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Compendium Reports on Oil Shale Technology

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COMPENDIUM REPORTS ON OIL SHALE TECHNOLOGY

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory—Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment, and
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs.

The study resulting in this report provides technical support to a program for the design and implementation of groundwater quality monitoring programs for Western oil shale operations. This report summarizes available data on oil shale resource recovery.

This document presents a summary of research and development related to oil shale operations. Topics considered are: mining, oil shale retorting, shale oil upgrading, organic and inorganic characteristics of oil shale products, and potential environmental controls (including water availability) on the oil shale industry. The summaries stress technologies which are proposed for Federal Oil Shale Leases U-a and U-b in eastern Utah. Thus Paraho and TOSCO retorting processes are considered in some detail. Other oil shale technologies, such as in situ development, are also discussed but in less detail.

The research summarized in this report is one component of the technical basis for developing monitoring programs for oil shale operations. As such, these technology summaries may be used by industrial developers and their consultants, as well as the various local, State, and Federal agencies with responsibilities in environmental planning and monitoring.

Further information on this study and the subject of monitoring development, in general, can be obtained by contacting the Monitoring Systems Design and Analysis Staff, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nevada.

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PREFACE

General Electric—TEMPO, Center for Advanced Studies, is conducting a 5-year program dealing with design and implementation of groundwater quality monitoring programs for western oil shale development. The type of oil shale operation being evaluated in this study is that presently proposed for Federal Prototype Oil Shale Leases U-a and U-b in Eastern Utah. This type of operation includes room-and-pillar mining, surface retorting utilizing Paraho and TOSCO II processes, and surface disposal of processed (or spent) oil shale. This effort is using a stepwise monitoring methodology developed by TEMPO.

This report represents a compilation of information on oil shale technology gathered to support the development of the monitoring program. Clearly, an understanding of the mining and industrial processes associated with oil shale operations is needed to effectively design environmental monitoring plans.

The technical information summarized in this document supports a companion report which describes the initial phase of the monitoring design study. This initial phase has resulted in the development of a preliminary priority ranking of potential pollution sources and their associated pollutants. This priority ranking will be utilized in subsequent phases of the research as the basis for defining monitoring needs and for ultimately designing the monitoring program.

In the next phases of this research program, a preliminary monitoring design is to be developed and implemented in the field. Initial field study results may lead to reevaluation of monitoring priorities. The final product of the 5-year program will be a planning document that will provide a technical basis and methodology for the design of groundwater quality monitoring programs for oil shale industrial developers and the various governmental agencies concerned with environmental planning and protection.

ABSTRACT

The development of western oil shale resources has been an evolutionary process in which production and environmental control technologies have evolved from current mining and petroleum industry practices. In addition, new technologies are being developed which are specific to shale oil recovery. The compendium or summary reports included in this document consider the various production processes (mining, retorting, and oil upgrading) and key environmental factors (organic and inorganic characterization, environmental control, and limitations) related to oil shale development. This state-of-the-art survey supports a study designing a groundwater quality monitoring program for oil shale operations such as that proposed for Federal Oil Shale Lease Tracts U-a and U-b. Hence, the reports emphasize technologies applicable to this development while also providing a general overview of oil shale technology.

This report was submitted in partial fulfillment of Contract No. 68-03-2449 by General Electric Company—TEMPO under the sponsorship of the U.S. Environmental Protection Agency.

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LIST OF ABBREVIATIONS

AA	atomic absorption spectrophotometry
ACS	American Chemical Society
ANFO	ammonium nitrate fuel oil
API	American Petroleum Institute
ATP	adenosine triphosphate
blox	biological oxidation
BOD	biochemical oxygen demand
Bu Mines	U.S. Bureau of Mines
C-a	oil shale lease tract Colorado-a
C-b	oil shale lease tract Colorado-b
COD	chemical oxygen demand
DDP	detailed development plan
DEA	diethanolamine
DEI	Development Engineering, Inc.
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetracetic acid
EIS	environmental impact statement
EOR	enhanced oil recovery
EPA	U.S. Environmental Protection Agency
ERDA	U.S. Energy Research and Development Administration
GC	gas chromatography
GC/MS	gas chromatography and mass spectrometry
GPC	gel permeation chromatography
H/C	hydrogen carbon ratio
HPLC	high pressure liquid chromatography
I.D.	inside diameter
LC	liquid chromatography
LC_{50}	acute toxicity of exposure resulting in 50 percent mortality
LC/MS	liquid chromatography and mass spectrometry
LD_{50}	median lethal dose
LERC	Laramie Energy Research Center
LHD	load haul dump
m/e	mass per electron

MS	mass spectrometry
NSF	National Science Foundation
N.T.U.	Nevada-Texas-Utah process
O.D.	Outside diameter
PAH	polycyclic aromatic hydrocarbons
Paraho-DH	paraho direct heating mode
Paraho-IH	Paraho indirect heating mode
POM	polycondensed organic matter
PSD	prevention of significant deterioration
RISE	rubble in-situ extraction
SSMS	spark source mass spectrometry
SCFSD	standard cubic feet stream per day
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
THF	tetrahydrofluoride
TLC	thin layer chromatography
TNT	tinitrotoluene
TOSCO II	The Oil Shale Corporation process
U-a	oil shale lease tract Utah-a
U-b	oil shale lease tract Utah-b
USDI	U.S. Department of Interior
W-a	oil shale lease tract Wyoming-a
W-b	oil shale lease tract Wyoming-b

Chemicals, Elements, and Other Terms

Å	angstrom
A	adsorbance
Ag	silver
Al	aluminum
As	arsenic
Ba	barium
Be	beryllium
C	Carbon
Ca	calcium
CH_4	methane
Cl^-	chloride ion
CO	carbon monoxide
CO_2	carbon dioxide
COH_b	carboxyhemoglobin

Cr	chromium
CS_2	carbon disulfide
Fe	iron
H	hydrogen
HC	hydrocarbon
HCl	hydrochloric acid
H_2O	water
HF	hydrofluoric acid
HS^-	sulfide ion
H_2S	hydrogen disulfide
H_2SO_4	sulfuric acid
K	potassium
λ	wavelength
Li	lithium
m-	meta
Mg	magnesium
Mn	manganese
Mo	molybdenum
N	nitrogen
n-	normal
Ni	nickel
NO_2	nitrogen dioxide
NO_x	nitrogen oxide
NH_3	ammonia
NH_4^+	ammonium ion
O	oxygen
o-	ortho
O_3	ozone
P	phosphorus
p-	para
Pb	lead
S	sulfur
Se	selenium
Si	silicon
SO_4=	sulfate ion
Ti	titanium
U	uranium
V	vanadium
Zn	zinc

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SECTION 1

OVERVIEW OF OIL SHALE DEVELOPMENT

WORLDWIDE OIL SHALE RESERVES

The combined total of the world's petroleum crude oil is estimated to be 318 billion cubic meters (m^3)(2 trillion bbl) in its ultimate resources (Norman, 1973). By about A.D. 2000, mankind will have consumed more than one-half of the recoverable petroleum resources (Hubbert, 1976). Even with enhanced oil recovery (EOR) techniques and additional significant discoveries during the next two decades, the world energy demand will require supplemental production of considerable quantities of oil from oil shale and tar sands. Though oil can be produced from coal, the technology to do so is, at this stage, less mature than that to produce oil from oil shale.

The world total of known oil shale resources is approximately 477 billion m^3 (3 trillion bbl) of oil. U.S. western shales of the Green River Formation alone exceed 318 billion m^3 (2 trillion bbl) of oil in place, as indicated in Table 1-1 (Donnell, 1977). The thickness of the Green River Formation ranges from about 3 meters (10 feet) to 610 meters (2,000 feet) with overburden thickness ranging from zero at outcrops to 490 meters (1,600 feet). The most economical deposits are at least 9 meters (30 feet) in thickness and yield at least 95 liters (25 gallons) of oil per 0.91 tonne (1 ton) of oil shale. The known resources of the high-grade shale are equivalent to 95,500 million m^3 (600 billion bbl) of oil (Figure 1-1), out of which at least 13 billion m^3 (80 billion bbl) of oil are recoverable by present technology (Yen, 1976a). For comparison, this amount of oil far exceeds the sum of the resources at Prudhoe Bay in Alaska and in the Continental Shelf reserves on the U.S. west coast.

Oil shale industries have developed over the past 100 years in France, Scotland, Sweden, Spain, South Africa, Australia, the Estonia S.S.R., China, and Brazil (Prien, 1976). Attempts in the United States to develop oil shale into a mature industry have lasted for more than 50 years (McKee, 1925). In the early days, there was even a journal devoted to this endeavor. However, progress has been slow toward realizing a fully matured oil shale industry. For example, the estimated supply of shale oil for 1985 is only 0.2 to 2.1 Quads (1 Quad = 27.8 million m^3 [175 million bbl] of crude, or 10^{15} Btu), the lower figure being more realistic. This means that shale oil probably will account for only about 1 percent of total oil consumption in 1985, as shown in Table 1-2 (Yen, 1976a). The constraint is imposed by two major factors:

1. The price of petroleum crude oil. In June 1977, the top price of crude was $13.50 per 0.2 m^3 (1 bbl). This price leaves little

TABLE 1-1. GLOBAL OIL SHALE RESOURCES[a]

Country	Billions of m^3	(Billions of bbls)
United States	318.0	(2,000.2)
Brazil	127.3	(800.8)
U.S.S.R.	17.9	(112.6)
Zaire	16.0	(100.6)
Canada	7.0	(44.0)
Italy (Sicily)	5.6	(35.2)
China	4.4	(27.9)
Morocco	0.6	(4.0)
Sweden	0.4	(2.5)
Burma	0.3	(2.0)
West Germany	0.3	(2.0)
Great Britain	0.2	(1.0)
Thailand	0.1	(0.8)

[a] From Donnell, 1977.

