenicity of crude shale oil with crude petroleum have been misdirected. The two materials are not comparable in the processing stream. To properly compare the carcinogenicity of crude shale oil with that of a petroleum product or intermediate, the same stages in processing must be used. As shown in Figure 6-1, the first refining step in the processing of crude petroleum and oil shale is to thermally treat the raw material. In both cases, the temperature of treatment approaches 482° *to 538*°C (900° to 1000°F) and during both these thermal processes PAH are formed. The next processing step is to hydrotreat the materials created in the thermal processes. For shale oil, this hydrogenation step has been proven to have two beneficial effects. It decreases the PAH content and reduces carcinogenicity as determined by biological testing. The preceding documented facts form the basis for industry's position on health effects of oil shale processing. That is, a commercial oil shale retorting facility using modern industrial hygiene practices and complying with the present Occupational Safety and Health (OSHA) and Mine Safety and Health Administration (MSHA) regulations will not expose workers or the environment to carcinogenic or toxic risks that are not presently acceptable in other modern energy-related industries.

Control technology—

The control processes described in this document may be used for guidance purposes when making an assessment of the best available control technology for various applications. The descriptions provide a convenient reference to technologies that are currently available and might be applicable to the oil shale industry.

The selection of control equipment for oil shale development must be addressed on a case-by-case basis. Each site and process will have different sets of economics impacting the type of control equipment selected. The BACT selection process requires consideration of practical engineering design coupled with an economic analysis. Allowances must be made for the development of innovative control technologies since the oil shale industry is developing innovative processing techniques at this time.

Spent Shale Disposal/Leachate—

The discussion of leachate gives the impression that natural leaching in significant quantities is inevitable at oil shale disposal piles. The following factors suggest very strongly that leaching will probably not occur:

1. The oil shale region is a semiarid region. There is not an abundance of natural water. The annual evaporation is typically greater than the annual precipitation.

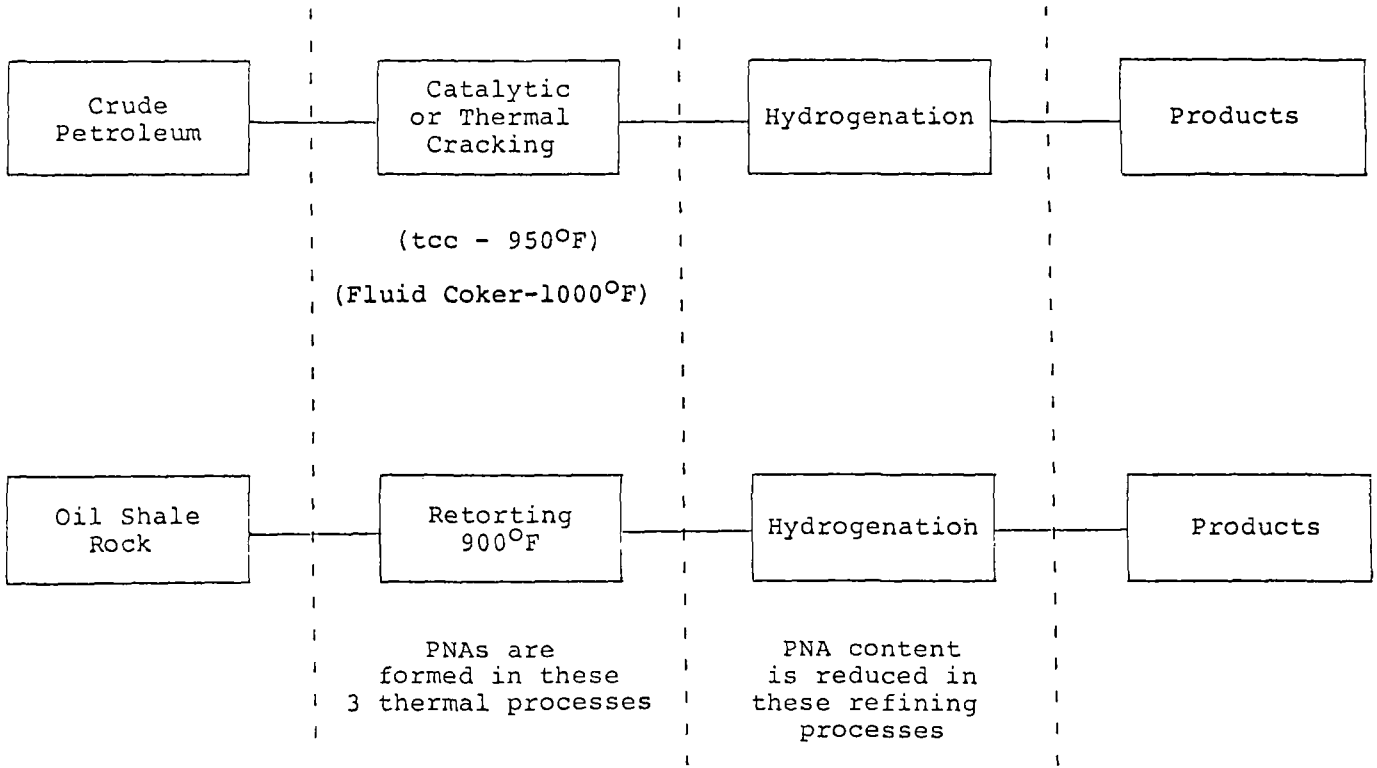

Figure 6-1. Polycyclic aromatic hydrocarbon formation — a comparison of petroleum and shale oil.

2. The retorted shale disposal area will be revegetated. Much experimental and field demonstration work has shown the viability of revegetating retorted shale disposal areas. The amount of vegetation presently occurring in the region is determined by the availability of water. This will also be the case of revegetated disposal areas. In other words, the plants will use all available water.
3. Retorted shale has a large capacity to store water. Thus, on those infrequent years when the precipitation exceeds the plant needs, there is storage capacity for the excess water.
4. The disposal piles will be constructed to provide layers of shale with very low permeability which will retard any water flow through the piles.

The Spent Shale Disposal section discusses some potentially serious problems that could result from careless disposal of retorted shale. However, industry's current plans for disposal of retorted shale show a careful and considered approach to those potentialities. Properly planned and managed revegetation efforts should go far in preventing harmful leaching.

Monitoring Methods—

Monitoring requirements as specified in the regulations should clearly state what is required of industry. Frequently, that statement is not made and the differentiation between the responsibilities of government and industry become blurred. It is therefore useful to gènerally define three types of environmental analyses in order to bring monitoring requirements into sharper focus. These environmental analyses are screening, monitoring, and research as follows:

1. *Screening* - Programs which are designed, conducted, and reevaluated by the developer to detect trends in *unregulated* baseline or indicator parameters. Screening programs are performed before and after operations to assess preexisting environmental conditions and the potential impacts of development upon the environment. Subject to constant change, screening could lead to either more or less intensive analysis than originally defined.
2. *Monitoring* - Programs which are defined and reevaluated by the EPA pursuant to law and regulation. The objective of monitoring programs is to characterize the impacts of operations on the environment in terms of regulated pollutants which are measured by known and proven methods. The operator is responsible for conducting, monitoring and reporting the results to demonstrate compliance with permit conditions. Monitoring programs should be subject to periodic reevaluations.
3. *Research* Programs which may be defined by either the EPA or the operator, but which are *not* regulatory requirements for monitoring. Suspect pollutants and unproven methods for sampling or analysis may be within the scope of research, but are *not* permit conditions. The funding of research programs should be considered on a case-by-case basis. Research, such as the determination of regional impacts of development, should be funded at least in part by the EPA.

Screening, monitoring and research programs should be site specific and process specific, to allow for the diversity in approach to development and to encourage innovation.

In addition, monitoring requirements should also be based on the following quidelines:

Monitoring requirements should be cost-effective, have clearly defined objectives, and specify what action may be taken as a result of monitoring findings.

Technically appropriate and accurate test methods for each prescribed parameter need to be defined by regulation.

Representative sampling should be defined, indicator variables should be selected and the frequency of sampling should be specified. Where warranted, the frequency of sampling should be reduced.

Air Impacts—

The size of the oil shale industry will most probably be determined by the PSD regulations. The number and size of plants located in any given area will be determined by consumption of the local Class II increment. The total size of the industry will be determined by consumption of the Class I increment in wilderness areas.

It is known that PSD increments will ultimately limit the size, siting, and the number of oil shale plants. However, because of limited available techniques for modeling and monitoring of air impacts, it is not known when this limit will be reached. The industry endorses continuing research to improve and validate such predictive methods, since the presently available methods are overly conservative. However, it must be recognized that refinement of these methods will only allow a more accurate prediction of *when* this limit of shale oil production will be met under the current regulations. This limit will still exist and should be acknowledged.

Research Needs—

The EPA oil shale research program should proceed from a written set of objectives. These objectives should be based on EPA's statutory obligations and be available for public review. Specific research needs should then be identified to meet these objectives. The priority of these identified needs should be set so that the greatest benefit can accrue from EPA's limited research budget. The priorities should be set considering the following factors:

The statutory authority given to EPA to regulate the research subject.

The need for EPA to know the research results before developing or modifying regulations concerning the research subject.

The availability of suitable facilities with which to perform the research.

The magnitude of the problem to be researched in comparison with the research cost.

The timing of the need for the research results.

In order to maximize the benefit obtained from all research, EPA's program should be coordinated with other Federal, State and industry programs. From an industry viewpoint, in view of the constraints imposed by the PSD increments, the single most important research need is development of a basinwide air quality model.

Standards—

The industry recognizes that EPA is developing specific performance standards for oil shale technologies. In so doing, EPA must recognize the following factors.

1. There are currently at least six generically different retorting processes under development. As more advanced technologies are developed there will undoubtedly be more. Since processes differ, a control technology and associated performance standard that might be appropriate for one may be totally inappropriate for another. This fundamental fact must be recognized when performance standards are set.
2. The control technologies being proposed for use on oil shale processes are technologies that have been developed in other industries. There is a high probability that these technologies will also work when applied to oil shale processes. However, the removal efficiencies that can reasonably be expected of these technologies when applied to oil shale have not been demonstrated. Until these demonstrations are made, it would be inappropriate to set removal efficiencies as performance standards.

3. Performance standards that have been developed in other industries have been based on well run plants operating under commercial conditions. No such experience exists in the shale industry.

When these factors are considered, it is apparent that the conditions used to set performance standards in other industries do not now exist in the oil shale industry. Until those conditions do exist and commercial operating data have been gathered, it will not be possible to set realistic performance standards for this emerging industry.

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SECTION 7
OIL SHALE TECHNOLOGY, EMISSIONS, AND SOLID WASTES

The Pace Company Consultants and Engineers, Inc.
A Division of Jacobs Engineering Group

This section provides a summary of oil shale technology for surface, modified *in situ*, and true *in situ* retorting methods. The major steps in producing oil from shale (feed preparation, retorting, recovery of products, and disposal of wastes) are briefly described.

Each of the major oil shale retorting processes is briefly described, with retort cross sections and process flow diagrams provided to illustrate the process.

OVERVIEW OF SHALE TECHNOLOGY

Mining

Except for true *in situ* oil shale processing, some degree of mining is required before retorting. In the case of modified *in situ* processes, this mining is limited to the development of access drifts and the formation of underground cavities into which the surrounding oil shale formation is explosively expanded. Surface retorting processes require that all of the raw shale to be processed be removed from the formation, crushed to the proper size, and transported to the retorting facility before retorting. In the latter case, the large scale mining operation that would provide raw oil shale to the retorting facility could be either an underground or surface process, depending on the geology and hydrology of the site and other economic factors.

Surface, or open pit mining, of Green River oil shale has never been attempted on a commercial scale; however, it appears to be applicable in some areas of Colorado, Utah, and Wyoming. Open pit mining involves excavating the overlying waste rock to expose the oil shale resource below. The oil shale and waste rock are "benched" down to a depth dictated by the economic limits or cutoff grade of the pit. The slope of the pit walls is determined by the stability of the rock being mined. Open pit mining has the advantage of recovering almost the entire resource (except the oil shale under the pit boundaries) as opposed to underground methods which have resource losses in the sills and support pillars.

In the Piceance Creek Basin of Colorado, nearly 80 percent of the oil shale resource is confined to the deposits in the deep central part of the basin. For this reason, underground mining systems with high volume and low cost will have to be used to mine the thick oil shale resource efficiently, unless the entire basin is mined as one grand-scale open pit.

Commercial-sized underground room-and-pillar mining systems have been used by the U.S. Bureau of Mines on the Naval Oil Shale Reserves by Union Oil at its Long Ridge site and by Colony Development Operation at the site of the semi-works retorting facility and at the Mobil Mine located adjacent to Anvil Points. Using this process, the oil shale is recovered by excavating the ore from equal-sized square openings approximately 18.3 by 18.3 m (60 by 60 ft), leaving columns or pillars that support the roof of the excavated rooms. Variations of the basic room-

and-pillar method can also be used effectively in oil shale. These include: advance entry and pillar mining, and chamber and pillar mining. Figure 7-1 is a conceptual multi-level room-and-pillar system that could be designed to mine the rich oil shale layers and leave the lean layers. This system leaves much shale in place as support pillars and is not appropriate for thicker shale deposits.

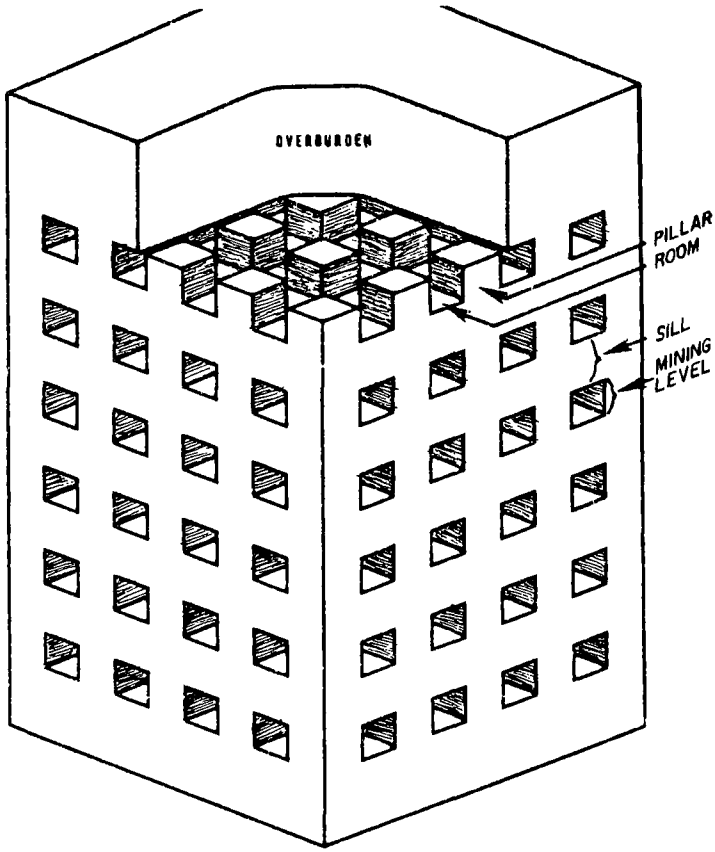


Figure 7-1. Multiple level room and pillar mining concept. (Source: Reference 1.)

Bulk underground mining could also prove to be a very efficient means of extracting oil shale at high volume with a minimum cost. Sublevel stoping is an example of a bulk underground mining method. Sublevel stoping involves blasting the oil shale into a stope (a high vertical column of ore) by means of fan rounds drilled from the sublevel and stope floor. Front-end loaders are then used to transport the broken muck from the stope to rail cars pulled by trolley locomotives. The muck is dumped from the rail cars into gyratory crushers at the shaft station and is hoisted to the surface.

Block caving using slushers is another method of bulk underground mining. The caving system is retreat in nature and starts within an economic distance from the main access area. A mining level is divided into panels, with each panel subdivided into blocks. Caved oil shale from an undercut level flows by gravity down finger

raises, is slushed along a slusher drift, and dropped directly into rail cars on the main haulage level. Instead of slushers, load-haul-dump units may be used to transport the ore from the finger raises to transfer raises, which in turn are used to load the ore trains.

Whatever method of mining is used, either surface or underground, the system must be capable of excavating large quantities of oil shale at a very low cost. The mine design must not only be cost effective, but must also comply with existing health and safety regulations and have minimal effects on the physical, biological, human, and mining environments.