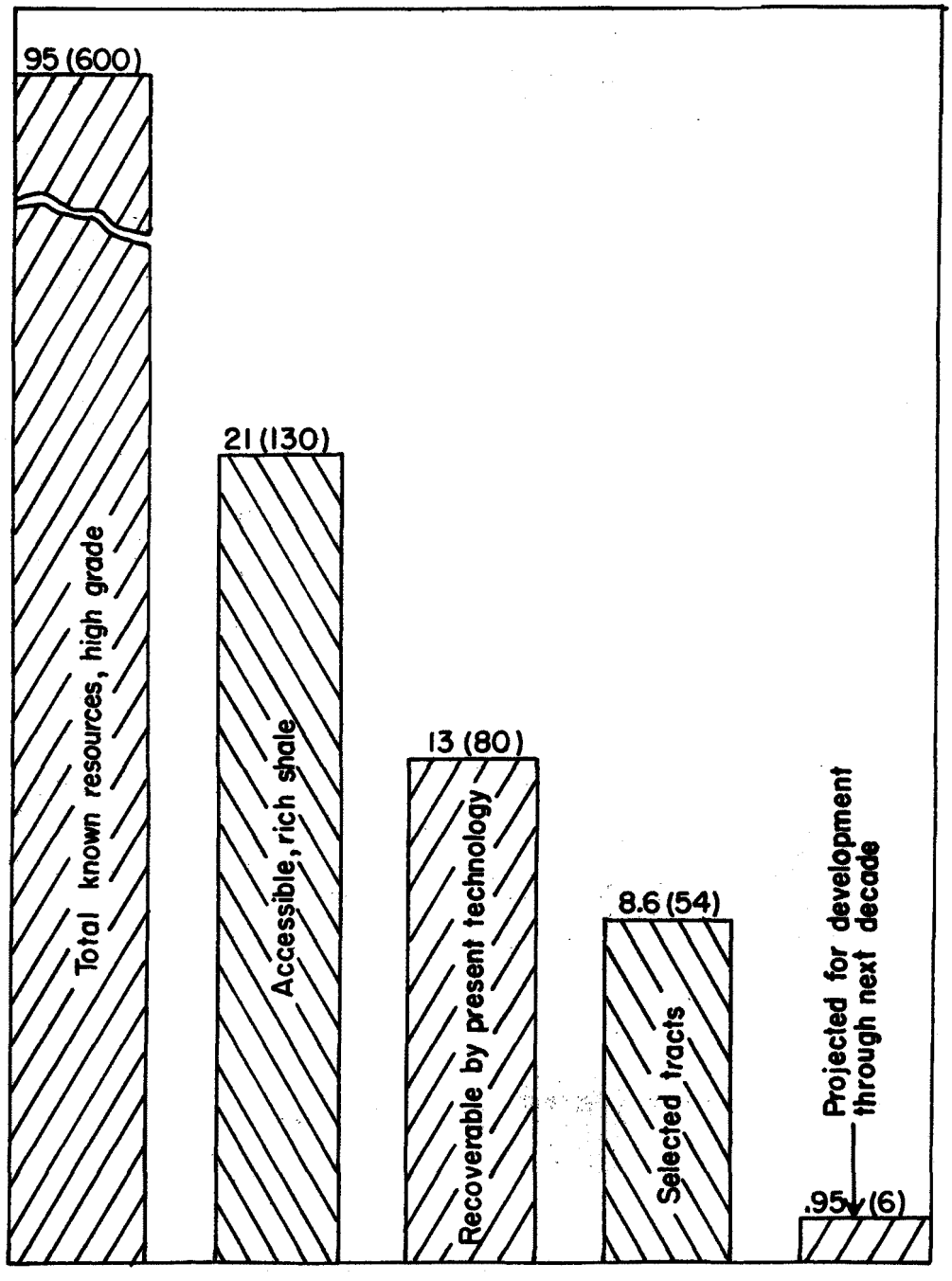

Figure 1-1. Oil shale resources (in billions of cubic meters [barrels] of oil) present on tracts that may be developed in the next decade, present on tracts designated by Federal Government (USDI, 1973), removable by present technology, accessible, and total high-grade resources (from Yen, 1976a).

TABLE 1-2. ESTIMATES OF SHALE OIL SUPPLY IN 1985[a]

Agency	Supply			
	Estimate dates	Quads	(millions of m^3)	(millions of bbl)
Federal Energy Administration Project Independence	11/74	2.1[b]	(58.4)	(367.5)
Ford Foundation	09/74	1[c]	(27.8)	(175)
National Petroleum Council	12/72	1.5[d]	(25.8)	(162.5)
National Petroleum Council	08/74	0.2	(5.5)	(35)
National Academy of Engineering	05/74	1	(27.8)	(175)
Joint Committee on Atomic Energy	05/74	0.2	(5.5)	(35)
Institute of Gas Technology	12/73	2.1	(58.4)	(367.5)
Commerce Technical Advisory Board	02/75	0.5	(14.0)	(87.5)
Exxon Energy Outlook	01/76	0.7[e]	(19.5)	(122.5)
Exxon Energy Outlook	02/77	0.5[e]	(14.0)	(87.5)

[a] The total energy demand for 1985 is estimated as 108 Quads (Q)(3.1 percent growth) or 125 Q (4.3 percent growth). Total domestic supply is approximately 94 Q and still requires 14 Q (based on 3.1 percent growth) from imports. Domestic oil supply is about 25 Q, and synthetic oil supply is estimated as 0.3 Q in 1985.

[b] Based on $11 oil accrued supply.

[c] Based on technological growth of pre-1974 status.

[d] This value is for Case I; for Cases II and III, 0.80 Q; and for Case IV, 0.20 Q. Case I is the most optimistic supply condition, and Case IV is the lowest level based on 1970 trends.

[e] Including synthetic oil from coal.

margin for extracting oil from shale. Thus the shale oil extraction industry hinges on the future international and national economic and political situation.

2. The availability of pollution control science and technology. Present data on the environmental impact of oil shale extraction, especially in relation to human health, are insufficient.

Currently, petroleum companies are becoming more optimistic about the commercial prospects of the 95.4 billion m^3 (600 billion bbl) of syncrude locked in the Green River Formation of the tristate area of Colorado, Utah, and Wyoming (Chemical Week, 1977). This optimism is based on technological and economic factors that may give shale oil a good chance to compete with conventional crude oil.

The speed with which western oil shale resources are developed is related to a variety of technological, economic, environmental, political, and legal factors. The following review of the present status of the four Colorado and Utah leases resulting from the Federal Prototype Oil Shale Leasing Program provides an overview of near-term plans (Table 1-3).

On August 30, 1977, the Department of Interior approved the revised Detailed Development Plan (DDP) for Tract C-b in Colorado. This plan calls for development using a modified in situ process. Ashland Oil and Occidental Petroleum, partners on Tract C-b, are initiating mine development at this time. However, several environmental groups (Environmental Defense Fund, Colorado Open Space Council Mining Workshop, and Friends of the Earth) have asked the U.S. Department of Interior (USDI) to prepare a supplemental environmental impact statement (EIS) on C-b (and C-a). The USDI felt that the original EIS was sufficient, so the request was denied.

On September 22, 1977, the USDI approved a modified in situ DDP for Colorado Tract C-a. Development is being pursued by Rio Blanco Oil Shale Corporation (Standard of Indiana and Gulf Oil Corporation).

The status of the Utah oil shale tracts (U-a and U-b) is somewhat more complex. Certain questions concerning the basic ownership of the tracts have arisen as a result of several recent legal actions:

- A suit is being pursued by the State of Utah against the U.S. Department of Interior in which Utah has laid claim to 157,255 acres of land (which includes Tracts U-a and U-b) as lands in lieu of State lands previously disposed of by the Federal Government. The U.S. District Court in Salt Lake City has ruled in favor of the State of Utah. This decision is being appealed by the Federal Government.
- Peninsula Mining, Inc. has filed for a preferential lease to the 157,255 acres obtained by the State of Utah as in lieu of lands in the above described decision.

TABLE 1-3. CURRENT OIL SHALE DEVELOPMENT PROJECTS

Project or location	Sponsor	Technique	Syncrude capacity m^3/day (bbl/day)	Estimated cost ($ million)
Federal Tract C-b (Colorado)	Occidental Petroleum and Ashland Oil	Modified in situ retorting (no surface retorting)	9,063 (57,000)	442
Colony Development (Colorado)	Atlantic Richfield and The Oil Shale Corp.	Room-and-pillar mining; TOSCO II retorting (heated ceramic spheres)	7,473 (47,000)	1,132
Federal Tract C-a (Colorado)	Gulf Oil and Standard Oil (Indiana)	Modified in situ retorting (with surface retorting)	239 (1,500)	93[a]
Multimineral (Colorado)	Superior Oil	Room-and-pillar mining; circular-grate retorting; recovery of soda and alumina	2,115 (13,300)	300[b]
Sand Wash (Utah)	The Oil Shale Corp.	Combination in situ and surface retorting	11,925 (75,000)	1,000
Parachute Creek (Colorado)	Union Oil of California	Room-and-pillar mining; direct heated rock pump retorting	1,240 (7,800)	123[c]
White River Shale Project (Utah) [Federal Tracts U-a and U-b]	Sun Oil, Phillips Petroleum, and Standard Oil (Ohio)	Room-and-pillar mining and surface retorting (Paraho and TOSCO II)	15,900 (100,000)	1,610[d]

[a] For 5-year development program with intermittent production in demonstration units; projected commercial capacity is 12,160 m^3/day (76,000 bbl/day).

[b] For the first module of stated capacity.

[c] For prototype module.

[d] Much smaller demonstration unit would be part of $246-million development program proposed as joint venture with ERDA.

- Recently (January 1977), a Colorado court ruled that under certain conditions unpatented oil shale mining claims could be valid claims. Unpatented claims exist on Tracts U-a and U-b.

As a result of these ownership issues, the White River Shale Project sought and received (on May 31, 1977) an injunction effectively suspending their lease agreement until these matters could be clarified. This injunction is being appealed by the Federal Government at this time.

Other than these activities, the Department of Energy has initiated a number of cost-sharing contracts with various industries—for example, the Equity Oil Company project for superheated steam recovery of leached zone oil shale by in situ method, the Talley-Frac Corporation and Geokinetics techniques for the true in situ recovery (present contract to Talley-Frac Corporation is for detonation and fracturing only), and the Occidental process of modified in situ shale recovery methodology. Other than the research and development effort of the Laramie Energy Research Center, different government laboratories such as Lawrence Livermore Laboratory, Sandia Laboratories, Los Alamos Scientific Laboratory, and Oak Ridge National Laboratory, as well as a number of universities, contribute greatly toward process modeling, resource recovery, and environmental aspects of oil shale development. Development plans by private industrial concerns, such as Colony, Union Oil, Superior, and TOSCO, are summarized in Table 1-3.

Thus the near-term future of western oil shale development is somewhat uncertain. However, petroleum specialists in government and industry have conjectured that by the end of this century, the U.S. economy and resources can easily develop an oil shale processing industry with an aggregate syncrude output of 160,000 m^3 to 320,000 m^3 (1 million to 2 million bbl) per day.

GEOLOGICAL SETTING OF UINTA BASIN

Oil shales from the Green River Formation of the Western United States were formed from the sediments deposited in the two Eocene lakes: Lake Uinta in Colorado and Utah and Lake Gosiute in Wyoming (Figure 1-2). During their life span of 6 million years, these lakes were chemically stratified into two stable zones (Bradley, 1931). The upper layer was relatively fresh and was able to support life. The lower layer, primarily a solution of sodium carbonates, was a strongly basic and reducing environment. This chemical environment contributed to the preservation of organic matter, largely from algal productivity in the upper layer of the lakes.

During much of the Eocene period, Lake Uinta covered a large area from central and northeastern Utah to northwestern Colorado. Within this large area, many types of environments existed. Sediments deposited in the western and southwestern parts of the Uinta Basin in Utah are lithologically and ecologically different from their stratigraphic equivalent to the east in the Piceance Creek Basin of Colorado. For example:

- The lower part of the Parachute Creek Member of the Green River Formation (the uppermost member of this formation) in the

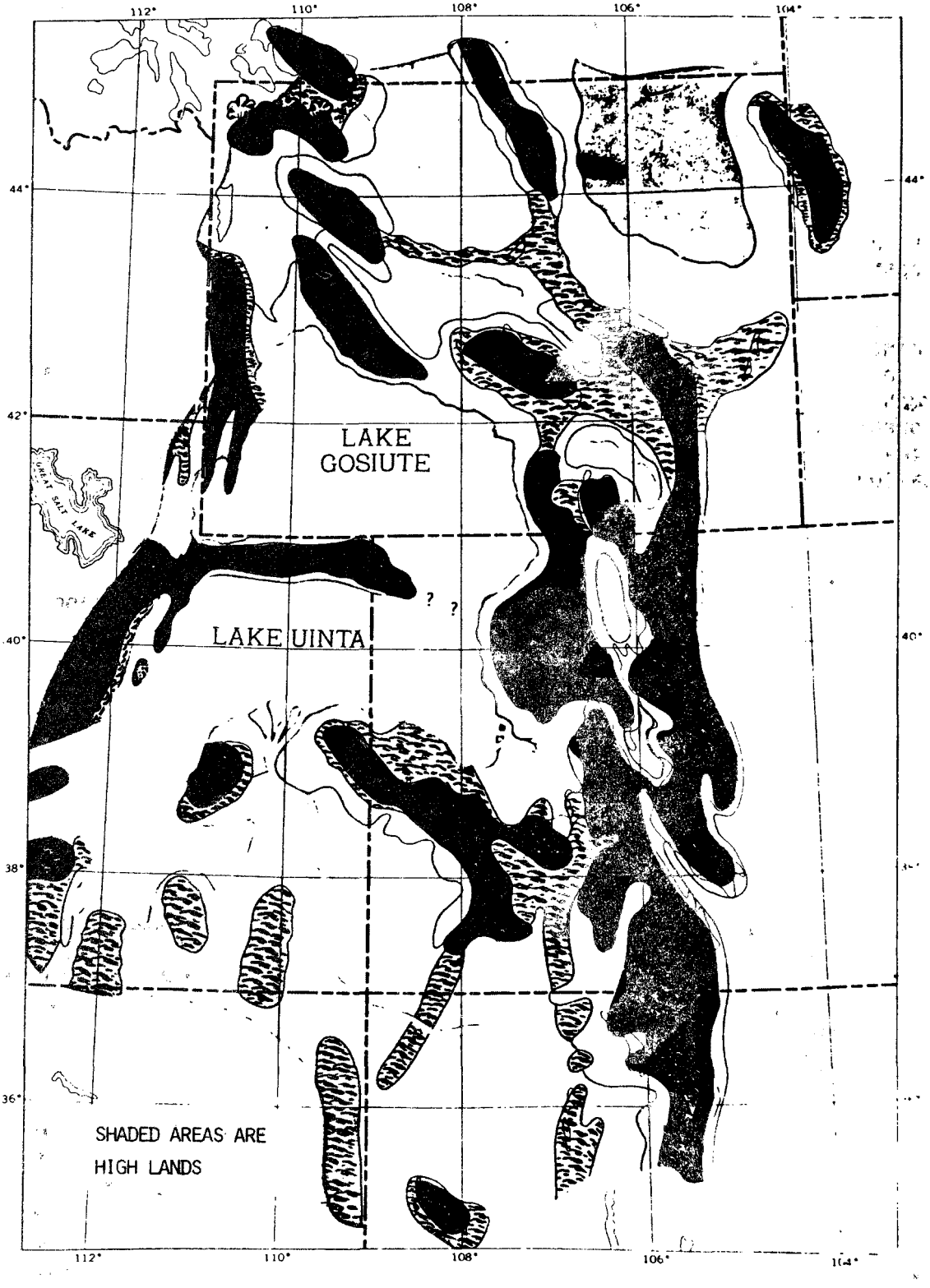

Figure 1-2. Paleogeography in late early to middle Eocene time (from McDonald, 1972).

Piceance Creek Basin contains bedded evaporites that are absent in the Uinta Basin.

- The Garden Gulch Member, which underlies the Parachute Creek Member, contains rich oil shales in the Piceance Creek Basin, while they are much thinner and rarer in the Uinta Basin.

The Uinta and Piceance Basins were allowed to follow differing developmental pathways because of the presence of the Douglas Creek Arch, which separates the two basins (McDonald, 1972).

The Piceance Creek Basin is economically very important because it contains the richest and thickest oil shale deposits in the world. The Parachute Creek Member contains most of the oil shale in the Green River Formation. Much of the oil in the Parachute Creek Member is contained in the Mahogany Zone (Figure 1-3). The rich brown color of the kerogen in these strata explains the name. Certain beds in this zone yield as much as 342 liters (90 gallons) of oil per 0.91 tonne (1 ton). The zone varies in thickness from less than 15 meters (50 feet) to more than 60 meters (200 feet).

The Uinta Basin has undergone less exploration and evaluation than the Piceance Creek Basin. The most important oil shale deposits are located in the eastern part of the basin, where they occur in a 122-meter (400-foot) thick sequence above and below the Mahogany Zone.

Most of the oil shale development in Wyoming occurred in Lake Gosiute. This lake was separated from Lake Uinta by the east-west-stretching Uinta Mountains, which contributed sediments to both lakes. The oil shales in Wyoming are located in two basins, the Washakie and the Green River. Both areas contain low-grade oil shale, i.e., the quantity is less than 57 liters (15 gallons) of oil per 0.91 tonne (1 ton). At times, Lake Gosiute was quite saline, resulting in large amounts of bedded trona or trona mixed with halite.

In conclusion, the deposits in Uinta Basin are most extensive and have not yet been fully explored. The Utah shales appear to have less trona-type materials than those found in Wyoming. The ownership distribution of western oil shale lands, which will play an important role in their development, is illustrated in Figure 1-4.

OIL SHALE

A number of diverse fine-grained rocks, termed oil shales, have been found to contain refractory organic material that can be refined into fuels. The organic material in these rocks is composed of a bitumen fraction (soluble in common organic solvents) consisting of about 20 percent by weight of identifiable organics, the remainder being insoluble kerogen. All oil shales appear to have been deposited in shallow lakes or seas that supported a dense algal biota. The composition and oil yields of some oil shales are listed in Table 1-4 (Yen and Chilingarian, 1976).

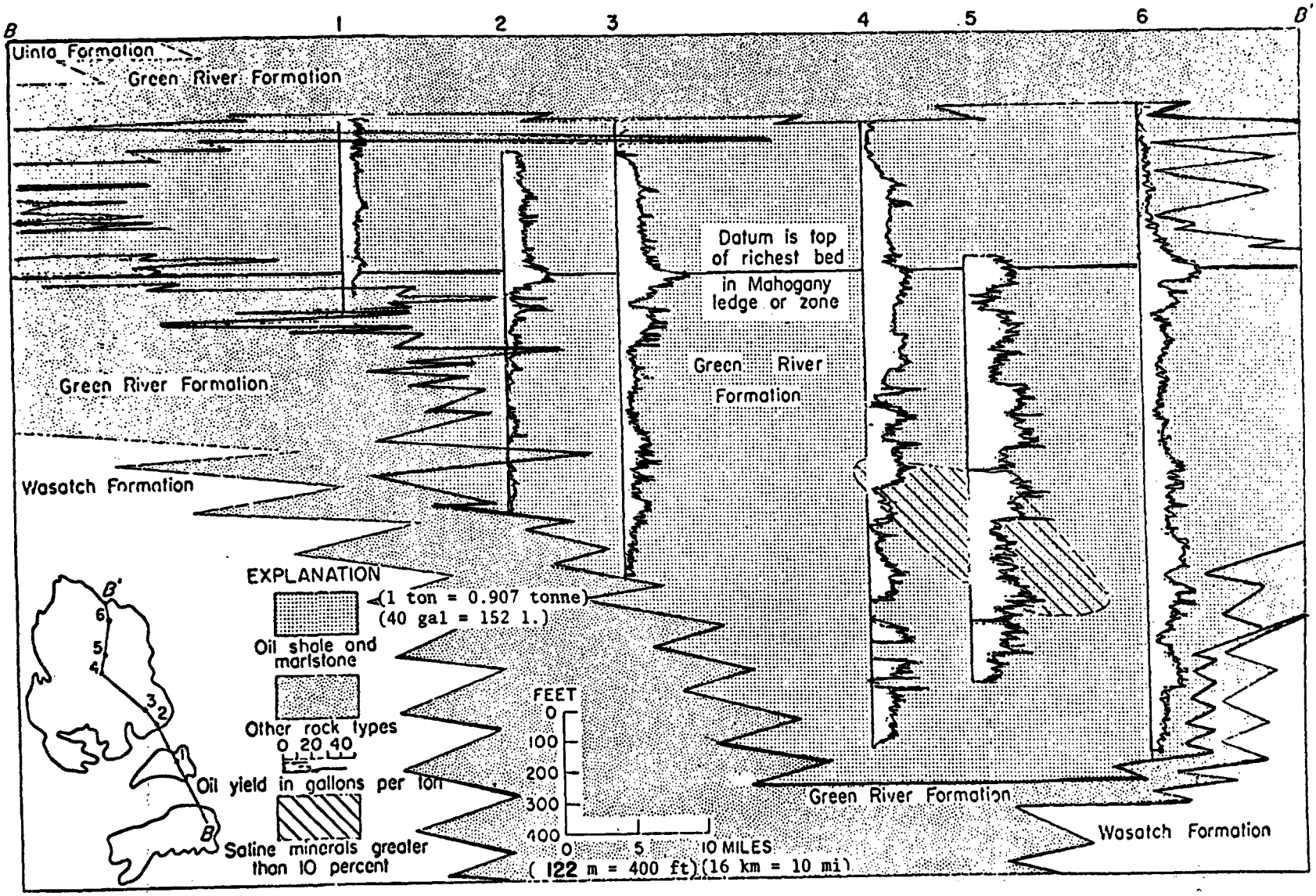

Figure 1-3. Cross section B-B' of Green River Formation in Piceance Creek Basin, Colorado (U.S. Department of Interior, 1973).