Crushing, Storage, and Transportation

Regardless of the particular surface process chosen for use in a project, raw oil shale must first be crushed to the appropriate size and transported to the retorting facility. Green River oil shale can be crushed by conventional crushing equipment, but the properties of the shale are such that selection of equipment should be made only after demonstration or previous experimental work has given assurance that crusher performance will be satisfactory. Oil shale tends to form slab-shaped fragments when crushed in jaw, gyratory, or toothed-roll crushers. This tendency is less pronounced when impact-type crushers are used. Fragments of rich oil shale are resilient, tough, and slippery, the latter characteristic making it difficult for smooth-roll crushers to nip or catch hold of individual fragments.

Crushing operations planned for large-scale demonstration or commercial facilities will generally consist of primary crushing at the mine site followed by secondary crushing near the retorting site. The small particle size required by some retorting processes will also necessitate tertiary operations in some instances. Primary crushers would reduce the mined ore to a manageable particle size, roughly 30.48 cm (12 in.). Dust generated by this operation would either be suppressed or collected in baghouses for later treatment.

Coarse ore would be transported to the retorting site either in trucks, by rail, or on covered conveyors. All commercial plans have proposed the use of covered conveyors. Dust generated by this operation would be collected at strategic locations and would either be retorted or discarded. The coarse ore would be stockpiled to provide for surge conditions and to allow the retorting facility to continue operating in the event of a temporary shutdown of mining operations. The proposed stockpiling procedure for small-scale operations would be containment in a silo or hopper, with discharge to the retorting plant from the bottom. Larger operations have proposed the use of open stockpiles, with the ore being removed to the retorting operation by bucket reclaimer units or underlying conveyor systems. Dust suppression techniques employing polymer or latex solutions have been proposed for use on these stockpiles.

Secondary (and tertiary) crusher units would prepare the ore for use in the retorting facility. Fine ore storage facilities would also be provided, but because of the relatively small size of the fragments, these would be enclosed to minimize dusting and eliminate exposure to detrimental environmental conditions.

Surface Retorting

All surface retorts are similar in that the retorting process actually occurs in a metal vessel in an above-ground facility. Such a configuration has the advantage that process flows and operating parameters can be easily controlled and manipulated; however, the surface processes also suffer the disadvantage that large quantities of raw oil shale must be mined, transported to the retort area, processed, and disposed of in an environmentally acceptable manner.

Literally hundreds of U.S. patents have been issued concerning surface retorting of oil shale. Despite the number and types of retorting processes described in the literature, no one process has yet been shown to be the best for all purposes. It is

probable that a combination of processes would best serve a commercial shale retorting industry.

Surface retorting processes can generally be divided into three classes: Direct-heated, indirect-heated, and combination. Direct-heated processes rely on internal combustion of fuel (generally recycle gas and/or residual carbon in the spent shale) with air or oxygen within the bed of shale in the retort to provide all the necessary process heat requirements. Nitrogen and products of combustion (if air is used for combustion) accompany the off-gas stream from the retort.

Indirect-heated retorting processes utilize a separate furnace for heating solid or gaseous heat-carrying media that are injected, while hot, into the shale in the retort to provide the process heat requirements. Hydrogen retorting processes are of the indirect-heated type, varying from the more conventional techniques in that the retorting is conducted in a hydrogen-rich atmosphere.

Combination processes do not actually operate in the direct- and indirect-heated modes at the same time. Rather, they are processes that may be either directly or indirectly heated, depending on the specific equipment configuration used.

In Situ Retorting

In situ processes are those in which the actual retorting, or conversion of organic matter in the oil shale to shale oil, occurs underground with a minimum of dislocation of the oil shale from its original position in the formation. *In situ* processes require at most only a limited amount of mining and solids handling, but they have the disadvantage that remote sensing must be used to monitor almost all process operating conditions, thus complicating the control problem. Though an *in situ* recovery process produces little waste material to dispose of aboveground, the retorted zone of spent shale left after retorting could present serious environmental problems of its own if not dealt with properly.

Discussions of *in situ* retorting often distinguish between "true" *in situ* processes, which involve only the drilling of wells, and "modified" *in situ* processes, which require some mining to develop the underground retort chambers. With the exception of Occidental Petroleum's work on a modified *in situ* process, the development of *in situ* processes has not advanced to as large a scale of production as surface retorting methods. There is, however, much interest in and a large potential application for both true and modified *in situ* methods.

In situ retorting involves the in-place heating of an underground shale formation under conditions wherein the flows of heat, vapors, and liquids can be controlled, resulting in the recovery of acceptable quantities of gaseous and liquid products from the resource. Typical Green River Formation oil shale occurs as competent, hard, nonporous rock formations with relatively little permeability. They are generally unsuitable for *in situ* retorting. It is therefore necessary to create permeability.

Joint patterns and fractures do occur in the formations, but the natural fractures are widely spaced and do not provide the massive fracturing and surface area necessary for successful *in situ* processing. In certain zones, water-soluble minerals (e.g. nahcolite, halite, etc.) occur. These occurrences are as bedded zones, nodules and spherical crystals, and disseminated crystals. These soluble minerals may be leached from the oil shale by natural groundwater or from a borehole resulting in some permeability of the remaining rock. Permeability for true *in situ* (borehole) is generally induced by explosive or hydraulic fracturing and propping techniques. Modified *in situ* methods create the greatest degree of permeability by mining out a portion of the formation and then explosively expanding the adjacent rock into the void. The key technical problem in modified *in situ* recovery is to develop the proper mining and blasting techniques that would optimize rock fragmentation in underground retorts, and thus permit the controlled flow of heat, gases, and liquids through retorts.

Once adequate permeability has been established (for either true or modified *in situ*), the oil shale can be heated to the necessary temperature by either direct or indirect heating techniques. All of the major projects currently underway involve the direct heating of the shale and utilization of the combustion of recycle gas and/or residual carbon on the spent shale to provide the necessary heat.

Spent Shale Disposal

Once oil shale is mined, crushed, and retorted, the spent shale must be used or disposed of in an environmentally acceptable manner. The composition and size range of the spent shale particles largely depends on the type of retorting process used, and these properties in turn determine the possible uses and the method and ease of disposal.

Even though the spent shale usually occupies a greater volume than the raw in-place shale, it would be desirable to place as much of the spent material as possible back in the mine. Unfortunately, the logistics of mining and the material handling costs may make such an option uneconomical. It is expected that with the proper moisture content, all or part of the spent shale can be returned to the mine and be packed completely to the roof. It will then set up similar to shotcrete. In this manner, mine subsidence would be prevented, and unsightly waste piles would be eliminated.

Disposal of spent shale in an open pit mine appears attractive. Once the open pit is large enough to accomodate both continued operation and spent shale backfilling, all of the spent shale can be returned to the pit. The pit can then be advanced with ongoing backfilling and reclamation.

Aboveground disposal of spent shale from underground mining/surface retorting operations is a potential alternative to returning spent shale to an underground mine, and one that has been proposed by several developers. This technique simply involves compacting and contouring the spent shale in the vicinity of the processing facility in canyons or valleys or on relatively flat terrain. A valley site allows for disposal of a large volume of material and the surfaces requiring stabilization and revegetation are relatively small. Furthermore, the bulk of the material is hidden from view. If the disposal site is in a natural drainage path, efforts must be made to reroute natural water flows and minimize or eliminate the natural leaching of water soluble material. Reclamation and revegetation, with appropriate planning, can be conducted along with the placement of spent shale, which will result in relatively small areas of unreclaimed spent shale at any point in time during active disposal.

During modified *in situ* operations, oil shale mined and removed to the surface may be processed in aboveground retorts, thus creating spent shale requiring disposal. For this situation, it has been proposed that some or all of the spent shale from the surface retorts could be slurried and injected into underground retorts in which retorting has been complete.

During recent years, much research has been conducted on dealing with the revegetation of spent shale. This research has indicated that the high salinity of the spent shale is one of the most important hinderances to revegetation. Other studies have shown that spent shale is deficient in both nitrogen and phosphorus, and therefore some degree of fertilization would be necessary for successful revegetation. It was also found that the surface temperatures that the black spent shale may attain — 60° to 66°C (140° to 150°F) — may adversely affect the revegetation process. Therefore, mulching may be required to revegetate successfully.

Retort Gas Treatment

The crude retort gas from an oil shale retorting unit consists of a mixture of shale oil vapors, particulate matter, light hydrocarbon gases, and a wide range of non-condensable gases such as hydrogen, carbon dioxide, and hydrogen sulfide. The first step in treating this stream is oil recovery. Two techniques are commonly pro-

posed to perform this operation — electrostatic precipitation and partial condensation (fractionation), although impact precipitators are also suitable for this purpose. The first approach is usually applied when the retort gas stream is largely composed of gases and the concentration of condensable oil droplets is rather dilute, such as from vertical kiln type retorts or *in situ* processes. The fractionation approach is most commonly proposed for use when treating streams with a fairly high concentration of oil droplets, such as those from a TOSCO II or Lurgi-Ruhrgas process.

The electrostatic precipitator oil recovery operation also removes significant quantities of water and particulate matter. The oil/water/solids stream is further treated by conventional separation processes to yield three separate streams. The water is sent to a foul water stripper for cleanup. The solids are either discarded or reinjected into the retorting unit, and the oil is further upgraded, if desired.

The fractionation operation yields several different product streams, from naphtha to residual oil and particulate matter. The bottoms product can be centrifuged to yield an oil residue and a sludge stream.

The gaseous overhead stream from the electrostatic precipitator or partial condenser oil recovery units is normally separated into product gas, low pressure gas (LPG), and butane. Depending on the retorting process used, the product gas may either be of a high or low heating value. In the latter case, it would most likely be used as a plant fuel and as a hydrogen plant feedstock. In either case, the stream may be further treated in a conventional amine scrubbing unit (or similar device) to remove hydrogen sulfide and carbon dioxide. The hydrogen sulfide-rich stream from this unit would then be treated in a Claus unit to recover elemental sulfur. An alternative approach would be to treat the entire gas stream in a Stretford unit to recover elemental sulfur directly. The LPG stream from the fractionator could be sold as product and the butane stream could serve as additional plant fuel.

Shale Oil Upgrading

Shale oil is the term applied to the liquid oil product recovered from the thermal decomposition (pyrolysis) of kerogen, the organic material present in the oil shale. Crude shale oil, sometimes called retort oil, is the liquid oil product recovered directly from the retort. Synthetic crude oil is the upgraded oil product resulting from the hydrogenation of crude shale oil.

The properties of crude shale oil from a retort are dependent on a variety of factors. One of the most important of these is retorting temperature, or more specifically, temperature history. Retorting pressure and atmosphere also have significant effects on the product oil properties, as do particle size and shale grade.

Table 7-1 is a summary of the properties of crude shale oil produced by various pilot plants and bench-scale operations. It should be noted that though these properties are indicative of what would be produced by a commercial facility, the oil samples investigated were not produced by an optimized process. Rather, they were generated during test runs on relatively small scales under operating conditions that may vary from those at a commercial installation.

Because of the high pour point, viscosity, and nitrogen and oxygen contents of crude shale oil, it is not a premium grade feedstock for a conventional refinery. To convert the raw shale oil into a more desirable feedstock, it must be upgraded, or partially refined, using proved refining techniques. Thus, there are three different levels of shale oil refining, any or all of which may be used for a particular situation:

Conversion to a pipelinable product to facilitate transport to a distant refining installation.

Upgrading to produce a low-sulfur, low-nitrogen, premium grade refinery feedstock.

Complete refining of crude shale oil or some intermediate into usable end products.

To produce a pipelinable product, several schemes are possible:

Coking — crude shale oil is heated to crack the hydrocarbons, producing a coke-like material plus a light oil that has a low pour point. This method is rather unattractive because of the severe losses resulting from production of low-value coke, with relatively small yields of product oil.

Addition of pour-point depressants — these are proprietary compounds that are said to reduce the pour point of crude shale oil.

Hydrogenation — hydrogenation may be used to remove sulfur and nitrogen compounds. The product oil may then be burned directly as fuel oil or further refined into other end products.

The complete refining of crude shale oil into usable end products has been successfully demonstrated by several investigators. Some of the most extensive research was conducted by Sohio and Gary Western Refining using crude shale oil

TABLE 7-1. PROPERTIES OF CRUDE SHALE OILS[a]

Property	Fischer Assay Samples	NTU	Gas Combustion	TOSCO	Union A	Union B	Paraho	Hydrotort
Carbon, wt. %	84.59	84.61	83.92	85.1	84.2	84.8	84.90	85.44
Hydrogen, wt. %	11.53	11.40	11.36	11.6	11.4	11.7	11.50	11.12
Oxygen, wt. %	—	1.10	1.67	0.8	2.2	0.9	1.40	—
Nitrogen, wt. %	1.96	2.10	2.14	1.9	2.0	1.7	2.19	1.88
Sulfur, wt. %	0.61	0.79	0.7	0.9	1.0	0.8	0.61	0.56
Gravity, °API	—	20.3	19.8	21.2	18.6	22.7	19.3	21.5
Specific Gravity	0.92	—	—	0.928	0.943	0.918	0.938	—
Arsenic, ppm	—	—	—	—	—	—	19.6	—
Nickel, ppm	—	—	6.4	6	—	—	2.5	—
Iron, ppm	—	—	108	100	—	—	—	71.2
Vanadium, ppm	—	—	6	3	—	—	0.37	—
C/H Ratio	7.3	7.42	—	7.34	—	—	7.38	—
Pour Point, °F	80	90	83.5	80	—	—	85	65
Heating Value, BTU/lb	18,508	—	—	—	18,600	18,530	—	—
Distillation								
5 vol. % at °F	—	—	378	200	390	234	—	—
10	336	—	438	275	465	330	520	278
30	518	—	607	500	640	551	680	430
40	—	—	678	620	710	—	750	—
50	655	—	743	700	775	711	810	568
60	685	—	805	775	830	—	840	634
70	705	—	865	850	980	—	—	682
80	—	—	935	920	—	848	—	712
90	—	—	1030	—	—	984	—	—
95	—	—	1099	—	—	1045	—	—

[a] Source: Reference 1.

from the Paraho retorting operation at Anvil Points, Colorado. A total of 1,360 tonnes (100,000 bbl) of crude shale oil was refined into a full range of military fuels, including heavy fuel oil, diesel fuel, JP-4, JP-5/Jet-A, and gasoline. While none of the fuels produced during the refinery runs met all specifications, the tests did demonstrate that it is feasible to produce a wide range of civilian and military fuels from crude shale oil if appropriate modifications are made and specific operational procedures are followed at a commercial refinery.

SURFACE RETORTING PROCESSES

Gas Combustion Retorting Process

The Gas Combustion retorting process involves the gravity flow of oil shale through a refractory-lined vertical kiln, with the shale feed rate being controlled by a grate mechanism located at the bottom of the retort. As the shale progresses through the retort, it passes through four functional zones, though there are no physical separations in the retort and no distinct division between the zones. A simplified flow diagram of the process showing these zones is provided in Figure 7-2.

The top zone, into which the 0.64 cm (1/4-in.) to 7.62 cm (3-in.) shale fragments enter through a continuous antisegregation feeder, is called the shale preheating or product cooling zone. In this stage, heat is transferred from the rising stream of hot product gas to incoming raw shale. Thus, this zone serves two purposes—first, to cool the product gases below the dew point of the contained product oil, which then condenses as a fine mist and is carried out of the top of the retort, and second, to preheat incoming shale to minimize the heat load on the process in subsequent heating zones.

Having passed through the first zone, the preheated shale enters the retorting zone, where it is heated to retorting temperature by hot gases rising from the combustion zone. As kerogen contained in the oil shale pyrolyzes, it yields oil (in vapor form), gas, and a residual carbonaceous product that adheres to retorted shale solids. The vapors are swept upward by the rising flow of hot gases.

Leaving the retorting zone, shale fragments pass into the hottest part of the retort, the combustion zone. In this zone, a mixture of recycle gas and air is introduced. Oxygen available from the injected air supports combustion of the carbonaceous residue present on shale fragments coming from the retorting zone. The oxygen present also supports combustion of hydrocarbon constituents in the injected recycle gas. As shown in Figure 7-2, the temperature in the retort at the combustion zone may reach 760° to 816°C (1400° to 1500°F). Hot flue gases produced in the combustion zone rise upward into the retorting zone to provide the heat necessary for pyrolysis.

The retorted and partially burned spent shale fragments then pass into the cooling or heat recovery zone. This area of the retort essentially serves as a countercurrent heat exchanger wherein heat from hot spent shale is transferred to cool incoming recycle gas. Like the topmost zone, this serves a dual purpose—first, to preheat the recycle gas and thereby reduce the heat load in the combustion zone, and second, to cool the spent shale to minimize handling problems and increase thermal efficiency.

The Gas Combustion process, being directly heated, requires the injection of oxygen (usually in air) into the retort to burn off residual carbon on the spent shale and thus provide the necessary heat for retorting. The injection of nitrogen in the combustion air dilutes the product gas and, after the liquid hydrocarbons are condensed from the stream, the remaining gas has a low heating value. Since the Gas Combustion process uses relatively coarse shale feed, and very little if any attrition occurs within the retort, the spent shale will have a particle size distribution very similar to that of the feed shale. This minimizes dusting problems encountered dur-

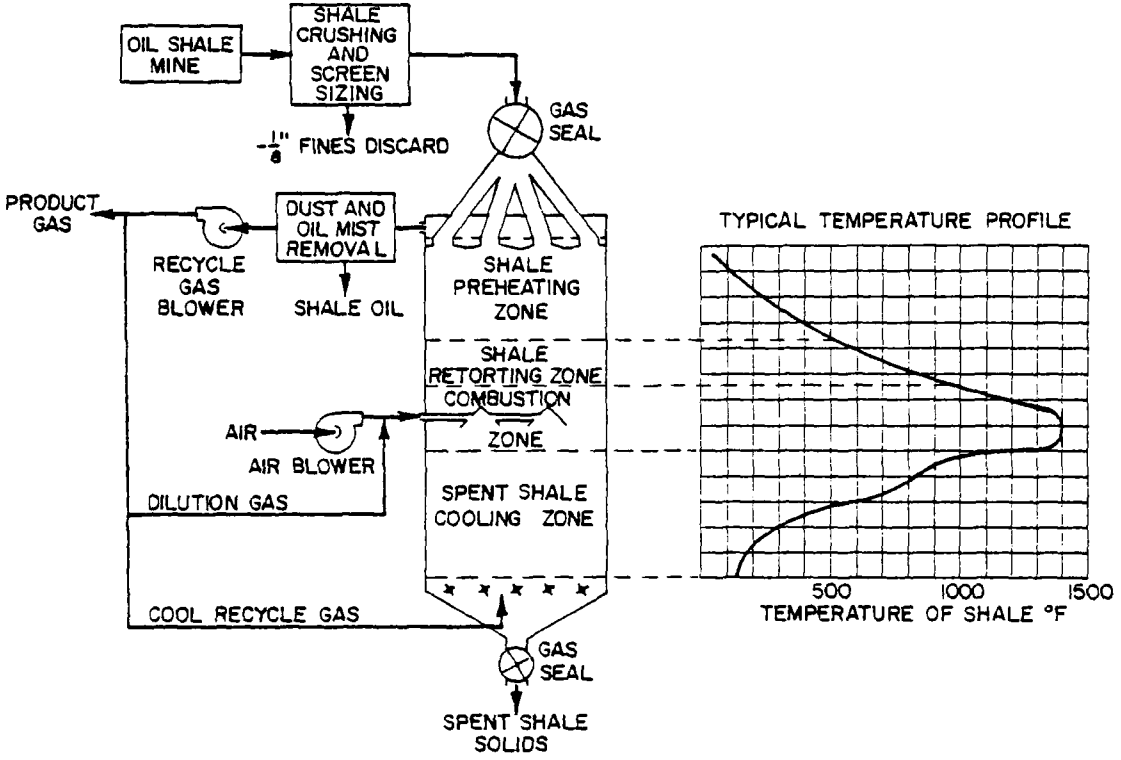


Figure 7-2. Gas Combustion retorting process.
(Source: Reference 1.)

ing the transportation and disposal of spent shale. Because some of the residual carbon on the spent shale is combusted in the retort, the spent shale product contains less residual carbon than that from indirect-heated processes and is lighter in color.

During six evaluation runs conducted on the 136-tonne (150-ton) Gas Combustion retort by the U.S. Bureau of Mines, the offgas following oil recovery had the average composition shown in Table 7-2.

TABLE 7-2. AVERAGE COMPOSITION OF OFFGAS FROM GAS COMBUSTION RETORT[a]

Orsat analysis component:	Vol. %
CO_2	24.2
Unsaturated hydrocarbons	1.7
O_2	0.3
CO	2.6
H_2	4.7
Saturated hydrocarbons	4.0
N_2	62.6

[a] Source: Reference 1.

TOSCO II Retorting Process

The TOSCO II retorting process configuration is shown in Figure 7-3. Raw oil shale, crushed to minus 1.3 cm (½ in.) is mixed with hot ceramic balls in a pyrolysis drum. In the semi-works plant, this drum is 2.44 m (8 ft) in diameter and approximately 4.57 m (15 ft) long. The 1.3 cm (½ in.) diameter balls enter the drum at approximately 650 °C (1200 °F), having been heated in a separate vessel. The heated balls are charged into the drum to mix with the incoming preheated shale at 260 °C (500 °F) in the proportion of about 2 tons of balls for every ton of shale. As the pyrolysis drum rotates, the balls come into contact with oil shale and heat it to approximately 482 °C (900 °F).

The shale oil vapors evolved during pyrolysis, the spent shale, and the ceramic balls exit together and are separated in an accumulator vessel. The shale oil vapor is quenched and then fractionated using conventional hydrocarbon fractionation equipment. The ceramic balls and the crushed oil shale are separated by a trommel, which is a heavy-duty, rotating cylindrical screen. The trommel operates within the sealed accumulator vessel. The balls are lifted by a bucket elevator to a ball heater, which is a direct-contact heat exchanger designed to heat the balls to about 688 °C (1270 °F). The spent shale leaving the pyrolysis drum goes through a special heat exchanger to cool the shale and produce steam for plant use. The spent shale is also quenched with water and moisturized to approximately 14 percent, a level determined to be optimum for disposal.

Hot flue gas from the ball heater is used to lift raw shale to a point at which it can subsequently flow by gravity into the pyrolysis drum. In so doing, the flue gas also preheats the raw shale to approximately 260 °C (500 °F).

Primary outputs from the TOSCO II process are product gas, shale oil, and fine spent shale. The fact that the process is indirectly heated accounts for the high heating value gas product, since there is no nitrogen dilution effect from internal combustion. On the other hand, the indirect-heated nature requires that the spent shale leave the retort still bearing the residual carbon left after pyrolysis. Direct-

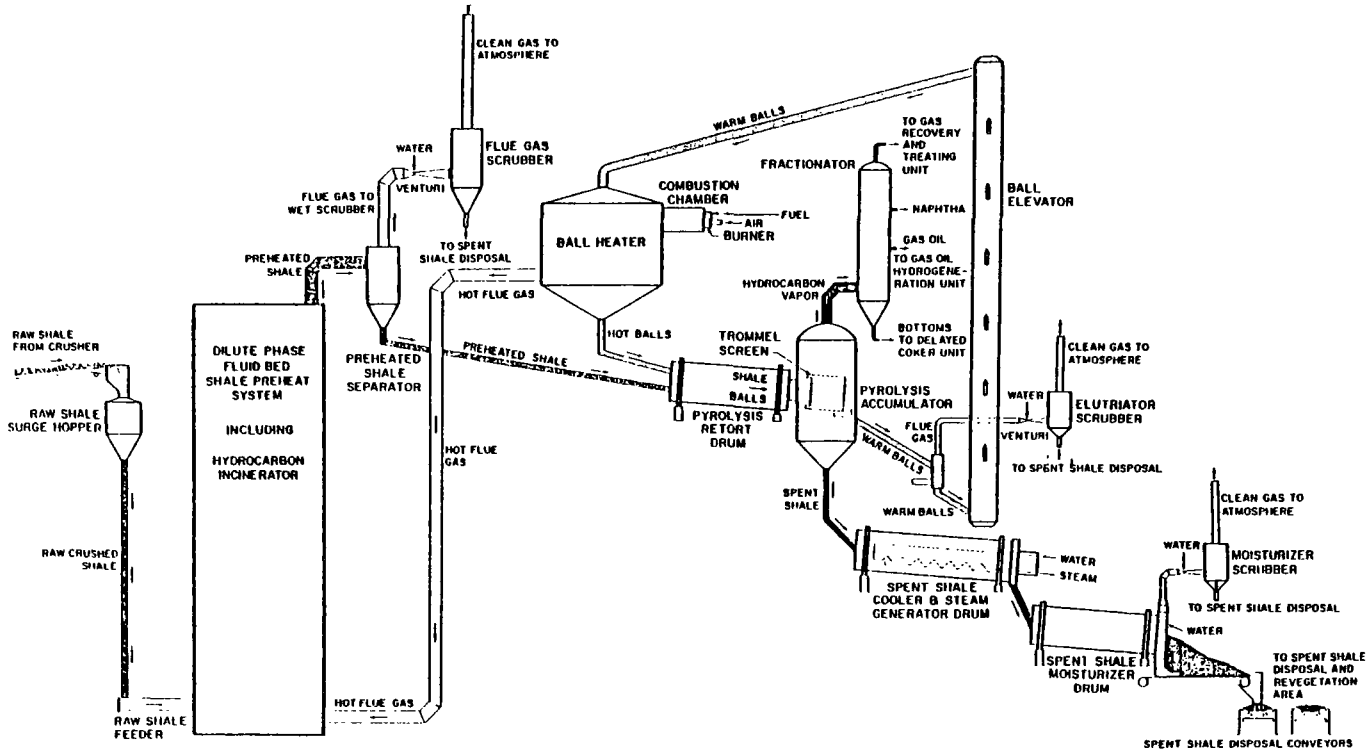


Figure 7-3. TOSCO II retorting process.

heated retorts, on the other hand, usually produce low heating value product gas, but make use of some of the residual carbon on the spent shale. The spent shale from the TOSCO II process is also distinguished from that of many other processes in that it leaves the retort as a fine powder, with the average particle size approximating .074 mm (200 mesh).

Primary sources of emissions from the TOSCO II process that require treatment before discharge are:

Crushing, mining, conveying systems

Shale preheat system

Shale elutriation system (final ball-shale separator)

Shale moisturizing system

Hydrotreating, sulfur recovery, and other upgrading units

Steam boilers

The shale preheating system serves as the primary vent for all of the thermal requirements of the process, and as such, emissions from this source represent the most significant flow of gaseous emissions. Emissions from this source will include typical products of combustion, as well as sulfur dioxide nitrogen oxides, particulates, hydrocarbons, and carbon monoxide. Though a variety of control devices have been considered to control these emissions, the most effective technique to minimize SO_2 and NO_X emissions is the use of low-sulfur clean fuels and proper burner control. This, however, would require combustion of the more valuable process products rather than low-value raw shale oil. The TOSCO II retorting process could be utilized at various throughput rates, locations, and in combination with a variety of additional equipment. Emission data are therefore project-specific, and data from one project would not necessarily apply to other projects. Emission data presented in the conditional PSD permit from EPA for the Colony Project have been summarized and are presented on Table 7-3 as an example only of potential emissions from a plant processing 59,870 tonnes/day (66,000 tons) of oil shale and recovering 6256 tonnes (46,000 bbl/day) of low-sulfur distillate.

Emissions from the shale elutriation system would be composed primarily of NO_X, carbon monoxide, and hydrocarbons. The levels of NO_X could be controlled by the use of clean fuels such as treated butane-butene from the gas treating plant, or by proper burner operation.

Emissions from the shale moisturizing system would be confined to particulate matter, CO_2, and possibly a small amount of hydrocarbon. Except for the sulfur recovery unit, all emissions from the oil and gas treatment system would be the result of fuel combustion. The properties of offgas, therefore, can largely be controlled by proper utilization of clean fuels.

The TOSCO II process will produce wastewater from the following major sources:

Pyrolysis of oil shale

Pyrolysis section steam condensate

Gas recovery section

This water would first be treated to remove the NH_3, H_2S, CO_2 gases and other volatile constituents and then be used to moisturize spent shale. The approximate composition of this moisturizing water is shown in Table 7-4.

The solid waste from the process will consist of spent shale with an average particle size of approximately 0.074 mm (200 mesh). Since the process is indirectly heated, the spent shale will also contain significant quantities of residual carbon, making the material black in color and possibly inhibiting revegetation efforts. Mulching, etc. would effectively reduce this tendency. In a commercial plant, however, residual carbon could be burned off to provide process heat. The chemical composition of typical spent shale from the process is shown in Table 7-5.

TABLE 7-3. AVERAGE RATES OF AIR EMISSIONS FROM PROPOSED COLONY PROJECT[a]
kg/hour (lb/hr)

Source	SO_2	NO_x	HC	Part.	CO
Crushing, mining, and conveying	—	—	—	25.13 (55.4)	—
Shale preheat system	23.13 (51.0)	596.4 (1314.8)	122.47 (270.0)	36.74 (81.0)	19.19 (43.9)
Shale elutriation system	42.77 (94.3)	51.44 (113.4)	0.14 (0.3)	17.15 (37.8)	1.27 (2.8)
Shale moisturizing system	—	—	—	17.37 (38.3)	—
Hydrotreating, sulfur recovery, and other upgrading units	58.88 (129.8)	47.99 (105.8)	1.0 (2.2)	6.67 (14.7)	5.85 (12.9)
Steam boilers	3.49 (7.2)	10.16 (21.6)	0.18 (0.4)	1.36 (2.9)	1.22 (2.6)

[a] Source: Data summarized from Reference 2.

Paraho Development

The Paraho retort is a refractory-lined, vertical kiln in which a moving bed of crushed oil shale, flowing downward through the kiln, is contacted with a countercurrent flow of hot gases having an adequate heat content to pyrolyze organic constituents in the shale and convey the resulting vapors out of the top of the retort. The process can be operated to utilize the residual carbon on the retorted shale as the source of retorting heat (direct-heated mode) or in a configuration whereby the retorting heat is provided by the recycling of product gas heated in an external furnace (indirect-heated mode). First to be discussed will be the direct-heated mode, since this is the configuration used in most of the earlier testing. Figure 7-4 illustrates the process. In this process, crushed oil shale feed of 0.95 to 8.9 cm (3/8 to 3½ in.) is charged to the top of the vertical kiln by an appropriate antisegregation feeding device. As the shale passes downward through the retort, it is contacted by an upward flow of gases near the top of the kiln, in the shale preheating and mist formation zone, the heat in the rising gases is transferred to the cool incoming shale, thereby preheating the solids and increasing overall thermal efficiency. Passing into the retorting zone, the solids encounter hot gases rising from the combustion zone. These gases heat the shale to a temperature such that the organic constituents are pyrolyzed. The vapors that are evolved are carried upward by the flow of gases.

The retorted shale then passes into the combustion zone, where air is injected in sufficient quantities to burn the residual carbon off the surface of the retorted shale. This combustion provides the necessary heat to pyrolyze the shale in the overlying retorting zone. In some cases, additional heat is supplied by injecting and burning a part of the product gas. Passing through the combustion zone, the shale enters the shale-cooling zone, where heat from the spent shale is transferred to a rising stream of recycle gas. The cooled shale is then discharged from the retort by a patented grate mechanism at the bottom of the vessel.

TABLE 7-4. APPROXIMATE COMPOSITION OF TOSCO II WASTEWATER USED TO MOISTURIZE SPENT SHALE[a]

Component[b]	Concentration (ppm)
Ca^{+2}	280
Mg^{+2}	100
Na^{+1}	670
NH_4^{+1}	15
Zn^{+2}	5
As^{+5}	(15-300 ppb)
Cr^{+6}	2
CO^{-2}	360
HCO_3^{-1}	100
SO_4^{-2}	850
$S_2O_3^{-2}$	90
PO_4^{-3}	5
Cl^{-1}	570
CN^{-1}	5
Phenols	315
Amines	410
Organic acids	1,330
Neutral oils	960
Chelate	5

[a] Source: Reference 3.

[b] Elements present in trace amounts include Pb, Ce, Ag, Mo, Zr, Sr, Rb, Br, Se, Cu, Ni, Co, Fe, Mn, V, Ti, K, P, Al, F, B, and Li.

TABLE 7-5. CHEMICAL COMPOSITION OF TOSCO II SPENT SHALE[a]

Component	Weight %
SO_3	2.63
Total carbon	9.83
Inorganic carbon	4.41
Organic carbon	5.41
SiO_2	33.07
Al_2O_3	9.14
Fe_2O_3	3.24
CaO	17.56
MgO	7.74
Na_2O	0.77
K_2O	1.39

[a] Source: Reference 4.