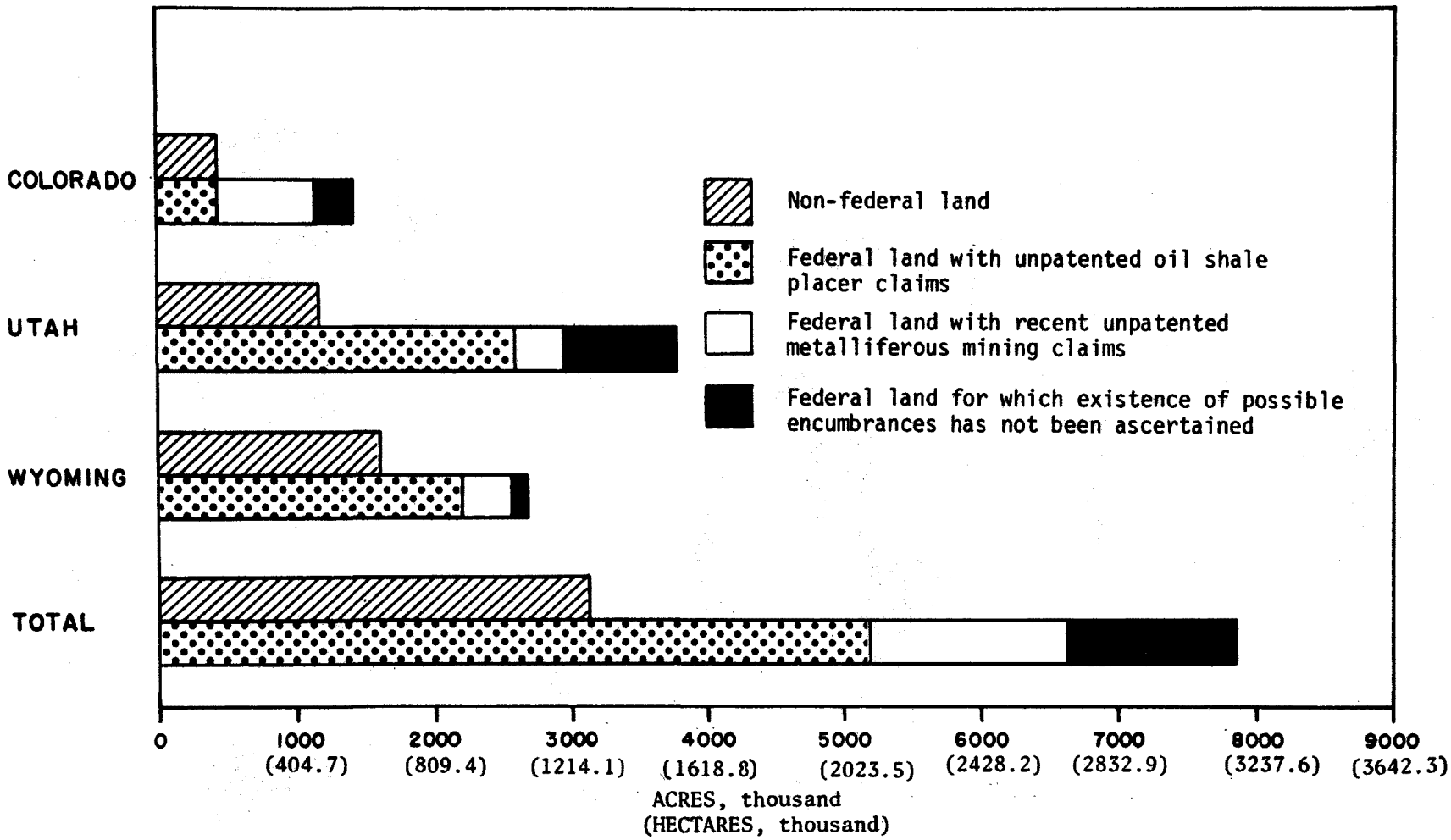

Figure 1-4. Oil shale lands—Green River Formation (National Petroleum Council, 1972).

TABLE 1-4. COMPOSITION AND OIL YIELD OF SOME OIL SHALES

Location of sample	Organic carbon (percent)	Sulfur (percent)	Nitrogen (percent)	Ash (percent)	Oil yield liters/0.91 tonne (gallon/ton)	
Kiligwa River, Alaska[a]	53.9	1.5	0.30	34.1	528.2	(139.0)
Piceance Creek, Colorado[a]	12.4	0.63	0.41	65.7	106.4	(28.0)
Elko, Nevada[b]	8.6	1.1	0.48	81.6	31.92	(8.4)
Dunnet, Scotland[a]	12.3	0.73	0.46	77.8	83.6	(22.0)
Ione, California[b]	62.9	2.1	0.42	23.0	197.6	(52.0)
São Paulo, Brazil[a]	12.8	0.84	0.41	75.0	68.4	(18.0)
Puertollano, Spain[a]	26.0	1.7	0.55	62.8	178.6	(47.0)
Shale City, Oregon[a]	25.8	2.2	0.51	48.3	182.4	(48.0)
Coolaway Mt., Australia[a]	81.4	0.49	0.83	4.4	760.	(200.0)
Soldiers Summit, Utah[b]	13.5	0.28	0.39	66.1	64.6	(17.0)
Ermelo, South Africa[a]	52.2	0.74	0.84	33.6	380.	(100.0)
New Glasgow, Canada[a]	7.92	0.70	0.54	84.0	9.4	(2.4)

[a]Data from Robinson, 1976.

[b]Data from McKee, 1925.

Oil shales interpreted in terms of material science can be classified as "composites"—tightly bound organics and inorganics as shown in Figure 1-5. An illustrated hypothetical structure is shown in Figure 1-6. The proportion of organics in oil shale rarely exceeds 25 percent by weight. The weight percentage, however, of organics for a typical oil shale yielding 95 liters (25 gallons) of oil per 0.91 tonne (1 ton) is only about 14 percent (Figure 1-7).

Kerogen constitutes the bulk of available organic material in oil shale. Therefore, any liberation of useful hydrocarbons depends on the degree to which kerogen can be converted to liquid fuel precursors. Green River kerogen consists of polycyclic subunits interconnected by long-chain alkanes and isoprenoids. This matrix also contains substantial amounts of entrapped uncondensed alkanes and fatty acids. The extensive cross-linking of these subunits produces the insolubility characteristic of kerogen (Yen, 1976b). The structure of kerogen of Green River oil shale has recently been elucidated by Young and Yen (1977) (Figure 1-8). Individual studies of clusters and bridges are presented in Figure 1-9 (Yen, 1976c).

The average composition of the bitumen from the Green River oil shale is summarized in Table 1-5. The major components are n-alkanes, branched and cyclic alkanes, aromatic oils, resins, and asphaltenes (Robinson, 1976). Biomarkers such as isoprenoids, stearanes, pentacyclic triterpanes, carotenes, and porphyrins have been identified (Figure 1-10).

The mineral composition has been recently reviewed and summarized. In general, there are carbonates, silicates, pyrites, and other sulfides (Shanks et al., 1976). Some of the minerals are listed in Tables 1-6 and 1-7.

The wide range of properties observed in oil shales from different areas prohibits development of all but a very generalized concept of their genesis. Nonetheless, certain factors appear to be necessary for deposition and collection of the inorganic and organic material that will, after burial, become oil shale. It is evident that oil shales result from the contemporaneous deposition of fine-grained mineral debris and organic degradation products derived from the breakdown of biota. Conditions leading to the collection and concentration of the organic and inorganic components of oil shales must then include abundant organic productivity, early development of anaerobic conditions, and longevity of the lake systems.

Oil shales probably developed in bodies of water, either marine or fresh, that were fairly calm, such as isolated marine basins, lakes, or deltaic swamps. The prevailing climate during deposition was fairly dry, similar to that considered favorable for coal formation.

Continued sedimentation, perhaps coupled with subsidence, provided overburden pressure that effected compaction and diagenesis of organically rich strata. Chemical activity at low temperature (less than 150°C [300°F]) resulted in loss of volatile fractions, ultimately producing a sedimentary rock with a high content of refractory organic residues.

OIL SHALE
- INORGANIC MATRIX
  - QUARTZ
  - FELDSPAR
  - CLAY (ILLITE AND CHLORITE)
  - CARBONATES (CALCITE AND DOLOMITE)
  - PYRITE AND OTHER MINERALS
- BITUMENS (SOLUBLE IN CS_2)
- KEROGENS (INSOLUBLE IN CS_2) (CONTAINING U, FE, V, NI, MO)

Figure 1-5. General scheme of oil shale components (adopted from Yen, 1975a).

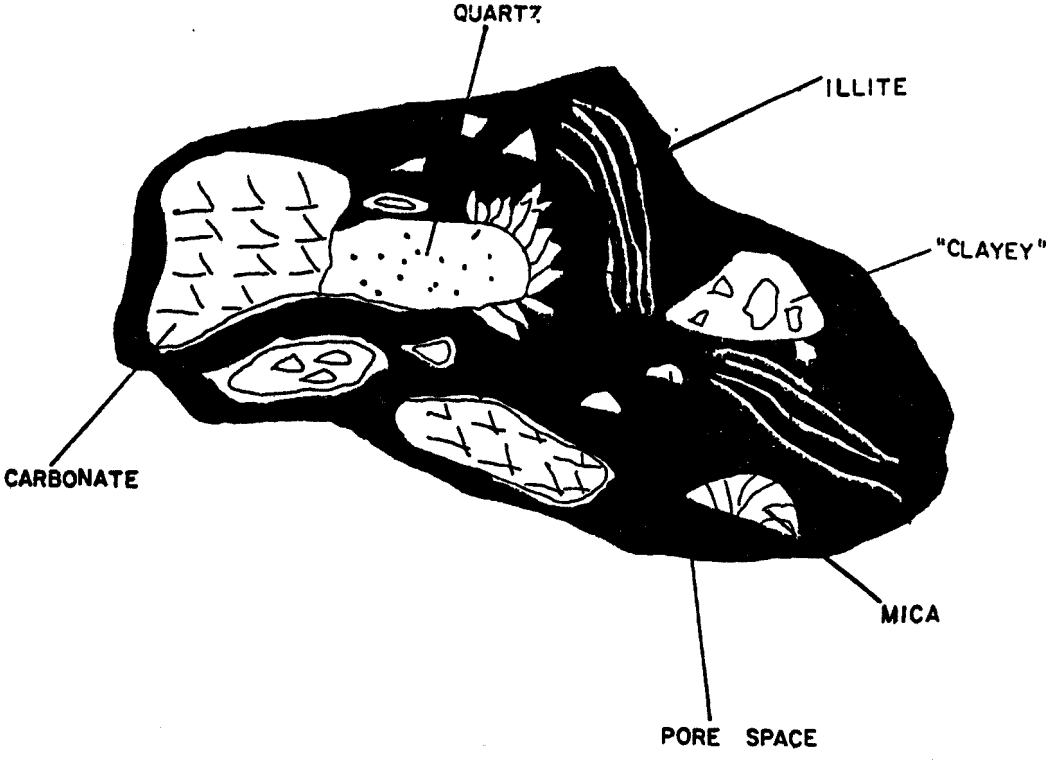

Figure 1-6. Schematic section of oil shale (Yen, 1977).