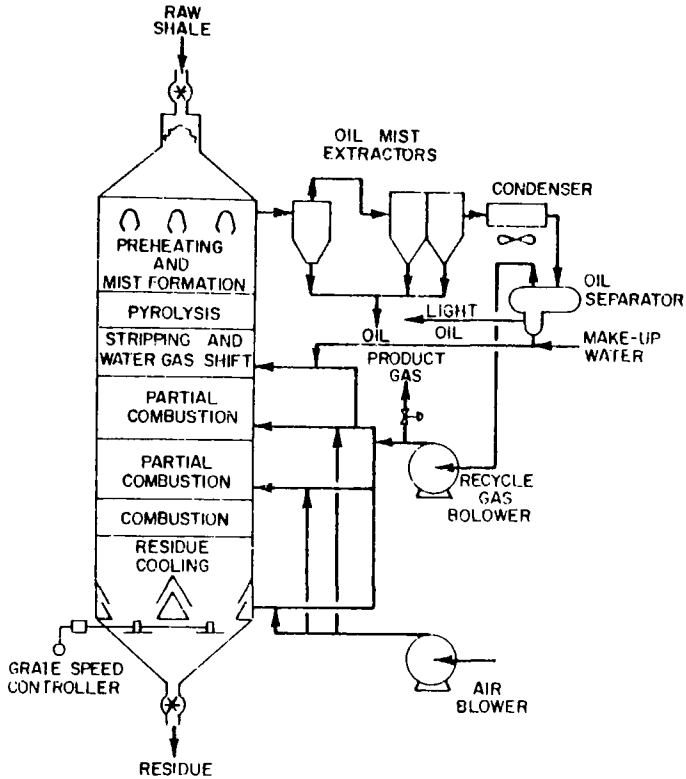


Figure 7-4. Diagram of Paraho retorting process. (Source: Reference 1).

The same basic flow regime is used in the indirect-heated mode, except that instead of injecting air and thus forming a combustion zone, only hot recycle gas is injected. This recycle gas is taken as a slip stream off the product gas line and heated externally in a furnace. The fuel for combustion in this furnace is usually product gas, but this could be augmented by burning residual carbon or spent shale.

The direct-heated mode of the Paraho process resembles other vertical kiln operations such as the gas combustion process, and as such, it would be expected to have similar emissions and effluents. Because of the effect of nitrogen dilution, the product gas from the Paraho process would have a heating value of approximately 890 kcal/scm (100 BTU/scf). The spent shale, since it undergoes very little if any attrition in the retorting operation, will emerge from the retort at essentially the same size it entered. This size range minimizes the dust problem when transporting and disposing of the spent shale. Since some of the residual carbon on the spent shale is used to provide heat for the retorting operation, the final spent shale from the retort will not be black, but rather gray in color. The composition of Paraho spent shale is shown in Table 7-6.

When operating in the indirect-heated mode, the Paraho process will produce product gas with a heating value of approximately 7832 kcal/scm (880 BTU/scf). However, the spent shale from the retort will contain all of the residual carbon produced by the pyrolysis process. As in the direct-heated mode, the shale fragments will undergo little if any attrition during the retorting operation and will thus leave

TABLE 7-6. COMPOSITION OF PARAHO SPENT OIL SHALES

Component	Paraho Indirect	Paraho Direct
	(In Weight %)	
SiO_2	23.1	28.0
CaO	15.3	18.3
MgO	6.5	6.5
Al_2O_3	8.0	6.9
Fe_2O_3	2.7	2.7
Na_2O	2.3	2.6
K_2O	2.4	6.6
SO_3	0.7	0.2
P_2O_5	—	—
Mineral CO_2	18.1	13.3
Organic C	1.84	2.18
Inorganic C	4.95	4.15
Texture	silty gravel	silty gravel
pH	10.9	11.1

Reference: Table 3-24.

the retort with approximately the same particle size distribution as the feed.

The composition of the gas stream from the indirect- and direct-heated retorting mode varies considerably. The estimated composition of this stream, following compression, cooling, and water knockout is shown in Table 7-7. The retort gas analysis is shown in Table 7-8.

The wastewater produced by the Paraho retorting process is comparable to that produced by other processes, as reported in the literature. Three separate wastewater streams were analyzed by EPA during test runs in 1976 (5). These streams are:

Cold condensate stream from the sample condenser at the pilot plant

Hot condensate stream from the bottom gas cooler of the semi-works plant

Process water separated from the crude shale oil

A summary of the data collected during these tests is shown in Tables 7-9 and 7-10. The BOD tests were conducted with great difficulty and little precision. Correlation with COD was poor. Thus, the values shown on the table should not be taken as definitive. Reference 5 also cites cautions regarding the values for total alkalinity and hardness.

Union Oil Development

All three of the processes developed by Union Oil are variations of an upflow vertical kiln retort using a rock-pump shale feeding mechanism. The retorts are known as Retort A, Retort B, and SGR-3 . In all three processes, the oil shale is pushed upward through the retort while the gas flow is downward. In Retort A, the heat for pyrolysis is generated by the internal combustion of residual carbon on the spent shale. In Retort B and the SGR retort, the heat is supplied indirectly by hot gases.

The Retort A process was developed through 1.8-, 45-, and 9000-tonne/day (2-,

TABLE 7-7. COMPOSITION OF PARAHO RETORT GAS PRODUCT[a]

Component	Direct-Heated (Vol. %)	Indirect-Heated (Vol. %)
N_2	61.0	1.8
O_2	0.1	—
H_2	4.9	36.6
CO	2.9	7.3
CO_2	22.8	21.2
H_2S	0.1	2.0
C_1	2.1	20.5
C_2's	1.1	6.1
C_3's	0.6	1.2
C_4's	0.3	0.6
H_2O	4.1	2.3
Total	100.0	100.0

[a] Source: Reference 6.

TABLE 7-8. AVERAGE COMPOSITION OF PARAHO RETORT OFFGAS[a]

Component	Direct-Heated (Vol. %)	Indirect-Heated (Vol. %)
H_2	2.5	24.8
O_2	—	—
N_2 + argon	65.7	0.7
CH_4	2.2	28.7
CO	2.5	2.6
CO_2	24.2	15.1
H_2S	0.266	3.5
NH_3	0.249	1.2
$C_2^=$	0.7	9.0
C_2	0.6	6.9
C_3	0.7[b]	5.5
C_4	0.4[c]	2.0

[a] Source: Reference 7.
[b] Includes $C_3^=$
[c] Includes $C_4^=$.

TABLE 7-9. INORGANIC ANALYSIS OF CONDENSATE STREAMS FROM THE PARAHO PROCESS[a]

Parameter	Cold condensate from pilot plant, direct mode (mg/l)	Hot condensate from semi-works plant, indirect mode (mg/l)
Cations:		
Calcium	60.74	39.16
Magnesium	<0.1	<0.1
Sodium	0.20	0.29
Potassium	0.08	0.18
Ammonium (NH_4^+)	5652-calc.	13440-calc.
Anions:		
Carbonates	30500-calc.	3030-calc.
Bicarbonates	31265-calc.	6280-calc.
Sulfate	113.6	1.65
Sulfide	<0.1	390
Chloride	TR	TR
Fluoride	0.35	0.10
Nitrate	118	1.0
Nitrite	0.02	<0.002
Nutrients:		
NH_3-N	14060-calc.	16800-calc.
TKN	31,400	—
Phosphate (total)	0.58	0.75
Gross parameters:		
BOD	12,000	4,850
COD	19,400	17,100
TOC	29,200	9,800-36,900
TIC	9,800	1,600
Oil & grease	502	33.3
Solids, total	22,000	429
Solids, upon evaporation	21,800	406
Solids, suspended	200	—
Total alkalinity	68,550	12,900
Hardness	152-calc.	98-calc.
Phenols	46	42
pH	9.8	9.5

[a] Source: Reference 5.

TABLE 7-10. ANALYSIS OF PARAHO CONDENSATE WATER AND PROCESS WATER[a,b]

Element	Cold Condensate Water from pilot plant, 3/10/76 0800-1,700 hrs (μg/ml)	Process Water from semi-works 3/15/76 1,500 hr (μg/ml)
Uranium	0.03	
Lead	0.7	0.2
Mercury	<0.01	<0.01
Praseodymium	0.008	
Cesium	0.01	0.01
Lanthanum	0.04	
Barium	0.1	2.0
Iodine	0.008	
Tin	0.05	
Molybdenum	0.3	0.1[c]
Zirconium	0.05	
Yttrium	0.007	
Strontium	0.1	3.0
Rubidium	0.4	
Bromine	0.02	0.009
Selenium	0.04	0.1
Arsenic	0.09	1.0
Gallium	0.04	<0.02
Zinc	0.2	0.4
Copper	0.1	0.2
Nickel	0.1	0.2
Cobalt	<0.01	<0.04
Germanium		<0.05
Iron	>10	5.0
Manganese	0.2	0.3
Chromium	0.07	0.3
Vanadium	<0.01	0.03
Titanium	0.9	0.3
Scandium	0.01	<0.05
Calcium	8	>10
Potassium	3	>10
Chlorine	0.4	2.0
Sulfur	3	>10
Phosphorus	0.2	5.0
Silicon	4	>10
Aluminum	0.2	0.8
Magnesium	3	>10
Sodium	51[b]	>10
Fluorine	−0.1	7
Boron	0.06	−5.0
Lithium	0.02	1.0

[a] Source: Reference 5.
[b] After extraction of organics, sample was thermally ashed @ 450°C for ½ hr in a laboratory furnace in a quartz crucible before analysis.
[c] Heterogeneous.

50-, and 10,000-ton/day) pilot plants that were operated before 1960. A view of the Retort A process is shown in Figure 7-5. The retort is an inverted cone fitted with a rock-pump shale feeder that pushes the oil shale upward through the vessel. Air is injected at the top of the retort to support combustion of the residual carbon on the retorted shale fragments in the upper portion of the retort. This combustion provides the heat necessary to retort the upward-flowing shale.

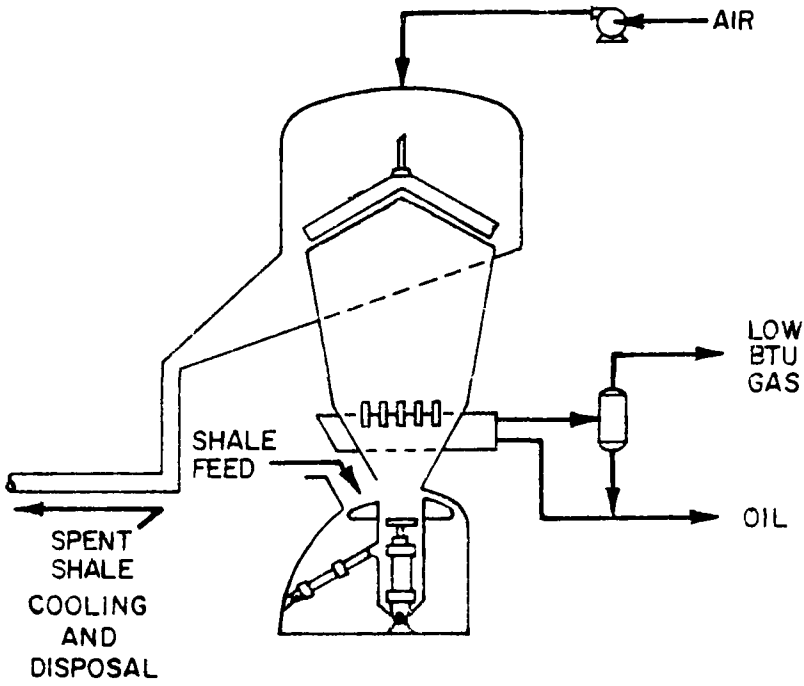


Figure 7-5. Diagram of Union Oil Retort A.
(Source: Reference 1.)

The crushed shale feed is removed from the hopper and transferred to the bottom of the retort by a shale feeder. As the shale enters the retort, it is contacted by a countercurrent flow of hot product gases leaving the combustion and retorting zones above. In this lower zone, the gas-cooling zone, heat is transferred from the hot gases to the cool incoming shale. The feed is preheated, and the oil vapors are condensed, resulting in higher thermal efficiencies. In addition, the recovery of the sensible heat in the gas also makes subsequent gas handling easier. Passing up through the retort, the preheated shale enters the retorting or pyrolysis zone. The gases passing downward in this area, having just left the combustion zone, heat the shale to a temperature such that organic material is pyrolyzed, producing shale oil vapor, product gas, and residual carbon on the surface of the shale. As the gaseous products of pyrolysis are evolved, they are swept downward by the flow of combustion gases.

The retorted shale fragments then enter the combustion zone where they encounter preheated combustion air passing down through the retort. This air sustains the combustion of the residual carbon that remains on the surface of the shale after retorting. Temperatures in this zone may reach 1093 °C (2000 °F), high enough to fuse a portion of the shale. In earlier versions of the retort, retorting spiral plows

were used to break clinkers and remove retorted shale. In later versions, these plows were not used. Herein lies one advantage of the Union rock-pump retorts. Since the spent shale will eventually overflow the top of the retort rather than pass through a discharge grate mechanism, the formation of large clinkers does not present as much of a problem as it does in typical gravity flow retorts.

The hot spent shale leaves the combustion zone and enters the topmost zone, the air preheat zone. In this area, heat from the spent shale is transferred to the cool incoming combustion air, thus preheating the air before entry into the combustion zone. Upon leaving this zone, the shale is pushed up over the top of the retort and falls into the ash disposal chute.

Below the gas cooling zone, in which some of the retort products are condensed, the retort walls are slotted to allow separation of the oil and gas from the incoming shale. A bustle surrounds this section, and the gas and oil pass through this bustle to the product recovery system. The shale feeder is constructed so that any fines that pass through the slots return to the feeding piston and are reintroduced into the kiln. Thus, the gas and oil collector does not become plugged with an accumulation of fines. The feeding mechanism is filled with oil to a level just below that of the slot edges, providing a liquid seal that prevents air from being drawn into the kiln through the shale feeder. The liquid oil level is determined by pressure in the retort. Oil drains through the retort exit line to the Roto-clone collector.

Retort B closely resembles Retort A, except that the heat for pyrolysis is supplied by hot recycle gas rather than internal combustion. Another difference is that the design of the rock-pump shale feeder is slightly altered to permit feed rates up to 9,072 tonnes/day (10,000 tons/day). Diagrams of the Retort B process are shown in Figures 7-6 and 7-7.

Sized and screened oil shale is drawn through a shale oil seal in the feed chutes and pumped into the bottom of the retort by the two rock-pump pistons. Shale oil product acts as a hydraulic seal in the feed chutes to maintain retort pressure. The solids pump, mounted on a movable carriage, is completely enclosed within the feeder housing and immersed in shale oil. The pump consists of two hydraulic piston and cylinder assemblies that alternately feed shale to the retort. While one cylinder of this rock-pump is filling with oil shale feed during a piston downstroke, the other cylinder is charging oil shale into the retort. When this operation is completed, the pump carriage is moved horizontally on rails until the full cylinder comes under the retort. This cylinder charges its oil shale upward into the retort while the other fills with shale from the other feed chute. The carriage is then moved back to its original position and the cycle is repeated. Seal plates outboard of each cylinder close off the idle feed chute to prevent discharge of shale into the feeder housing.

The oil shale moves uniformly up through the cone to form a free-standing pile on top of the retort bed. Retorted shale falls by gravity from the top of the vessel, but it may be assisted by a lightweight rake rotated above the top of the bed. The retorted shale is then discharged into a collection and cooling system. The top of the retort cone is enclosed by a pressure dome, permitting operation at a nominal 1.10 kg/cm^2 (15 psig). As in the Retort A, a series of vertical slots around the perimeter of the lower cone wall provides the openings for disengaging the condensed oil and retort vapors from the solids bed.

The composition of Retort A offgas is given in Table 7-11. Emission data for the Union B retort and associated facilities for a modular oil shale facility contained in the proposed conditional PSD permit from EPA to the Union Oil Co. are summarized on Table 7-12. The modular project will consist of mining 13,750 tonnes/day (15,156 tons/day) of oil shale and producing 1,224 tonnes of oil/day (9,000 bbl/day).