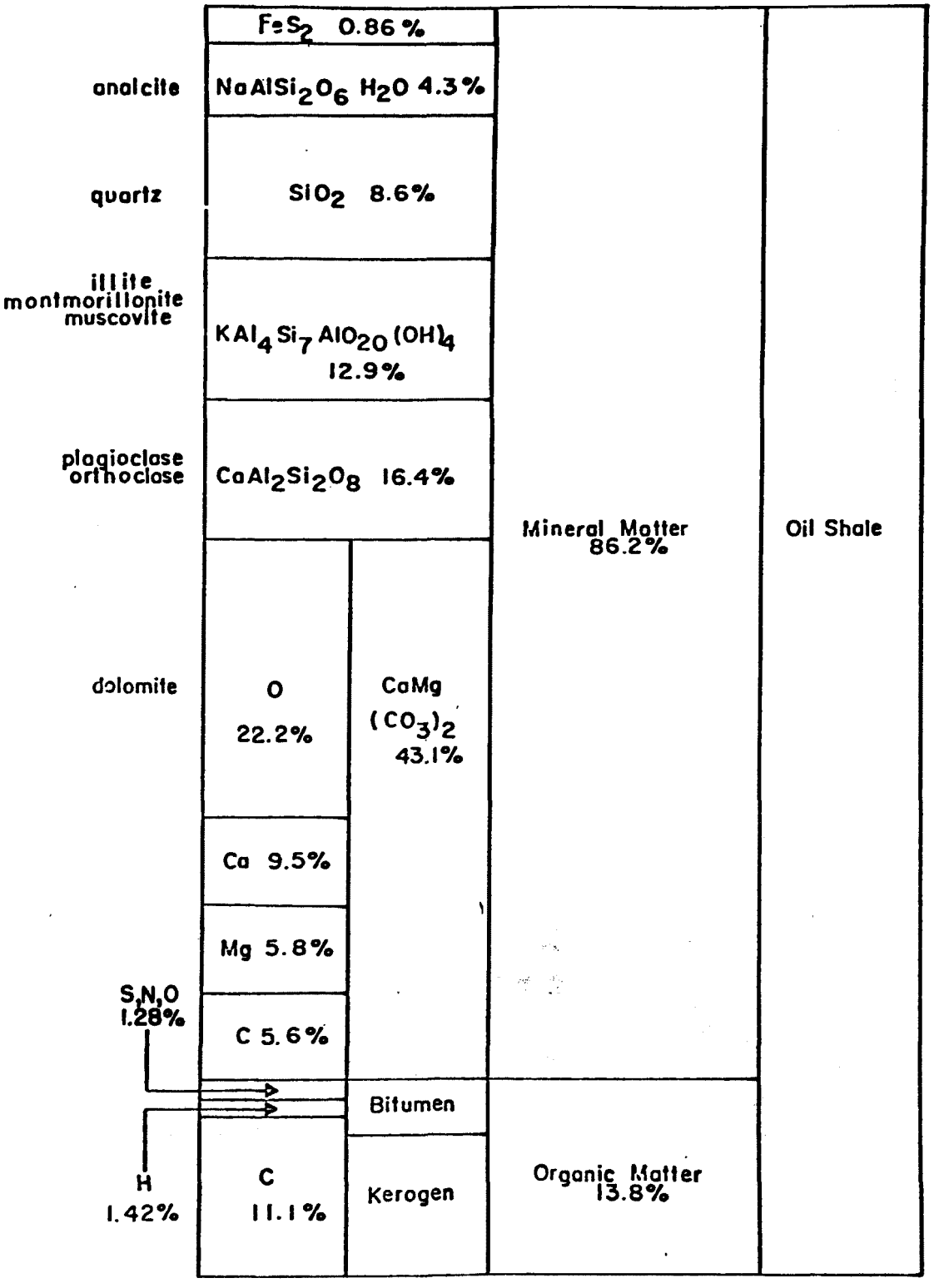

Figure 1-7. Chemical analysis of a Green River oil shale (Yen and Chilingarian, 1976).

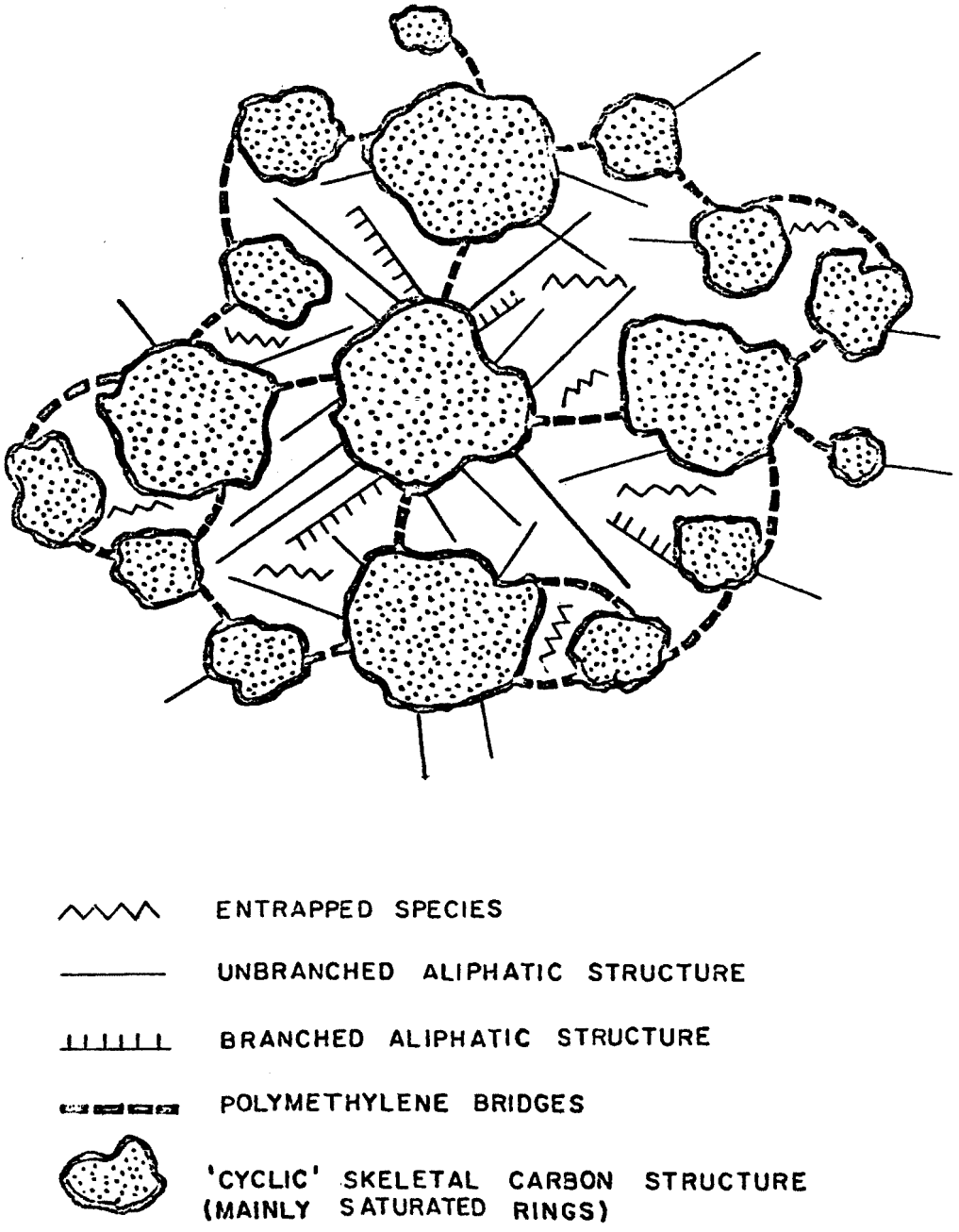

Figure 1-8. Kerogen structure of Green River oil shale (Young and Yen, 1977).

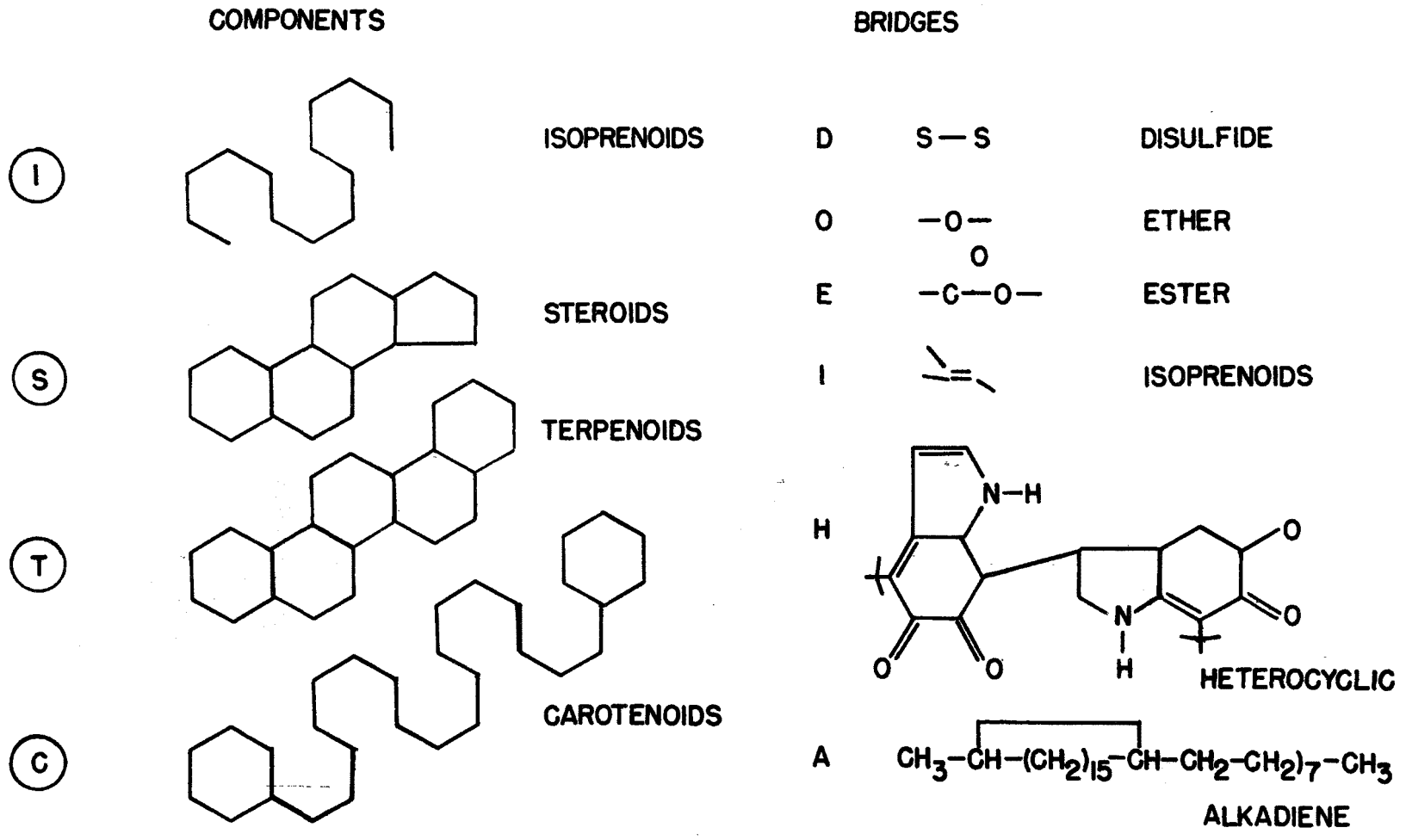

Figure 1-9. Components and bridges of a Green River oil shale kerogen (Yen, 1976c).

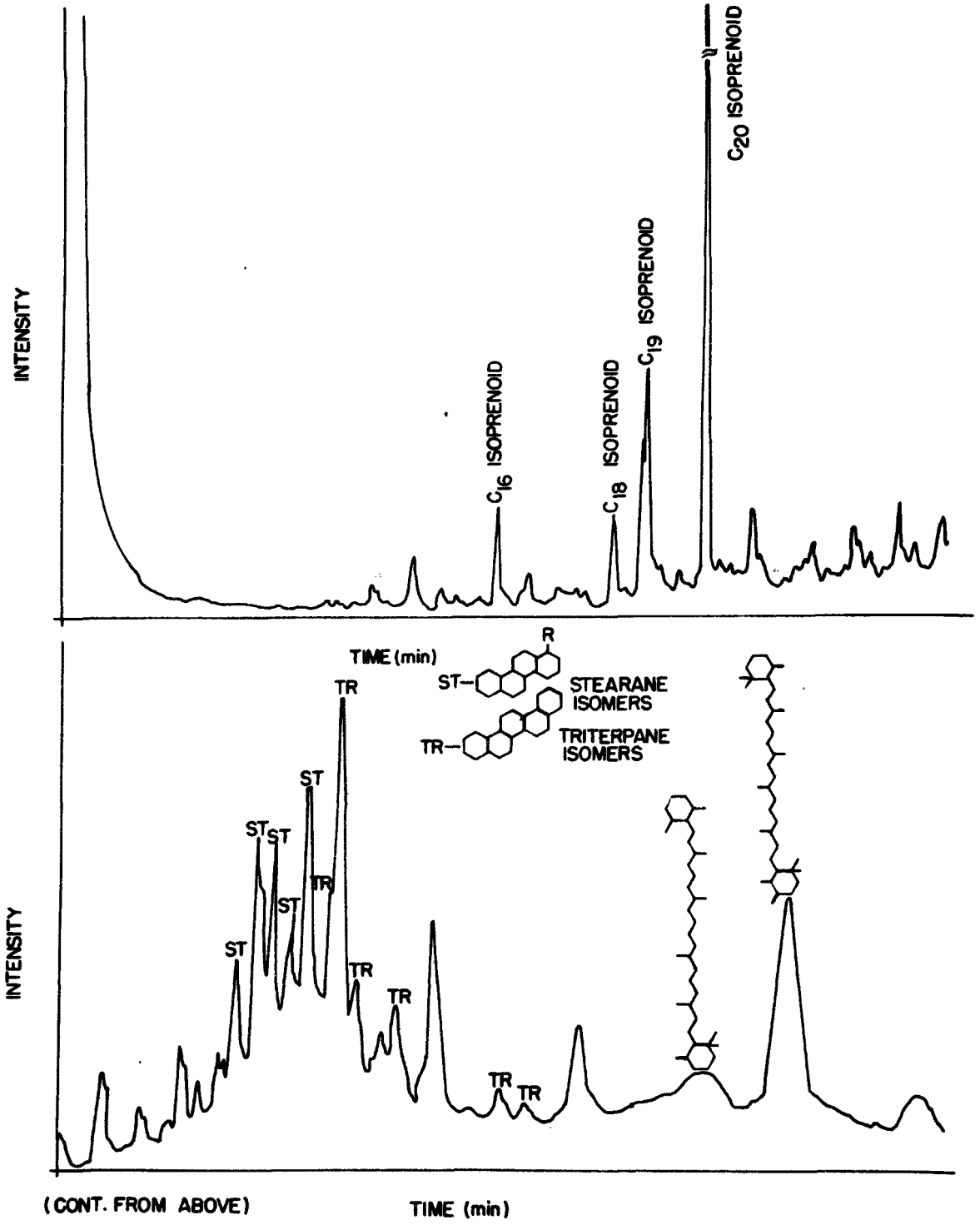

Figure 1-10. Biomarkers in Green River oil shale bitumen (Yen, 1973).

TABLE 1-5. COMPOSITION OF BITUMENS IN GREEN RIVER OIL SHALE (Yen, 1977)

Classes of components	Percent by weight	Principal components
N-alkanes	3.4 - 3.9	C_{13}-C_{35} with C_{17} and C_{29} as maxima Odd-to-even predominance at 3:1 or 4:1
Branched and cyclic alkanes	23.6 - 30.3	Chain isoprenoids (farnesane, pristane, and phytane) C_{27}, C_{28}, C_{29} stearanes C_{30} and C_{31} pentacyclic triterpanes C_{40} carotanes
Aromatic oil	2.7 - 3.3	Alkyl benzenes Alkyl tetralins Mixed aromatic and naphthenic compounds
Resins	54.4 - 57.4	M.W. ~625 Indanones Tetralones, acetylindanes Hydroxypyrrole, diketopyrrole
Asphaltenes (including fatty acids)	9.0 - 12.5	M.W. ~1,320 Porphyrins C_{10}-C_{34} fatty acids (n, iso, anti-iso) C_{27}-C_{29} sterols

TABLE 1-6. CARBONATE MINERALS IN GREEN RIVER FORMATION (Shanks et al., 1976)

Name	Formula	Abundance
Single carbonates		
Calcite	$CaCO_3$	Ubiquitous
Nahcolite	$NaHCO_3$	Abundant
Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	Abundant
Magnesite	$MgCO_3$	Rare
Wagscheiderite	$Na_2CO_3 \cdot 3NaHCO_3$	Rare
Thermonatrite	$Na_2CO_3 \cdot H_2O$	Rare
Siderite	$FeCO_3$	Rare
Aragonite	$CaCO_3$	Rare
Compound carbonates		
Dolomite	$CaMg(CO_3)_2$	Ubiquitous
Shortite	$Na_2Ca_2(CO_3)_3$	Widespread
Barytocalcite	$BaCa(CO_3)_2$	Widespread
Dawsonite	$NaAl(CO_3)(OH)_2$	Abundant
Northupite	$Na_2Mg(CO_3)_2 \cdot NaCl$	Abundant
Pirssonite	$Na_2Ca(CO_3)_2 \cdot 2H_2O$	Abundant
Gaylussite	$Na_2Ca(CO_3)_2 \cdot H_2O$	Abundant
Ankerite	$(Mg_{0.85}Fe_{0.15}Ca)(CO_3)_2$	Abundant
Eitelite	$Na_2Mg(CO_3)_2$	Rare
Bradleyite	$MgNa_3CO_3PO_4$	Rare

TABLE 1-7. SILICATES IN THE GREEN RIVER OIL SHALE (Shanks et al., 1976)

Name	Formula	Abundance
Simple silicates		
Quartz	SiO_2	Ubiquitous
Orthoclase	$KAlSi_3O_8$	Widespread
Plagioclase	$Na(Ca)Al_{0-2}Si_{2-3}O_8$	Widespread
Albite	$NaAlSi_3O_8$	Widespread
Acmite	$NaFeSi_2O_6$	Rare
Zoolites		
Analcite	$NaAlSi_2O_6 \cdot H_2O$	Widespread
Natrolite	$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	Rare
Clays		
Montmorillonite	$Al_4(Si_4O_{10})_2(OH)_4$	
Illite	$K_{0-2}Al_4(Si_{8-6}Al_{0-2})O_{20}(OH)_4$	Widespread
Kalite	$H_4Al_2Si_2O_9$	Locally abundant
Stenvenite	$Al_{0.06}Fe_{0.04}Mg_{2.81}Li_{0.04})$ $(Si_{3.98}Al_{0.02})O_{10}(OH)_2Na_{0.04}$	Locally abundant
Longhlinite	$H_{16}Na_2Mg_3Si_6O_{24}$	Locally abundant

There is almost no dispute that the genesis of kerogen and bitumen is biological, largely derived from the lipid fraction of algae. Taphonomic and biostratinomic processes allowed further conversion of the fossilized material. The geochemical deposits are summarized in Table 1-8.

TABLE 1-8. CLASSIFICATION OF MAJOR OIL SHALES (Yen, 1975b)

Location	Type	Age	Source
Large lake basins	Green River Formation	Eocene	Cyanophycea
	Stanleyville Basin, Congo	Triassic	
	Albert Shale, New Brunswick	Mississippian	
Shallow seas on continental platform and shelves	Alaskan Tasmanite, Brooks Range	Mississippian	Unknown—may be red algae
	Phosphoria Formation	Permian	
	Monterey Formation	Miocene	
	Irati Shale, Brazil	Late Permian	
Small lakes, bogs, lagoons, associated with coal-forming swamps	NSW Torbanite	Devonian	Xanthophyceae *Botryococcus braunii*
	Fusan, Manchuria	Tertiary	

DEVELOPING WESTERN OIL SHALE RESOURCES

By 1977, there was still no large-scale commercial production of domestic shale oil. The balance between energy supply and demand controls the position of oil shale in the U.S. energy market. The oil embargo in 1973-74 and the subsequent increase in petroleum prices by OPEC intensified the concerns over energy supply and simulated the interest in developing oil shale as a source of domestic oil supply (Smith and Jensen, 1976).

Federal land ownership is one of the factors that affects oil shale development. More than 80 percent of the oil shale lands underlain by the Green River Formation, containing the richest and thickest deposits, are owned by the Federal Government. In 1973, the Department of Interior's Prototype Oil Shale Leasing Program was launched. Four tracts of commercial shale oil production were leased in 1974 by bonus bidding. Of the privately held land, two-thirds is owned by the five major oil companies (Union, Exxon, Texaco, Mobil, and Conoco). The locations of oil shale development activity are indicated in Figure 1-11.