Because of its relative simplicity and encouraging process economics, the Retort B process was selected in 1976 as the process to be demonstrated on a commercial

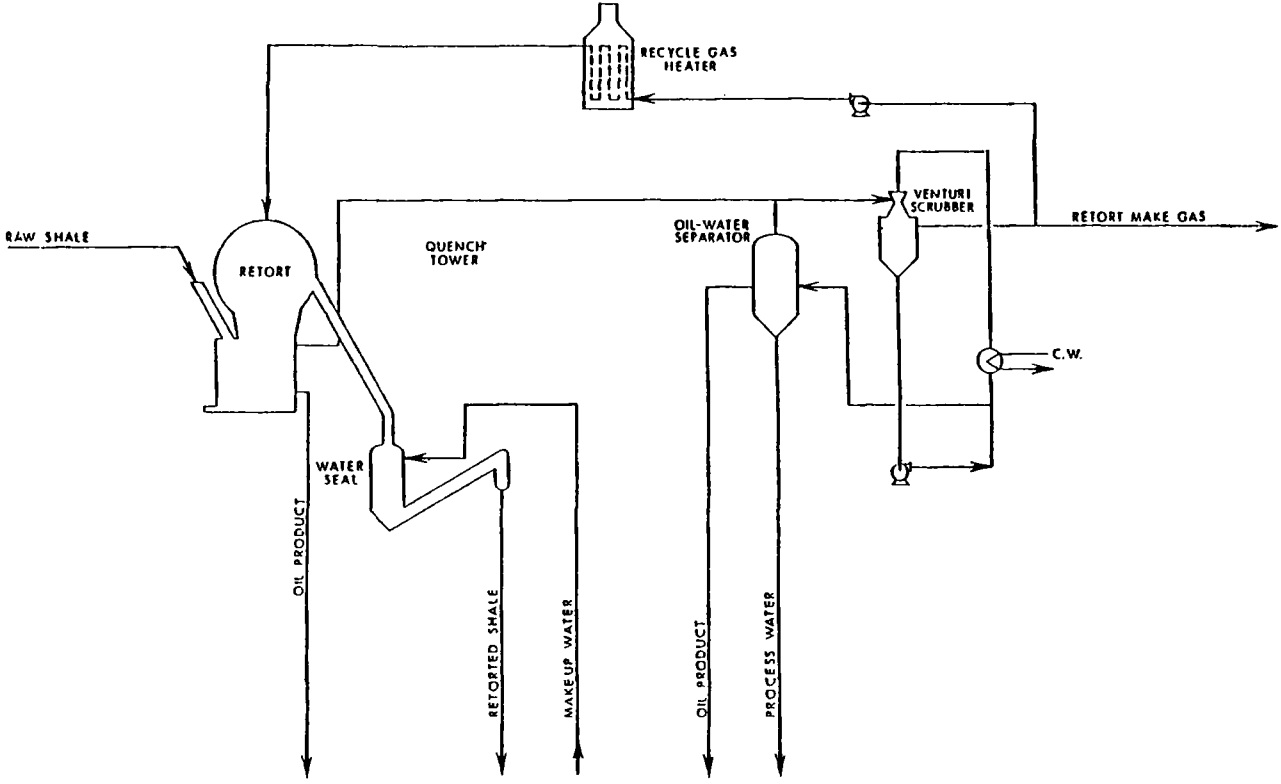


Figure 7-6. Process Flow Diagram Union Retort B Process.

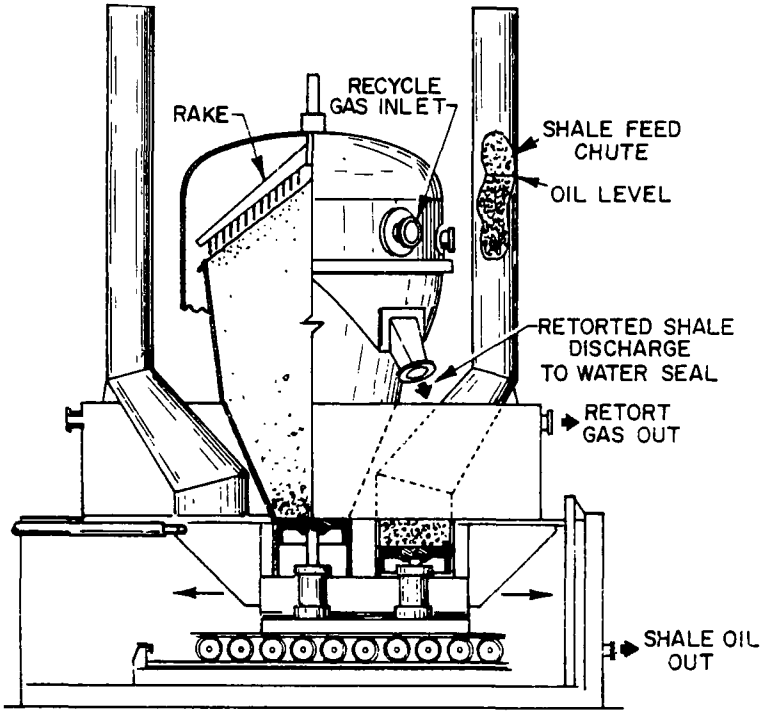


Figure 7-7. Diagram Union Oil Retort B.
(Source: Reference 1.)

TABLE 7-11. COMPOSITION OF UNION A OFFGAS

Component	Vol. %
H_2	2.2
O_2	2.2 air
N_2 + argon	57.6
CH_4	0.9
CO	4.6
CO_2	30.3
H_2S	0.1
$C_2^=$	0.6
C_2	0.4
$C_3^=$	0.4
C_3	0.2
$C_4^=$	0.3
C_4	0.1
CS	0.1

Source: Reference 7.

TABLE 7-12. SUMMARY OF DESIGN EMISSIONS FOR THE UNION B RETORT AND RELATED FACILITIES
kg/hr (lb/hour)

Source	SO_2	NO_X	Part.	CO	HC
Mining, conveying, crushing, etc.	—	6.12	14.28	3.76	—
	—	(13.5)	(31.5)	(8.3)	—
Retorting and product handling	36.80	38.99	0.64	22.98	11.4
	(81.11)	(85.96)	(1.42)	(50.66)	(25.13)
Spent shale disposal	—	—	0.99	—	8.12
	—	—	(2.2)	—	(17.9)

scale. In early 1977, a process was announced that, when retrofitted to a Retort B prototype unit, would further improve the economics of the process by utilizing the residual carbon left on the spent shale. This process, known as SGR-3, provides for the combustion of the residual carbon in a separate vessel, thus producing enough hot flue gas to supply all of the retort heat requirements. This technique provides for the production of a 8,720-kcal/scm (980-BTU/scf) product gas from the retort while maintaining a high thermal efficiency (83 percent) by using the residual carbon on the spent shale. Following the removal of C_4 plus hydrocarbons and acid gases from the gas stream, the heating value is reduced to approximately 7,120 kcal/scm (800 BTU/scf). This value can be increased to more than 8,900 kcal/scm (1,000 BTU/scf) by methanation. A flow diagram for the process is shown in Figure 7-8.

Because of the design of the rock pump feed mechanism, all of the proposed Union Oil processes utilize fairly large shale fragments of 5 cm to 0.3 cm (2 to 1/8 in.). As in the other vertical kiln type processes, very little attrition occurs during the retorting process, and thus the spent shale fragments leave the retort essentially the same size as they entered. The spent shale from the direct-heated Union retorts would be gray in color, having had some of the residual carbon burned off. The indirect-heated retorts, on the other hand, would discharge shale still containing the residual carbon. The SGR-3 process employs a separate spent shale combustor unit. The spent shale from these processes, therefore, would be light-colored, containing very little if any residual carbon. The composition of the spent shales is shown in Table 7-13.

The composition of the product gas from the retort largely depends on the mode of heating. Indirectly heated retorts will produce a high-BTU gas product whereas the product from direct-heated retorts will have a low BTU content because of nitrogen dilution. The product gas composition from the SGR-3 process is shown in Table 7-14. Composition of the flue gas from the combustor in the SGR-3 process is shown in Table 7-15.

Superior Oil Development

The retorting process that the Superior Oil Co. proposes to use in its multi-mineral extraction facility features a circular traveling grate retort. The design features of the process are shown in Figures 7-9 and 7-10. Figure 7-11 is a diagram of the Superior retorting process. In the process, a layer of crushed and sized oil shale is placed on a continuous belt or grate. This grate is designed so that gases can flow through both it and the shale bed. As the shale circulates within the doughnut, it encounters separate zones in which it is heated, retorted, cooled, and dumped.

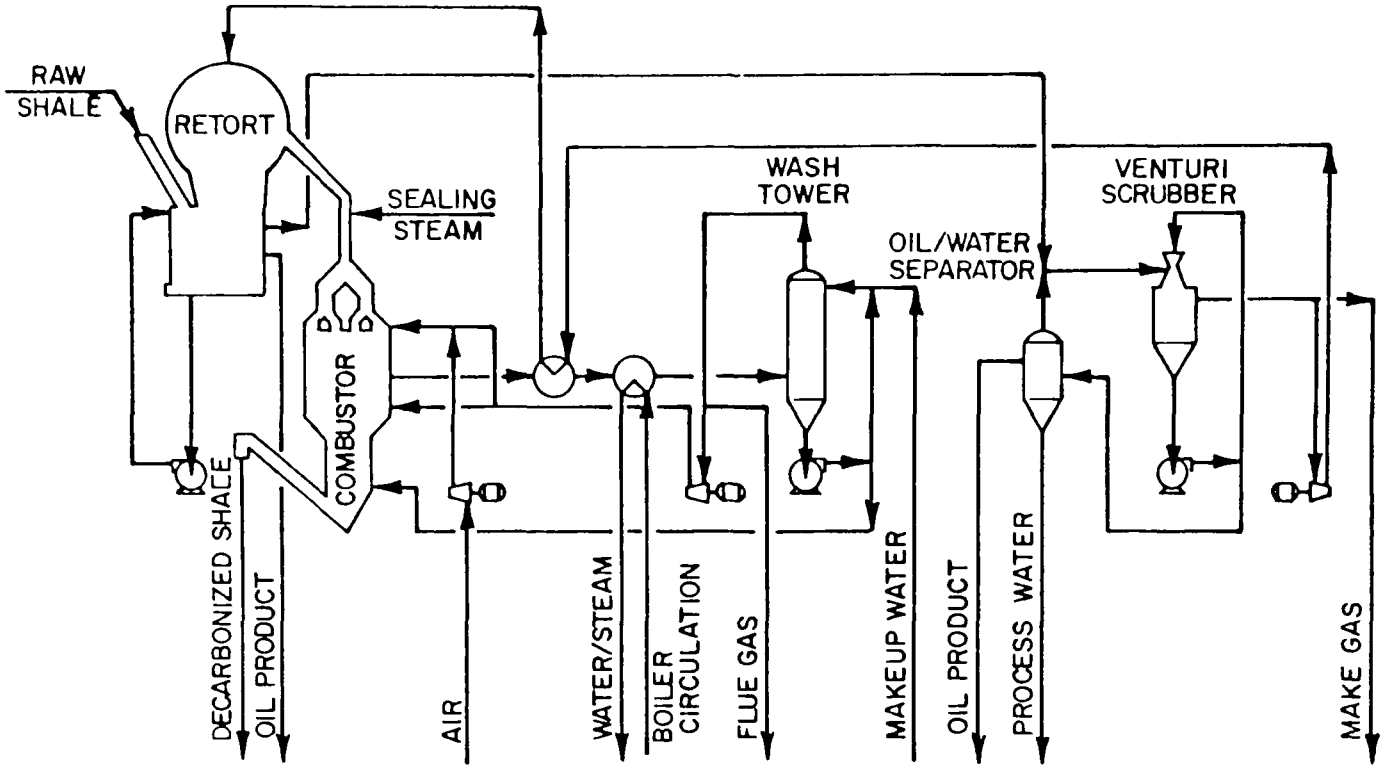


Figure 7-8. Diagram of Union Oil SCR-3 retorting process.
(Source: Reference 1.)

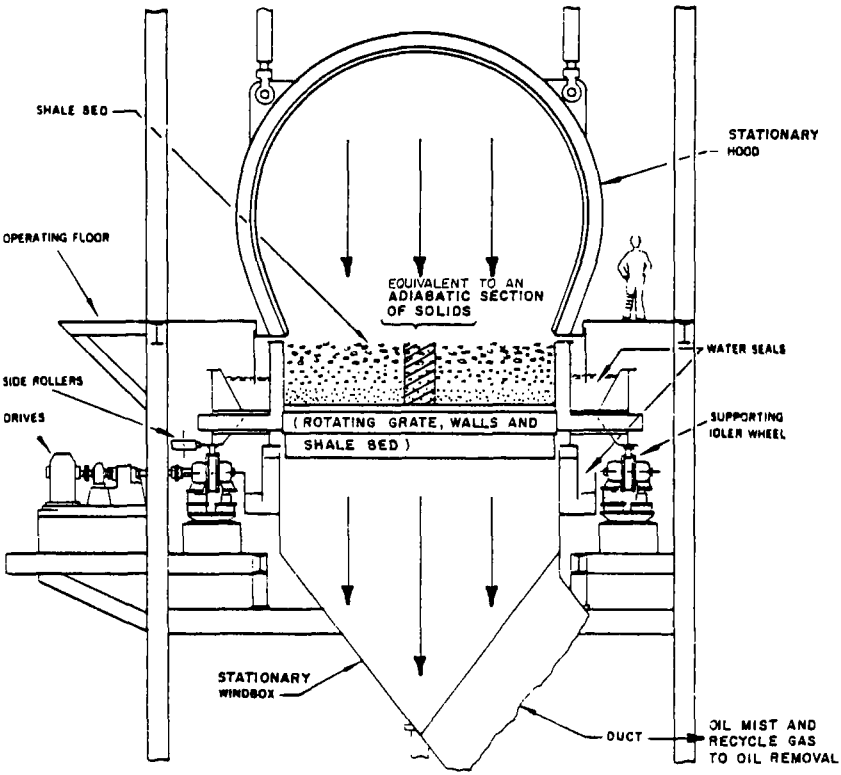


Figure 7-9. Cross sectional view of Superior retort.

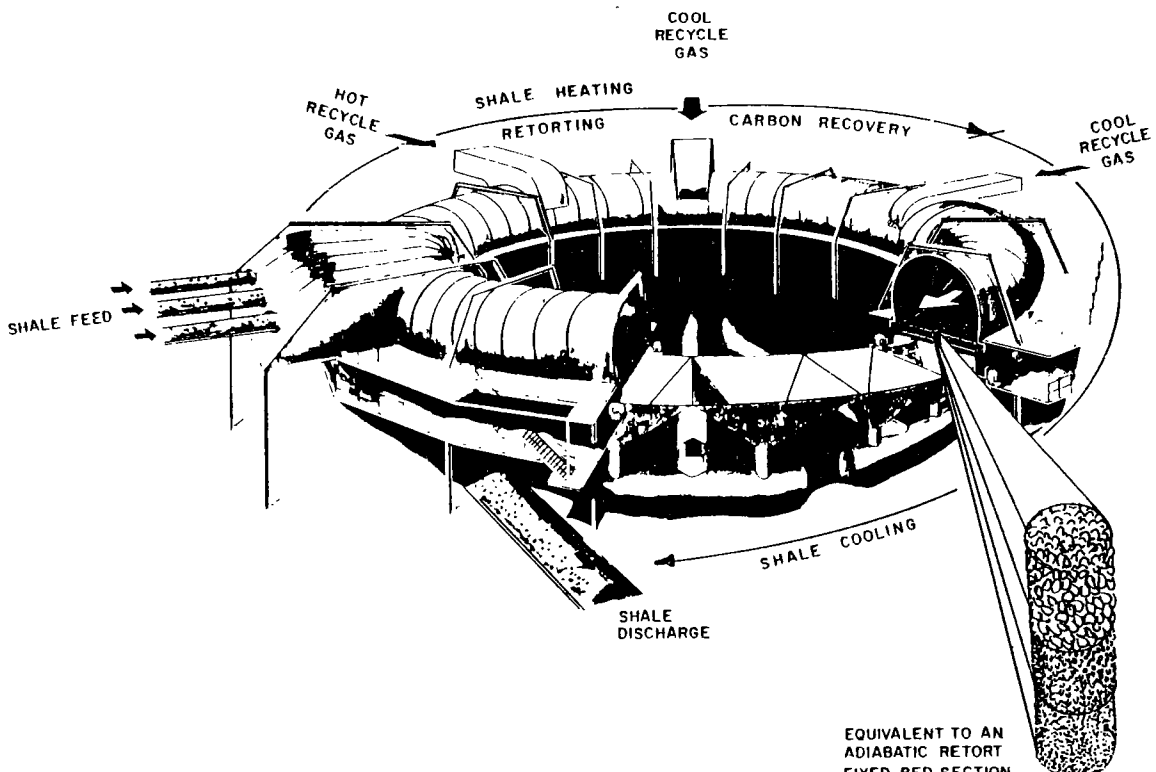


Figure 7-10. Functional design of Superior retort.