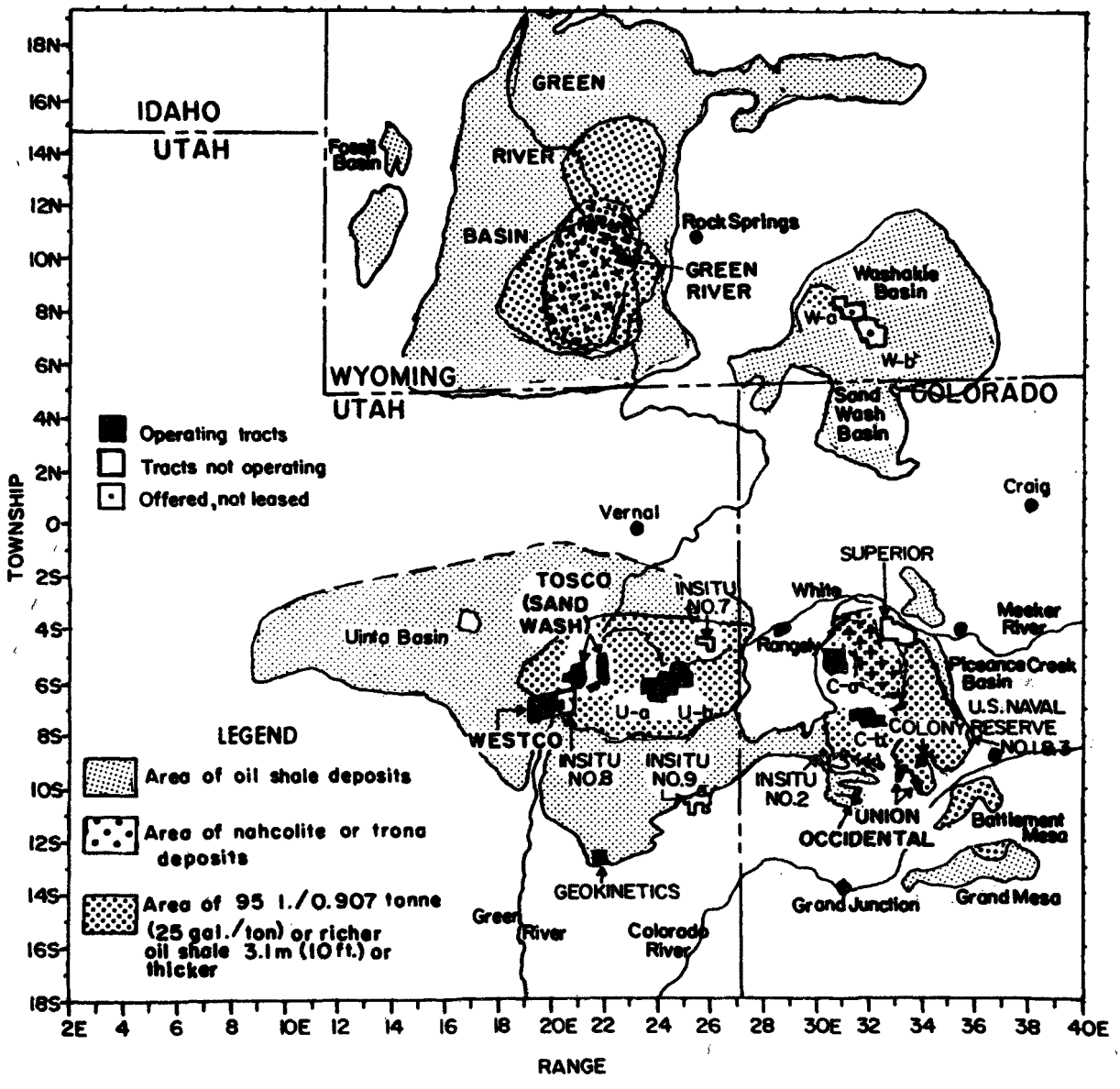

Figure 1-11. Current oil shale development activity in tristate area.

The recovery of shale oil from oil shale is based on the principle of retorting (thermal decomposition) of the kerogen and bitumen within the oil shale matrix. In general, surface retorting processes can be classified as external heating or internal heating by:

- Hot gases (BuMines gas combustion DEI kiln, Union Oil, N.T.U., TOSCO)
- Hot fluids (Cameron-Jones [Petrosix])
- Hot solids (TOSCO II, Lurgi-Ruhrgas).

The most desirable process for retorting oil shale should have as many of the following characteristics as possible (Carpenter et al., 1977):

- It should be continuous
- It should have a high feed rate per unit cross section area of retort
- It should have high oil recovery efficiency
- It should require a low capital investment and possess a high operating time factor (low down-time) with low operating costs
- It should be thermally self-sufficient—that us, all heat and energy requirements should be supplied without burning any of the product oil
- It should be amenable to enlargement into high-tonnage retorts rather than to a multiplicity of small units
- It should require little or no water because the Green River oil shale deposits are located in an arid region
- It should be capable of efficiently processing oil shale of a wide range of particle sizes to minimize crushing and screening
- It should be mechanically simple and easily operable.

The classification of all in situ (subsurface) processes has been summarized (Yen, 1976a). There are currently two versions of in situ processes; one is the modified in situ, and the other is the true in situ process. The modified in situ process is currently being developed by the Occidental Petroleum Corporation, and it seems promising as a viable additional technique for oil shale production (see Table 1-3). In general, in situ retorting processes can be classed as follows:

- Subsurface chimney
  - Hot gases (Atlantic Richfield, McDonnel Douglas, Continental Oil, Mobil Oil)
  - Hot fluids (Shell Oil, Cities Service Oil, Garrett Corp.)
  - Chemical extraction (Shell Oil)
- Natural fractures
  - Unmodified (Shell Oil, Marathon Oil, Resources R&D)
  - Enlarged by leaching (Shell Oil)
- Physical induction – no subsurface voids (Woods R&D Corp.).

The results of the Federal oil shale lease offerings are summarized in Table 1-9. The Utah Tracts U-a and U-b are jointly located in the eastern part of the Uinta Basin, close to the White River. Development plans include conventional room-and-pillar mining and aboveground (ex situ) kerogen extraction methods.

Among the conventional retorting methods, the Paraho process is considered an improved version of the gas-combustion process. The Paraho gas combustion process was originated by the U.S. Bureau of Mines at Anvil Points, Colorado, and was improved by a consortium of six petroleum companies (Mobil, Humble, Pan American, Sinclair, Continental, and Phillips). In 1972, Development Engineering, Inc. (DEI) leased the Anvil Points facilities for oil shale retorting, and in 1973, the Paraho Oil Shale Project of 17 companies was developed. This retorting process produced 1,590 m^3 (10,000 bbl) of shale oil for the Navy in a 56-day continuous run in 1975 at the operating capacity of 408 tonnes (450 tons) per day.

Another process is employed by The Oil Shale Corporation (TOSCO). In 1964, TOSCO initiated the Colony Development Operation, which included Sohio, Cleveland Cliffs, Atlantic Richfield, and TOSCO (later Ashland Oil and Shell Oil replaced Sohio and Cleveland Cliffs). TOSCO II uses an externally heated configuration. A semiworks plant of 907 tonnes (1,000 tons) capacity per day near Grand Valley, Colorado, operated until 1972. Both Paraho and TOSCO II processes are projected for use on the U-a and U-b leases. The retorting will mainly use the available Paraho technology (85 percent) supplemented by TOSCO II (15 percent) for fines.

TABLE 1-9. RESULTS OF FEDERAL OIL SHALE LEASE OFFERINGS

	Area (hectares)	Recoverable resource estimate (millions of m^3)	(millions of bbl)	High bonus bid ($ million)	Original lessee
Colorado					
C-a	2,060	200	(1,300)	210	Rio Blanco Oil Shale Project (Standard of Indiana, Gulf Oil Corp.)
C-b	2,062	116	(723)	118	Atlantic Richfield, Ashland Oil, Shell Oil, The Oil Shale Corp. (TOSCO)[a]
Utah					
U-a	2,073	53	(331)	76	Sun Oil Co. and Phillips Petroleum Co.[b]
U-b	2,073	43	(271)	45	Sohio[b]
Wyoming					
W-a	2,070	57	(359)	None	-
W-b	2,070	57	(359)	None	-

[a] Present lease partners are Ashland Oil and Occidental.

[b] White River Shale Project will jointly develop Tracts U-a and U-b.

SECTION 1 REFERENCES

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SECTION 2

MINING PROCESSES

The recovery of oil from oil shale resources involves tremendous quantities of materials that must be mined. A mature oil shale industry of 160,000 m^3 (one million bbl) per day would require mining of 1.3 million tonnes (1.4 million tons) of oil shale, and disposal of 1.1 million tonnes (1.2 million tons) of spent shale per day (Steele, 1976).

Either underground mining or surface mining may be employed for oil shale recovery. Largely because of the depth of the major oil shale deposits, most oil shale extraction is expected to be by underground mining. Surface mining may be applicable to 15 to 20 percent of the shale reserves (Prien, 1974). The advantage of the usually lower cost of surface mining is offset by the more efficient applicability of underground processes to the mining of higher quality oil shale, commonly located at depths of over 200 meters (over 600 feet).

In situ development is an alternative to conventional resource recovery procedures, but it is still somewhat in an experimental stage of development. These three major mining processes (underground, surface, and in situ) are discussed in the following subsections.

UNDERGROUND MINING

The actual experience in mining oil shale has involved underground mining techniques. Underground mining results in less surface disturbance than surface mining and is desirable and practical for mining deep oil shale deposits.

Cameron Engineers, Inc. studied the technical and economic feasibility of mining the deep, thick oil shale deposits of Colorado Piceance Creek Basin (Hoskins et al., 1976). Four mining systems were evaluated and selected as the most promising for further underground mining considerations. These four mining methods are:

- Room-and-pillar mining
- Sublevel stoping with spent shale backfill
- Sublevel stoping with full subsidence
- Block caving using load haul dump (LHD).

The general features of these mining approaches are presented in the following paragraphs.

Room-and-Pillar Method

Room-and-pillar mining is the most suitable method for mining deep (460 meter [1,500 feet] or less), thick (9 to 27 meters [30 to 90 feet]), high-grade (125 liters per tonne [30 gallons per ton]) oil shale deposits.

Major advances in underground mining of oil shale by using this method have been achieved by the Bureau of Mines in its oil shale program (East and Gardner, 1964). Commercial scale room-and-pillar mining of oil shale was demonstrated by the Bureau of Mines at Anvil Points, Colorado, during 1944 to 1956. The Bureau of Mines research program for room-and-pillar mining endorsed changes to rotary drilling in the mine headings and benches. Their investigations have also looked into the use of modern haulage and loading equipment and other operational improvements based on advances in quarry and open-pit mine engineering. Mine safety procedures have also been studied as part of the Bureau of Mine studies. This technique has been improved through subsequent work by the Union Oil Company at Parachute Creek (1956 to 1958), the Colorado School of Mines Research Foundation (1964 to 1967), and the Colony Development Operation at Grand Valley, Colorado (U.S. ERDA, 1976b) (1965 to present). Room-and-pillar mining is proposed for Oil Shale Tracts U-a and U-b by the White River Shale Project (White River Shale Project, 1976). Mining techniques for modified in situ development (studied by Occidental Petroleum at Logan Wash, Colorado) and room-and-pillar mining are the only mining systems that have been tested on the oil shales of the Green River Formation.

The first step in the development of a room-and-pillar operation is to excavate the entrance through which mining equipment will be transported. The contour and shape of adits are dictated by the topographic nature of the particular oil shale deposits. Once the adits have been established, mine development proceeds by drilling horizontal holes along the sides of the room to be excavated. An ammonium nitrate-fuel oil (ANFO) mixture is the explosive commonly used. The shale rubble is loaded on ore trucks with front end loaders for conveyance outside the mine. Backhoe or other digging equipment is used to scrape away the remaining shale. After all the shale is removed from the room, roof bolts are installed to strengthen the mine roof. Pillars of shale rock left in the mining zone support the roof against failure while mining continues from room to room (Figure 2-1). According to the experiences of the Bureau of Mines and other prototypes, optimum room-and-pillar sizes at Anvil Points, Colorado were both 18x18 meters (60x60 feet) (Schramm, 1970). This results in a resource extraction level of 75 percent with 25 percent remaining in the supporting pillars. The pillar size used for a particular situation, however, is dependent upon the depth at which material is being mined. For Oil Shale Tracts U-a and U-b, rooms and crosscuts are planned to be 18.3 meters (60 feet) wide. Entries with a width of 15.2 meters (50 feet) to 16.8 meters (55 feet) are planned. The pillar widths within the panels will be 18.3 meters (60 feet) to 24.4 meters (80 feet). Entry pillars will be 18.3 meters (60 feet) wide and their height will be determined by panel access requirements and the statutory maximum distance between crosscuts.