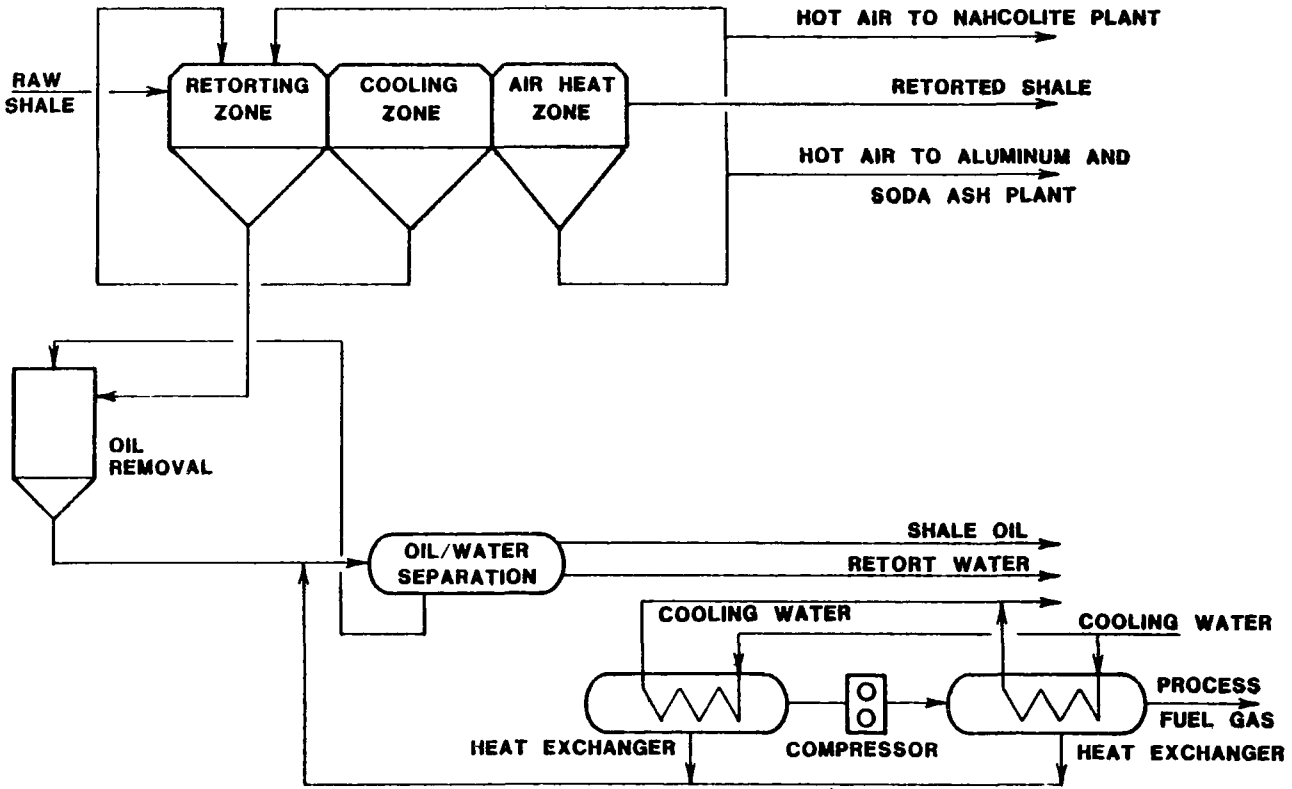


Figure 7-11. Diagram of Superior retorting process. (Source: Reference 9.)

TABLE 7-13. COMPOSITION OF UNION SPENT OIL SHALES

Component	Union A	Union B (in weight %)	Union SGR
SiO_2	35.3	31.5	39.2
CaO	27.2	19.6	27.3
MgO	9	5.7	8.2
Al_2O_3	8.5	6.9	8.9
Fe_2O_3	7.3	2.8	3.8
Na_2O	5.5	2.2	3.7
K_2O	2.8	1.6	2.7
SO_3	0.1	1.9	1.4
P_2O_5	2.2	0.4	0.5
Mineral CO_2	1.6	22.9	3.1
Organic C	0.5	4.3	0.3
Inorganic C	—	—	—
Texture	graded gravel to silty gravel	silty gravel	silty gravel
pH	12.5-13.0	8.7	12.5

TABLE 7-14. COMPOSITION OF PRODUCT GAS FROM UNION SGR-3 PROCESS[a]

Component	Vol. %
H_2	25
C_1	24
C_2	10
C_3	8
C_4	5
C_5	2
C_6	1
CO	5
CO_2	16
H_2S	4

[a] Source: Reference 8.

TABLE 7-15. COMPOSITION OF COMBUSTOR FLUE GAS FROM SCR-3 PROCESS[a]

Component	Amount
N_2, mol. %	71
CO_2, mol. %	28
O_2, mol. %	0.5
SO_2, ppm	5
NO_X, ppm	300

[a] Source: Reference 8.

The hot gases that pass through the shale in the retorting zone are heated externally; these gases are products of combustion from burned product gas. In one zone of the retort, some of the residual carbon on the spent shale is burned off.

Both circular and straight grates have long been in commercial use for iron ore pellet sintering, cooling, and other kiln applications. Superior's process development effort focuses on adaptation of the circular grate process for oil shale retorting. This effort included construction and operation of an adiabatic fixed-bed retort designed to simulate the conditions encountered by a section of solids as it travels through the separate processing zones in the circular grate. The adiabatic retort tests identified the significant process variables and their effect(s) on cost responses such as throughput rate, thermal efficiency, product yield, etc. Cost sensitivity analyses established optimum ranges in which to design and operate the circular grate oil shale pilot retort that was later constructed.

The pilot circular grate retort operations defined design and scale-up information for the oil removal system that had never been tested in prior circular grate applications. Pilot plant operations also confirmed the mechanical reliability of solids flow on four types of shale. The primary results of this process development effort have been:

Attainment of thermal efficiency for the cross-flow circular grate which approaches those achieved in countercurrent flow devices.

Product oil yields more than 98 percent of Fischer assay.

Development of a proved oil recovery system.

Optimized throughput and gas rates/ton of oil shale processed.

Lurgi-Ruhrgas Process

The Lurgi-Ruhrgas process features the use of heat-carrier solids of small particle size, such as sand grains or spent shale solids derived from the retorting process. Figure 7-12 is a simplified diagram of the process. The hot solids are mixed with finely crushed (0.6-cm or 1/4 in.) raw oil shale in a sealed, screw-type conveyor. The organic constituents are pyrolyzed during the mixing which occurs in this device. Upon leaving the screw conveyor, the effluents are separated into solid and gaseous components in a collection bin. A portion of the spent solids is recycled to a lift pipe, and the remainder is discarded. In the lift pipe, the hot spent shale is contacted with air at approximately 400 °C (750 °F), raising the material pneumatically and simultaneously burning the carbon residue on the shale surface. The combustion gases and hot spent shale are separated at about 650 °C (1200 °F) in a collecting bin, and the solids are mixed again with incoming oil shale in the screw conveyor. Between 6 and 8 pounds of heat-carrying solids are circulated and mixed with each pound of raw oil shale.

Since no air is injected into the retorting area, the gas product from the process has a high heating value. Furthermore, the oil yield from the process typically ranges between 95 and 110 percent of Fischer assay. Since the residual carbon on the spent shale is mostly utilized in the process, the overall thermal efficiency is quite high.

Because the Lurgi-Ruhrgas process is indirectly heated, the product gas has a high heating value; but unlike other indirectly heated retorts such as the TOSCO II process, residual carbon utilization is an integral part of the retorting process, and therefore the spent shale will be rather light in color and contain relatively little residual carbon. Like the TOSCO II process, the Lurgi-Ruhrgas process used raw oil shale feed with a particle size of less than 0.6 cm (1/4 in.). No public information is yet available regarding the final spent shale characteristics, but it is reasonable to assume that some degree of attrition will occur, thus leading to a somewhat smaller average particle size in the final spent shale.

The primary atmospheric emission stream from the Lurgi-Ruhrgas process is flue gas from the combustion of residual carbon on the spent shale. This stream will

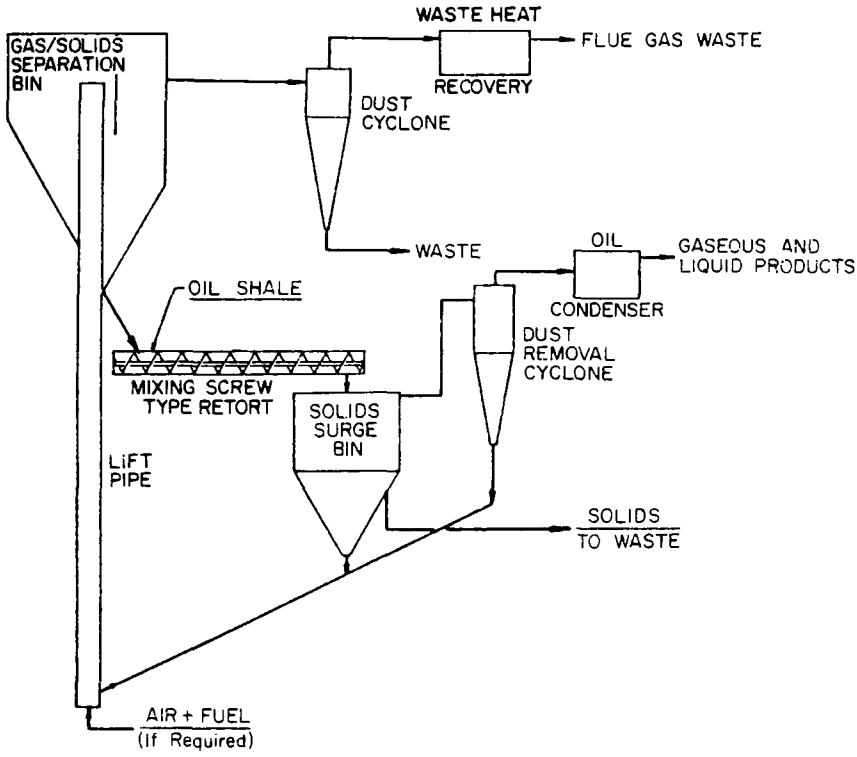


Figure 7-12. Lurgi-Ruhrgas retorting process. (Source: Reference 1.)

contain typical products of combustion, along with some sulfur dioxide (SO_2), nitrogen oxides (NO_X), and particulates. During pilot plant tests conducted thus far, particulate loading averaged 80 mg/m^3, and this level could be controlled with available technology. The SO_2 content detected during these tests was approximately 10.5 ppm. This low level may be attributable to the absorption of SO_2 by the CaO and MgO formed in the spent shale during the retorting process. Under the expected operating conditions for large-scale installations, the NO_X level is not expected to exceed 100 ppm (10). The offgas is shown in Table 7-16, in volume percent.

The major source of liquid waste from the process is the gas condensate produced during the pyrolysis of oil shale. This stream would contain minor amounts of ammonia, sulfur, oil, and phenols. The stream could either be used to moisturize spent shale or be treated with existing technology before disposal or reuse. The properties of this stream are shown in Table 7-17.

The fine spent shale from the Lurgi-Ruhrgas process would be light in color because of the utilization of residual carbon. This would perhaps enhance revegetation efforts. Recent studies have indicated that spent shale similar to that from the

TABLE 7-16. COMPOSITION OF LURGI-RUHRGAS OFFGAS[a]

Component	Vol. %
H_2	18.5
N_2 + argon	7.7
CH_4	11.9
CO	2.7
CO_2	25.0
H_2S	46.2 g/NM^3
$C_2^=$	12.0
$C_3^=$	8.9
C_4	C_4^+ 13.3
SO_2	0.06 gNM^3

[a] Source: Reference 7.

Lurgi-Ruhrgas process may be moistened to achieve some degree of cementation, thus minimizing erosion effects on disposal piles (4).

TABLE 7-17. PROPERTIES OF LURGI-RUHRGAS CONDENSATE WASTEWATER[a]

Constituent	Amount %
Total hydrocarbons (including phenols)	0.4 wt. %
Dust	0.03 wt. %
Ammonia	1.7 wt. %
Sulfur	0.05 wt. %
Phenols	0.026 wt. %
pH	9.3

[a] Source: Reference 10.

IGT HYTORT Process

The HYTORT process developed by IGT has been scaled up from laboratory and bench-scale to a Process Development Unit (PDU) with a capacity of 22 tonnes (24 tons) per day. The process has been developed to process eastern Devonian as well as Western Eocene shales to produce either a synthetic crude or synthetic natural gas (SNG).

Eastern Devonian shales, although they may have a similar organic carbon content, produce a much lower yield of oil plus gas when retorted by conventional methods (as indicated by Fisher Assay) than do western Green River Formation oil shales. This is probably due to the lower hydrogen/carbon ratio of the eastern shale as well as to structural differences in the two types of shale. The Institute of Gas Technology found that by retorting eastern shales under high hydrogen partial pressure the oil and gas yield could be significantly increased.

Based on the encouraging results obtained thus far in laboratory and bench-scale tests, IGT has prepared preliminary process designs for the HYTORT process. A commercial HYTORT plant would consist of three basic sections: the retort and associated solids handling system; the hydrogen plant and other utilities; and the shale oil or SNG upgrading equipment. A block flow diagram for a plant producing syncrude from eastern Devonian shale is shown in Figure 7-13.

Raw shale would be crushed to the size range required by the HYTORT reactor, with undersize material returned to the land reclamation site. Process shale would be fed to the high-pressure HYTORT reactor through liquid-sealed lockhoppers, patented IGT devices. The shale would move downward, counter-current to the hydrogen-rich gas flow, through the HYTORT reactor. A small amount of oxygen would be injected into the reactor near its center for heat balance purposes. Spent shale would be removed from the reactor through liquid-sealed lockhoppers.

Product gas from the retort, containing a mist of partially-condensed shale oil and water would be scrubbed to recover water and raw shale oil. Acid gas constituents would then be removed, and by-product sulfur and ammonia recovered. A bleed stream of the clean gas would be sent to the steam reformer, to convert hydrocarbon gas constituents into hydrogen. The balance would be recycled directly to the HYTORT reactor. All of the makeup hydrogen requirements for hydroretorting and catalytic hydrotreating would be produced in this fashion.

Raw shale oil would be catalytically hydrotreated to produce a low-sulfur, low-nitrogen refinery feedstock product and a plant utility fuel stream. A supplementary acid-treating step could be added to reduce the product nitrogen content further. A net syncrude yield of approximately one-half barrel per ton of shale would typically be produced with eastern Devonian shale.

The major source of pollutants in the process plant would be the water produced by the chemical reactions in the hydroretorting and,to a lesser extent, the catalytic hydrotreating steps. Table 7-18 shows estimated production rates of these substances from the hydroretorting step in a 6,285 tonnes (46,214 bbl) per day plant processing eastern Devonian shales. It is anticipated that in a commercial plant a zero discharge concept could be employed and that internal water streams would be extensively treated. Net water usage would result from cooling tower evaporation and drift, and from water on the spent shale.

The main identified sources of air pollutants for the HYTORT process are:

Shale handling and crushing facilities.

Claus sulfur plant and process gas vents.

Flue gas from plant boilers and fired heaters.

These sources produce pollutants in the form of particulates, SO_2, NO_X, light hydrocarbon gases, and CO. An estimate of emission rates of these pollutants from a 6,285 tonnes (46,214 bbl) per day syncrude plant operating on eastern Devonian shale is shown in Table 7-19.

IN SITU RETORTING PROCESSES

Occidental Modified *In Situ* Process

The modified *in situ* (MIS) recovery process developed by Occidental Oil Shale, Inc. (Oxy) involves the mining of approximately 15 to 25 percent of the retort volume and rubblizing the remaining shale into the void. Vertical longholes are drilled, loaded with an ammonium nitrate-fuel oil explosive, and detonated with timing delays in a fashion that explosively expands the rock mass to fill the entire volume. After rubblization, ignition of the retort is initiated by injecting a small amount of supplemental fuel at the top of the retort to heat the rubble pile to approximately 500 °C (900 °F). The heat released retorts the top shale to produce shale oil, some gas, and a residual carbon left on the shale. This carbon then becomes part of the required fuel. Either steam is added along with the combustion air or

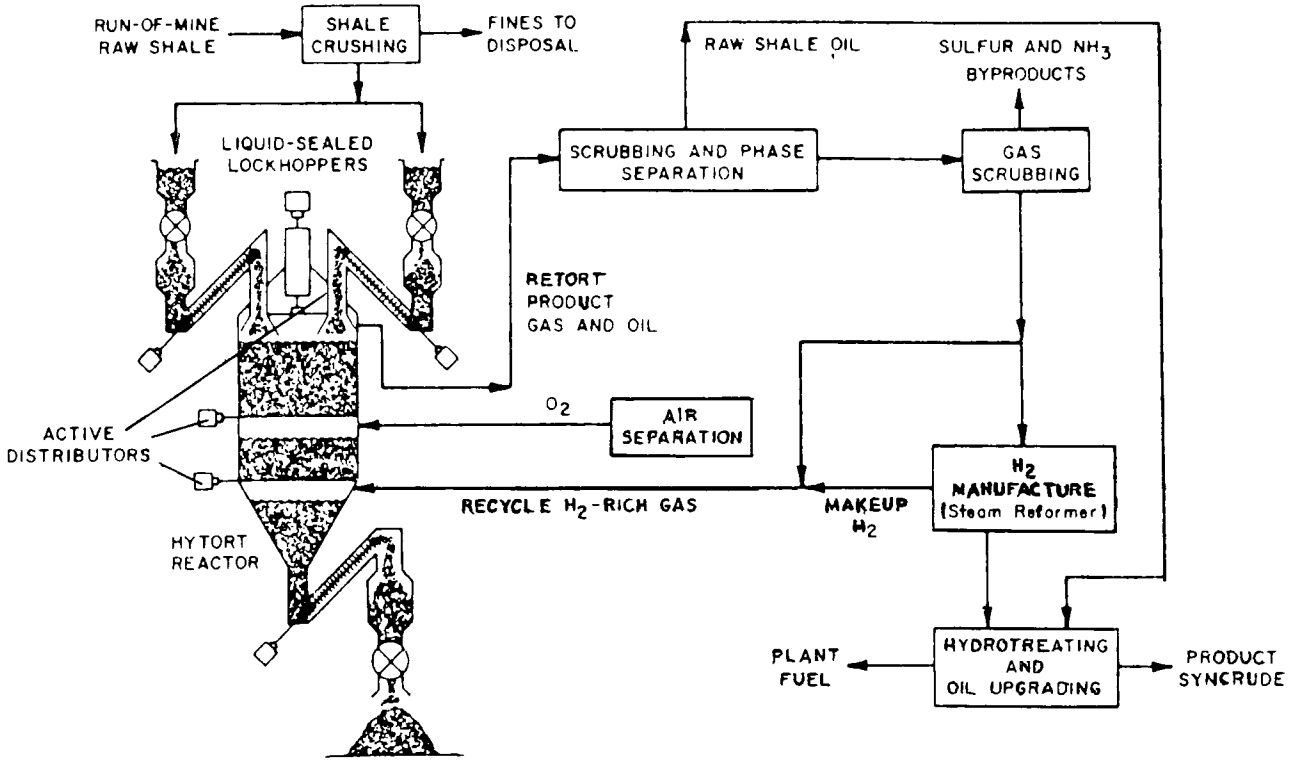


Figure 7-13. HYTORT™ commercial plant concept.
(Source: Reference 11.)

TABLE 7-18. WATER POLLUTANT LOADING FROM HYDRORETORT REACTORS[a]

Pollutant	Production Rate kg/day	(lb/day)
Oxygenated Compounds		
Alcohols	307	(677)
Acetone	1,011	(2,229)
2-butanone	661	(1,457)
2-pentanone	78	(171)
Acetic Acid	6,608	(14,572)
Propanoic Acid	1,944	(4,286)
Butanoic Acids	389	(857)
Pentanoic Acids	661	(1,457)
Phenol	451	(994)
Cresols	389	(857)
Xylenols	214	(471)
Total	12,711	(28,028)
Sulfur Compounds		
H_2S	73,857	(162,860)
Methyl Mercaptan	272	(600)
Ethyl Mercaptan	389	(857)
Thiocyanate (SCN)	54,987	(121,250)
Miscellaneous	3,498	(7,714)
Total	133,003	(293,281)
Nitrogen Compounds		
Ammonia	76,505	(168,700)
Acetonitrile		
Tolunitrile	12	(26)
Pyridine	233	(514)
Methyl Pyridines	292	(643)
C_2-Pyridines	233	(514)
C_3-Pyridines	175	(386)

(continued)

Table 7-18. (continued)

Pollutant	Production Rate kg/day	(lb/day)
Pyrolle	2,177	(4,800)
Methyl Pyrolles	739	(1,629)
C_2-Pyrolles	350	(771)
C_3-Pyrolles	117	(257)
C_4-Pyrolles	20	(43)
Aniline	972	(2,143)
Methyl Aniline	661	(1,457)
C_2-Anilines	50	(111)
Quinoline	39	(86)
Indole	39	(86)
$C_6H_{13}N$	156	(343)
$C_7H_{15}N$	428	(943)
$C_8H_{15}N$	280	(617)
$C_9H_{17}N$	389	(857)
Total	87,207	(192,298)
Hydrocarbons		
Benzene	311	(686)
Toluene	583	(1,286)
Total	894	(1,972)
Trace Organic Constituents	1,088	(2,400)

a Source: Reference 12.

part of the offgas may be recirculated to control the oxygen concentration in the incoming air. The oil and water vapor condenses in the coal rubble below the retorting zone and flows to the bottom of the retort where it is collected in a sump and pumped to underground storage. The gas not consumed to the system has a potential for power generation significantly in excess of the plant needs.

The product shale oil flows downward ahead of the combustion zone and is collected in a sump at the bottom of the retort. Pipelines carry the shale oil from the sump to surface storage facilities. A conceptual diagram of an Oxy retort is shown in Figure 7-14, and a flow diagram for the commercial process is shown in Figure 7-15.

Retorts 7 and 8 are now being developed at Oxy's Logan Wash test site near DeBeque, Colorado. These two retorts, operated simultaneously, constitute a net increase of greater than 100 tons per year of certain effluents. The facility is, therefore, considered a modified source and is subject to the PSD process. A conditional PSD permit was issued by EPA on November 1, 1979. Table 7-20 gives the air emissions allowed by the permit.

The total offgas flow will pass through a contact condensor and reduce by 60

TABLE 7-19. ESTIMATED EMISSIONS FROM COMMERCIAL HYTORT PLANT
Tonnes (Tons) Per Year[a]

Source of Emissions	Particulates		SO_2		NO_X		CO		Light Hydrocarbon Vapors	
SCOT Tail Gas Unit	0.19	(0.21)	3.15	(3.47)	0.58	(0.64)	5	(6)	83	(92)
High Pressure Boiler	1.62	(1.79)	0.52	(0.57)	4.87	(5.37)	9	(10)	468	(516)
Steam Reformers	3.18	(3.50)	1.01	(1.11)	9.52	(10.49)	92	(101)	1,372	(1,512)
Hydrotreater Preheaters	0.28	(0.31)	0.09	(0.10)	0.85	(0.94)	8	(9)	122	(135)
Shale Crushing & Handling Equipment	6.37	(7.02)	—	(—)	—	(—)	—	(—)	—	(—)
Fluidized Bed Incinerator	0.28	(0.31)	0.03	(0.03)	0.28	(0.31)	3	(3)	41	(45)
Totals	11.92	(13.14)	4.79	(5.28)	16.10	(17.75)	117	(129)	2,087	(2,300)

[a] Source: Reference 12.

percent the condensable hydrocarbons. Three steam plants will be at the site, but only two will operate at any one time. Two heater treater units will operate at the head of Logan Wash on an intermittent basis. The offgas consists primarily of gases from shale pyrolysis, carbon dioxide and water vapor from the combustion of carbonaceous residue, carbon dioxide from the decomposition of inorganic carbonate (primarily dolomite and calcite), and hydrogen from the water gas reaction as well as N_2. A pilot combustor and pilot FGD system will be built and tested for retorts 7 and 8. Table 7-21 gives the composition of the retort gas assuming the MIS retort producing 56,874 barrels per day crude shale from an assumed 147,600 tonne/day (164,000 tons/day) of shale of approximately 113.5 l/tonne (25 gal/ton) assay oil shale. Table 7-22 shows a typical process water analysis from Retort 6.

Rio Blanco MIS Process

The Rio Blanco MIS process removes about 50 percent of the shale from underground and the remainder is explosively rubbled into the resulting void, then retorted. The mining is done from the bottom level of the target zone and a rectangular-shaped room is created. A pattern of blast holes is then drilled from the surface, loaded with explosive, and sequentially fired to optimize rubble size and thus create an optimum void volume. Some of the vertical blast holes are then used for down-hole burners and injection of air, steam, and water. The retort is then ignited and retorting progresses downward through the retort. Quench water can be used to control outlet gas temperature. Retort water is kept from mingling with mine seepage by bulkheads and separate collection drifts. A Modular Development Phase (MDP) mine diagram is shown in Figure 7-16.

Rio Blanco intends to use this process on Federal lease Tract C-a. Estimated particulate and SO_2 emissions from the Modular Development Phase on Tract C-a are shown in Table 7-23. The estimates include emissions from all mining, processing, waste disposal, and vehicular movement during the MDP. Estimates of other emissions are not available.

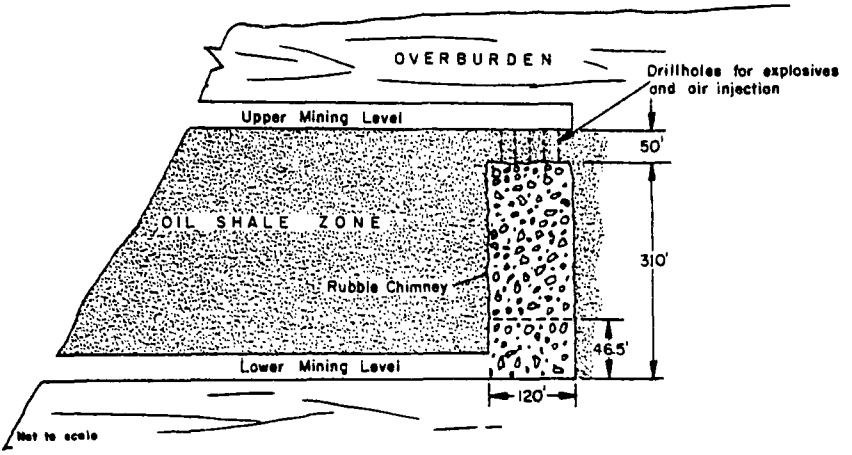
Multi-Mineral Integrated *In Situ* Process

The Multi-Mineral Integrated *In Situ* Process for the recovery of shale oil and associated minerals consists of three steps: underground mining and nahcolite recovery; retorting and hydrocarbon recovery; and leaching and soda ash/alumina recovery.

The process involves creating large underground chambers (stopes) by sequential blasting and removal of the oil shale from the stope. Gravity flow extraction is through funnel-like openings at the base. The stopes are separated by walls of unbroken oil shale. Their dimensions are variable, depending on the rock character and zone thickness. Extracted oil shale is crushed and screened into two sizes with the larger size being backfilled into the stope. The smaller size is then crushed and screened to separate nahcolite from the oil shale. Rejects from this operation are stored on the surface for future processing.

After backfilling with the top size, the stopes, full of sized oil shale, become underground retorts. The oil shale is retorted by hot gas introduced into the top of the retort and extracted at the base. The shale oil formed, along with the pyrolysis gas and water, is directed to a collection sump where the oil, water and gas are separated. The oil is pumped to the surface for marketing. After the oil shale has been retorted, residual carbon is left on the spent shale. The carbon is converted into a low-to-medium BTU gas which will be used for on-site electrical power generation. A simplified flow diagram is shown in Figure 7-17.

After the shale in the retort is cooled, soda ash and alumina are leached from the stope by spraying water over the top of the retorted shale and collecting this water as pregnant liquor at the base. This can be done in more than one stope simultaneously in a countercurrent process. The pregnant liquor is then pumped to the surface for recovery of the alumina and soda ash.



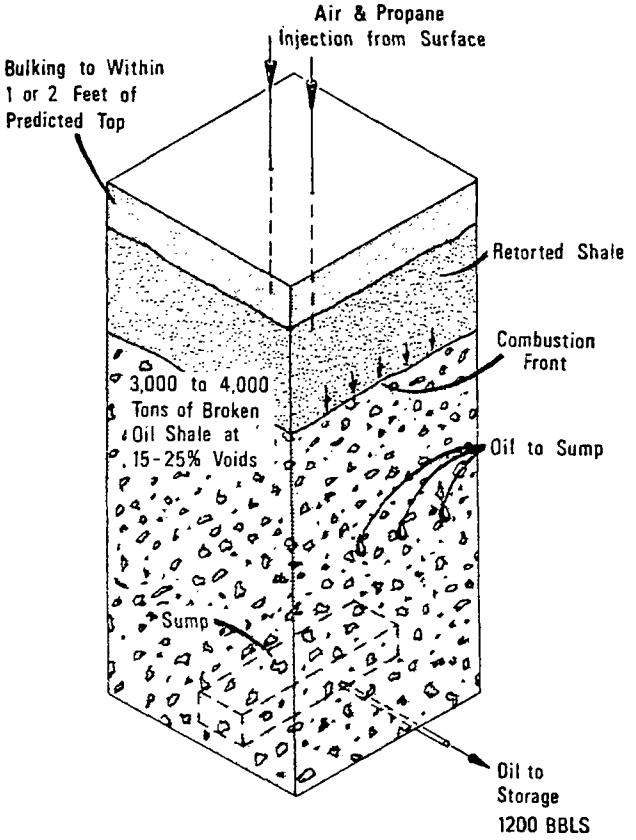


Figure 7-14. Occidental's Modified *in situ* retorting process.

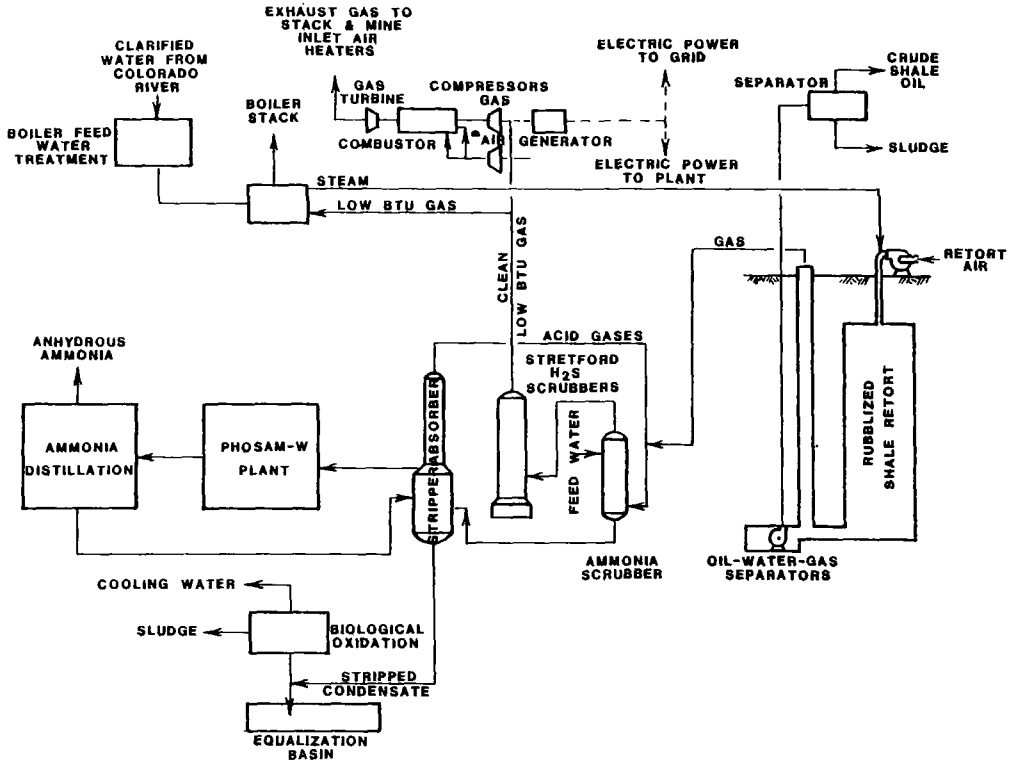


Figure 7-15. Flow diagram of Oxy MIS plant.

TABLE 7-20. OXY LOGAN WASH RETORTS 7 & 8 AIR EMISSIONS RATES
kg/hr (lb/hr)

Location	SO_2	H_2S	NO_X	HC	Particulates	CO
Retort stack	nil	169.2 (376)	nil	69.3 (154)	nil	1,638 (3,640)
Other sources[a]	13.9 (31)	nil	23.4 (52)	3.2 (7)		.9 (2)
Total	13.9 (31)	nil	23.4 (52)	70.7 (157)	3.2 (7)	1,638:9 (3,642)
Total tonnes/year (tons/year)[b]	80 (90)	986.4 (1,096)	135 (150)	410.4 (456)	16.2 (18)	9,561.7 (10,613)

[a] Includes boilers, heater-treaters, hot water circulators, and mine vent.

[b] Based on 8 months of operation.

TABLE 7-21. COMPOSITION OF MIS RETORT GAS[a]

Constituent	MWt	Raw Retort Gas Mass %	Raw Retort Gas Volume %	Cooled & Scrubbed Gas Mass %	Cooled & Scrubbed Gas Volume %
N_2	28	43.930	44.699	51.244	55.338
CO_2	44	38.153	24.704	40.471	27.865
CO	28	0.759	0.772	0.885	0.958
H_2	2	0.298	4.246	0.348	5.271
CH_4	16	0.650	1.158	0.758	1.763
C_2'S	29	0.315	0.309	0.267	0.383
C_3'S	43	0.232	0.154	0.271	0.191
C_4^+	60	0.618	0.309	0.721	0.364
O_2	32	0.086	0.077	0.100	0.095
H_2S	34	0.184	0.154	0.201	0.179
NH_3	17	0.369	0.618	—	—
H_2O	18	14.405	22.800	4.633	7.594
Total		100.	100.	100.	100.
H[b] (dry basis)		0.835		0.796	
C (dry basis)		14.245		13.76	
MWt		28.49			30.29
Gas rate, wet, 10^3 lb/hr:		6,366			5,482[c]
dry, 10^3 lg/hr:		5,449			5,229

[a] Source: Reference 6.

[b] Not including hydrogen in the water vapor and H_2S.

[c] About 46 x 30^3 lb/hr CO_2 are removed in gas treatment.

Geokinetics Horizontal *In Situ* Process

Geokinetics has dubbed its process LOFRECO, an acronym for "Low Front End Cost." Figure 7-18 depicts a schematic of the LOFRECO retort. Rubblization is achieved by detonating explosives within a pattern of blastholes, whereupon the overburden is lifted. The bottom of the retort is sloped to provide drainage into a sump from which product shale oil is pumped. Air injection holes and offgas holes are drilled at opposite ends of the rubblized zone. The oil shale is ignited at the air injection wells, and air is injected to establish and maintain a burning front that occupies the full thickness of the fragmented zone. As the front moves towards the offgas wells, oil shale ahead of the front is pyrolized and product oil drains to the sloping bottom of the retort to the production wells. Residual coke in the spent shale provides fuel for the burn front, the progress of which is monitored by thermocouples set in wells.

TABLE 7-22. TYPICAL ANALYSIS OF OXY RETORT 6 PROCESS WATER[a]

Parameter mg/l		2/15/79
Total Alkalinity (mg/l as $CaCO_3$)		8,000
Carbonate, (mg/l as $CaCO_3$)		1,500
Bicarbonate, (mg/l as $CaCO_3$)		6,500
Total Dissolved Solids		11,200
Total Suspended Solids		170
Sulfate		970
Chloride		110
Fluoride		33
Phenol		48
Nitrate		460
Oil & Grease		280
Silica		39
Sodium		3,400
Potassium		59
Arsenic		0.44
Iron	<	0.5
Magnesium		3
Manganese	<	0.02
Calcium		5
Boron		5
Vanadium	<	0.1
Copper	<	0.02
Molybdenum		0.06
Lithium		2
Zinc		0.02
Aluminum	<	0.1
Barium		2
Strontium		2
Lead	<	0.02
Nickel	<	0.02
Cadmium	<	0.02
Ammonia, as N		1,000
Sulfite		180

[a] Source: Reference 13.

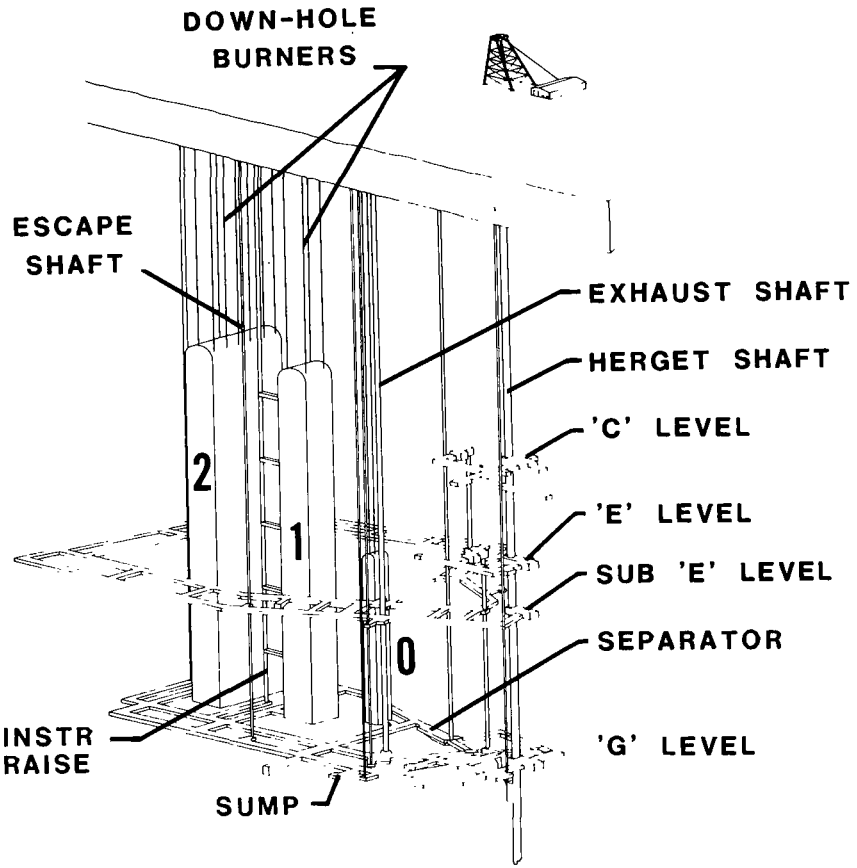


Figure 7-16. RBOSC Modular Development Phase Mine diagram.

Equity BX *In Situ* Process

The Equity BX Process involves the injection of superheated steam into the leached zone to retort oil shale *in situ*. Figure 7-19 is a flow diagram detailing the basic elements of project equipment and instrumentation. The operating sequence is as follows: water is produced from the leached zone and stored in the water storage pit until it can be processed in the water treatment plants. After treatment, water is fed to two steam generators capable of producing dry steam at 112 kg/cm^2 (1,600 psig) and 318 °C (605 °F). These two streams of dry steam are then fed to the superheater where the steam is superheated to 539 °C (1,000 °F) at 105 kg/cm^2 (1,500 psig). From the superheater, the steam is distributed to eight injection wells, the quantity going to each being proportionately controlled by automatic control valves. The steam is injected into the injection wells through insulated steel tubing which is suspended in steel casing perforated at the top and bottom of the leached zone. After the steam enters the leached zone, it gives up its heat and is produced as water accompanied by retorted oil and gas at production wells.

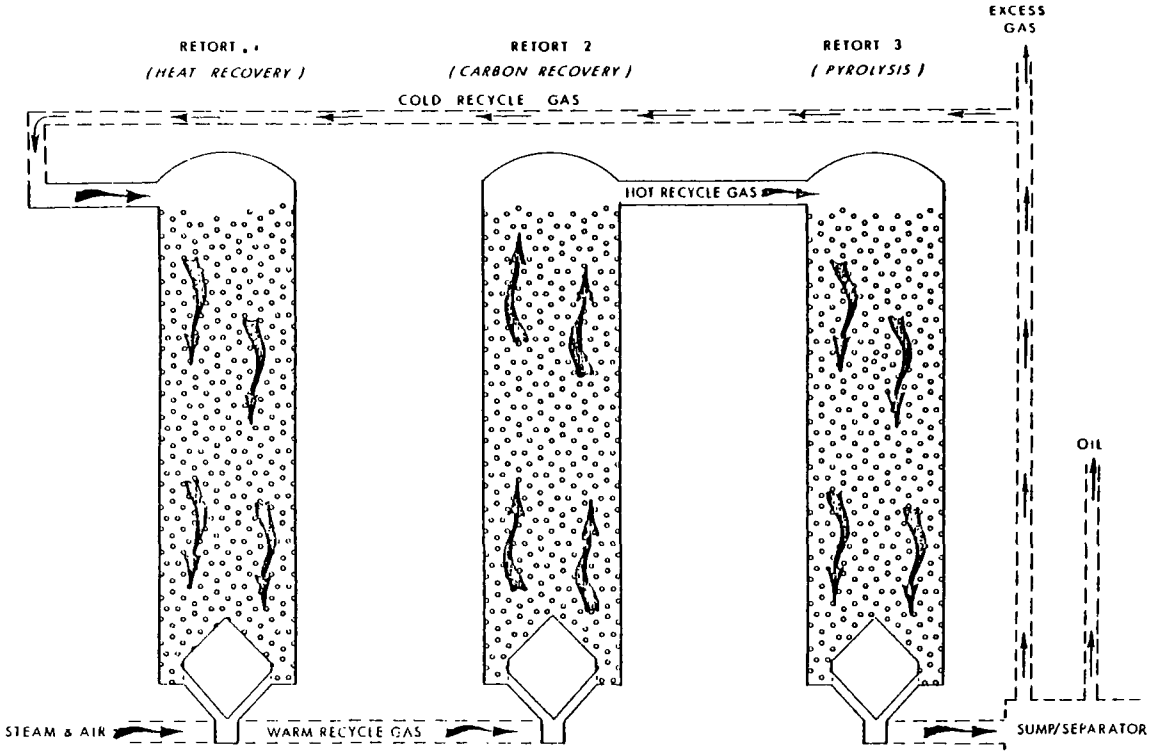


Figure 7-17. Multi Mineral Integrated *in situ* process.

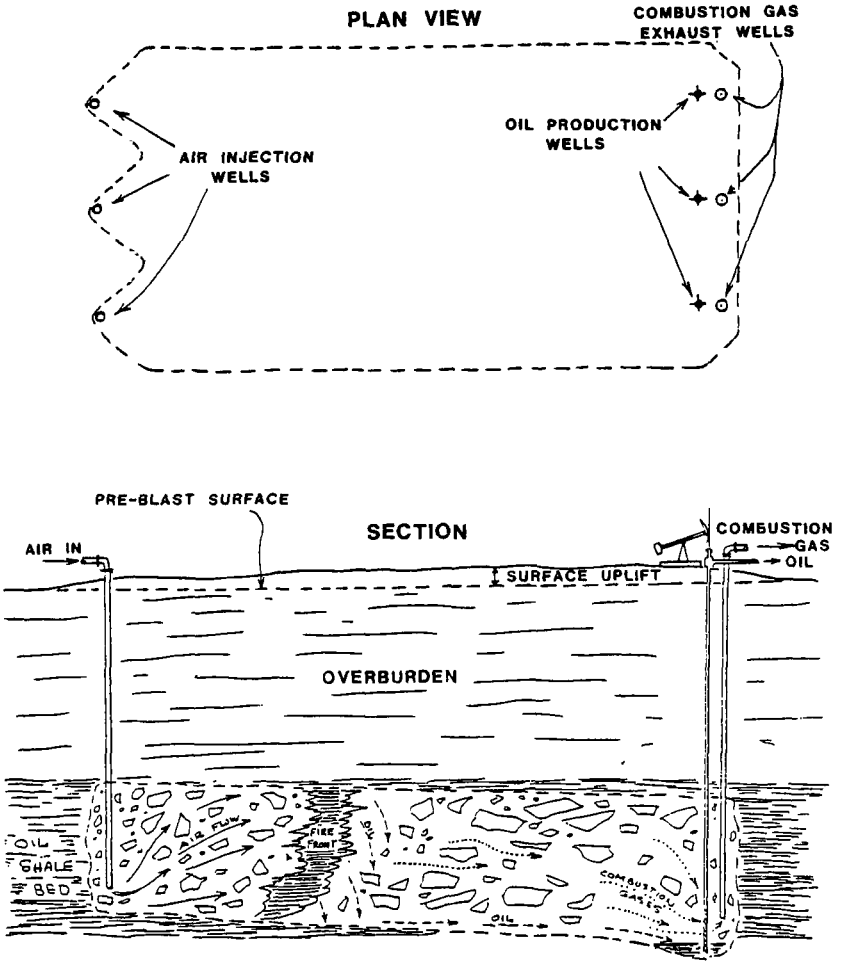


Figure 7-18. Plan and section of a typical Geokinetics horizontal *in situ* retort.

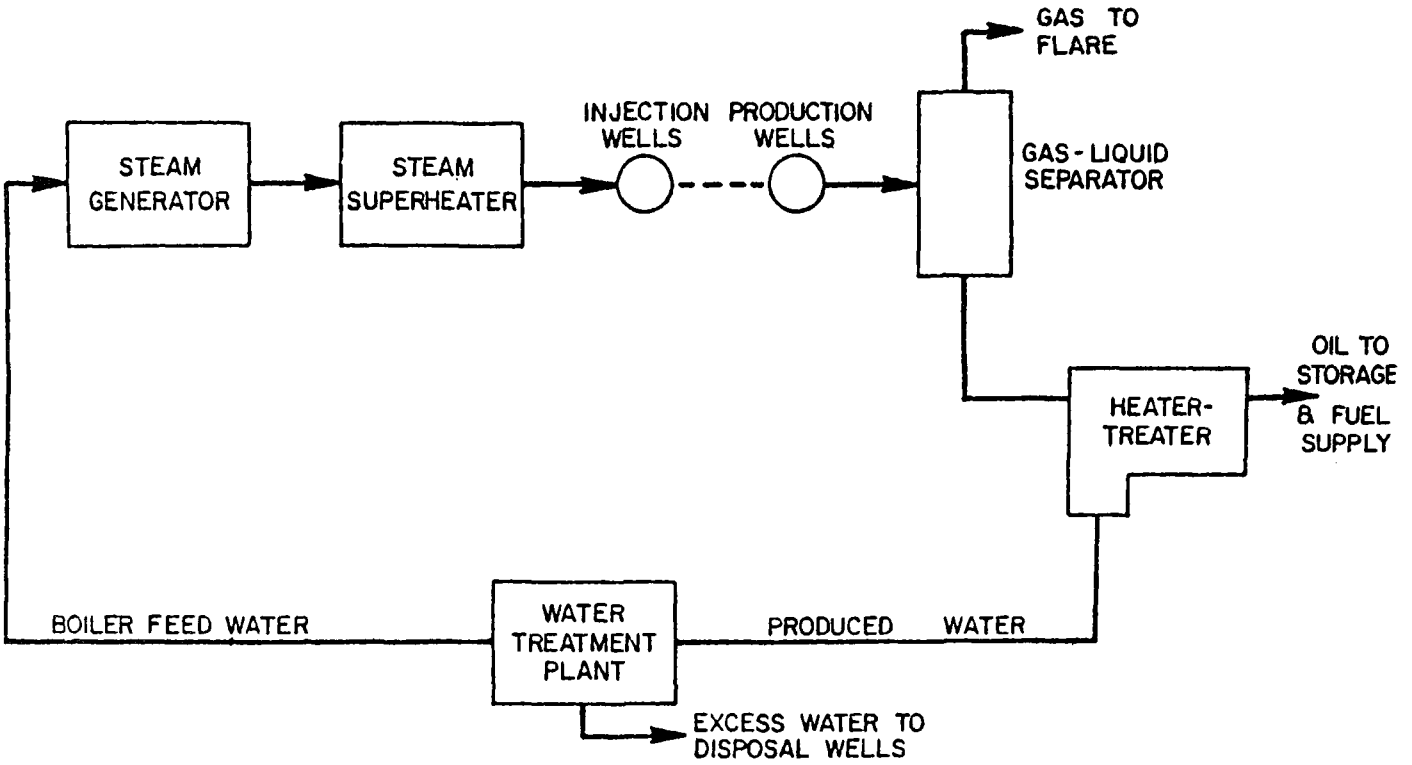


Figure 7-19. Equity Oil/DOE BX *in situ* shale project flow diagram.

TABLE 7-23. RIO BLANCO MDP ESTIMATED EMISSIONS[a]
kg/hr (lb/hr)

Source	Particulate	SO_2
1. Thermal oxidizer scrubber	4.99 (11.0)	75.80 (167.1)
2. Steam boiler	0.32 (0.7)	7.53 (16.6)
3. Shaft construction		
a. Mine vent	0.73 (1.6)	— —
b. Vehicular movement	2.45 (5.4)	— —
c. Storage tank	— —	— —
d. ROM ore handling	2.76 (9.1)	— —
Total	12.61 (27.8)	83.33 (183.7)

[a] Source: Reference 14.

Each production well is equipped with a "gas lift" system to assist in producing the production wells, the product stream goes through a free water knockout and a heater treater to separate oil, gas, and water. Water is returned to the water storage pit for reuse, oil is stored, and gas is recovered for use as steam-generator fuel gas.

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