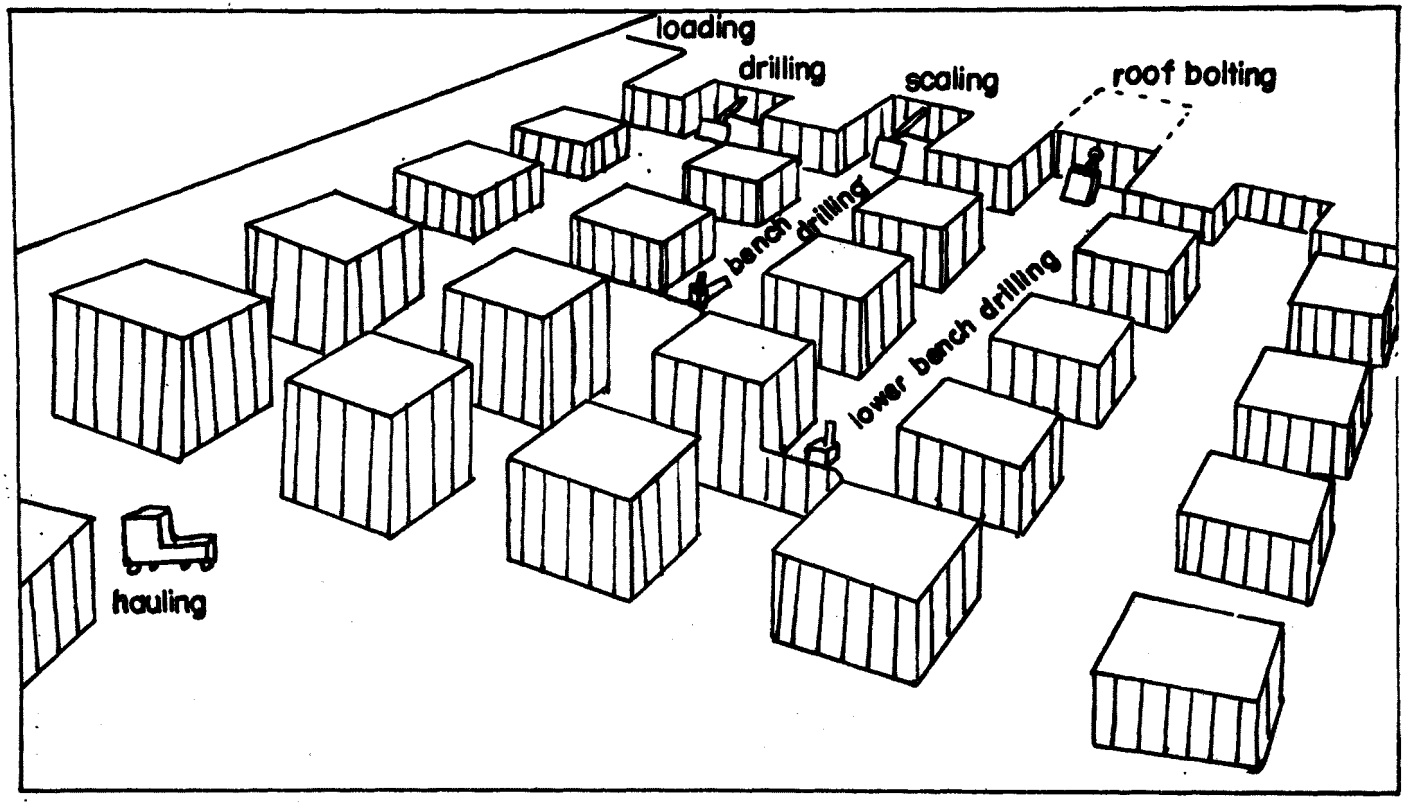


Figure 2-1. Underground room-and-pillar mining operation (modified from U.S. ERDA, 1976a).

Usually, a thick oil shale deposit (18 to 24 meters [60 to 80 feet]) is mined in two steps. The upper bench with a 9- to 12-meter (30- to 40-foot) height is mined first. Then the lower bench is developed in a similar procedure, except that the blast holes are drilled vertically instead of horizontally (Figure 2-1).

Several alternatives exist for the resource contained in the pillars after completion of a room and pillar operation. These include:

- Leave the pillars in place
- Pull the pillars and recover for surface retorting
- Rubble the pillars and recover by in situ processing.

Economics and subsidence after mine collapse will dictate the viability of these alternatives.

Other Underground Mining Methods

Block-Caving Method—

The block-caving method is employed for recovery of much thicker and larger bodies of resource than those for which room and pillar methods are applicable. Generally, a large block of ore is first partly severed by driving a series of horizontal passages, known as slusher drifts, through it or by a series of finger raises (Figure 2-2). A finger raise is a vertical or inclined passage connecting two or more working levels. Pillars are left to support the mine roof. The block is then undercut by removing a horizontal slice at the bottom. The unsupported column of ore breaks and caves under its own weight, and the broken ore is drawn off gradually from below. The development work is conducted on three levels: the level at which the ore is undercut, the "grizzly" level at which the ore is drawn, and the haulage level at which the ore is transported to the shaft.

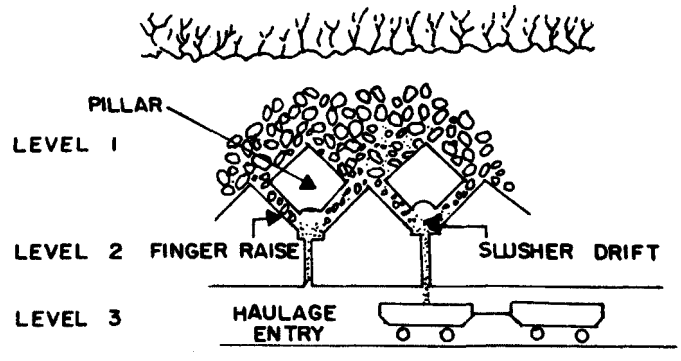


Figure 2-2. Block-caving mining concept (Hoskins et al., 1976).

Cut-and-Fill Stoping Method—

Mining operations proceed upward through the resource body in this method. After a slice of ore is cut off, the broken material is removed and the stope is filled with overburden accumulated from previous cuts until the floor of the chamber is within 1 meter of the roof. The miners stand on the waste material to make the next cut. The operation is thus conducted in cycles, consisting of breaking off material, removing the broken ore, and filling the empty space with waste. The filling is carried out mainly to support the walls of the stope.

Cut-and-fill stoping may utilize two variations: the horizontal and the inclined. In the horizontal cut-and-fill method, the back and filling are maintained practically horizontal. In the inclined method the back and filling are kept parallel to each other and the stope faces are inclined at about the angle of repose of the waste material; this permits the use of gravity to remove the ore and to fill the excavated workings with waste material.

A sublevel inclined cut-and-fill method involves a block of ore first subdivided into three horizontal sections by driving drifts throughout the length of the block (Figure 2-3). Mining operations begin in the upper section and retreat in a horizontal direction toward the shaft. The excavation in the upper section is kept ahead of that in the lowest section. After the ore is broken off and removed, each excavated section is filled up to the roof with waste material brought from above by gravity.

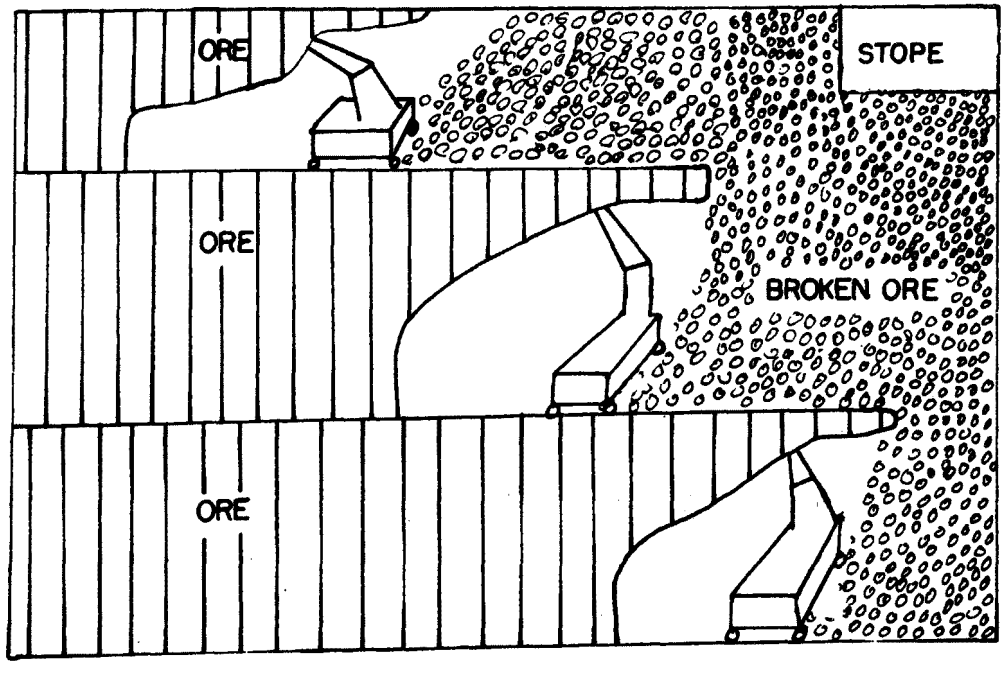


Figure 2-3. Sublevel inclined cut-and-fill stoping mining concept (modified from U.S. ERDA, 1976a).

SURFACE MINING

Surface mining is an economical method for recovering shale deposits that lie close to the ground surface. The economic use of surface mining is a function of the stripping ratio, i.e., the ratio of the amount of overburden material that must be removed to that of the resource recovered. The other important factor is, of course, the grade of the oil shale recovered. An oil shale deposit can be economically surface-mined when the stripping ratio is in the range of 0.5 to 2.5 (Prien, 1974, 1976; Steele, 1976). There are two basic types of surface mining: stripping and open pit.

It has been estimated that overburden will have to be disposed of away from the mine site during the first 10 years of operation. After that period, mined-out pit areas will be available for the disposal of overburden while allowing mining to proceed. Factors that affect this time frame are the stripping ratio, production rate, thickness and grade of shale, etc. (Prien, 1976).

Stripping Method

This is a common surface-mining process for extraction of coal in the Western United States. This mining approach is suitable only for oil shale deposits that are within 300 meters (1,000 feet) of the surface with very low stripping ratio (less than 0.5).

Explosives are used to loosen the overburden, and large draglines are commonly used to remove it. Power shovels are employed to excavate the exposed ore seam and load the shale onto trucks. The overburden is stored at a nearby site until the mined area is large enough to allow backfilling operations without interfering with mining advance. A typical strip mining operation is shown in Figure 2-4. The block-and-cut modified strip mining method (Figure 2-5) can provide high-quality land reclamation after the resource is removed. The overburden from the first mining area is removed, and then the resource is cut away. Mining proceeds in the neighboring zone, with the overburden being deposited and contoured in the first mined area. Mining progresses laterally through additional cuts, with the overburden in each area moved to backfill the preceding cuts on a continuous basis. Finally, the spoil from the initial mining zone is used to backfill the last mined areas.

Open-Pit Method

Open-pit mining is a highly developed process that is widely used in mining other ores and may be practical for oil shale in some areas. For western oil shale deposits, surface mining will be primarily of the open-pit type. It is suitable for deeper deposits than is strip mining and can be used where the stripping ratio is between 0.5 and 2.5 (National Petroleum Council, 1972). The preliminary development plans for Oil Shale Tract C-a included the primary mining approach (Rio Blanco Oil Shale Project, 1976).

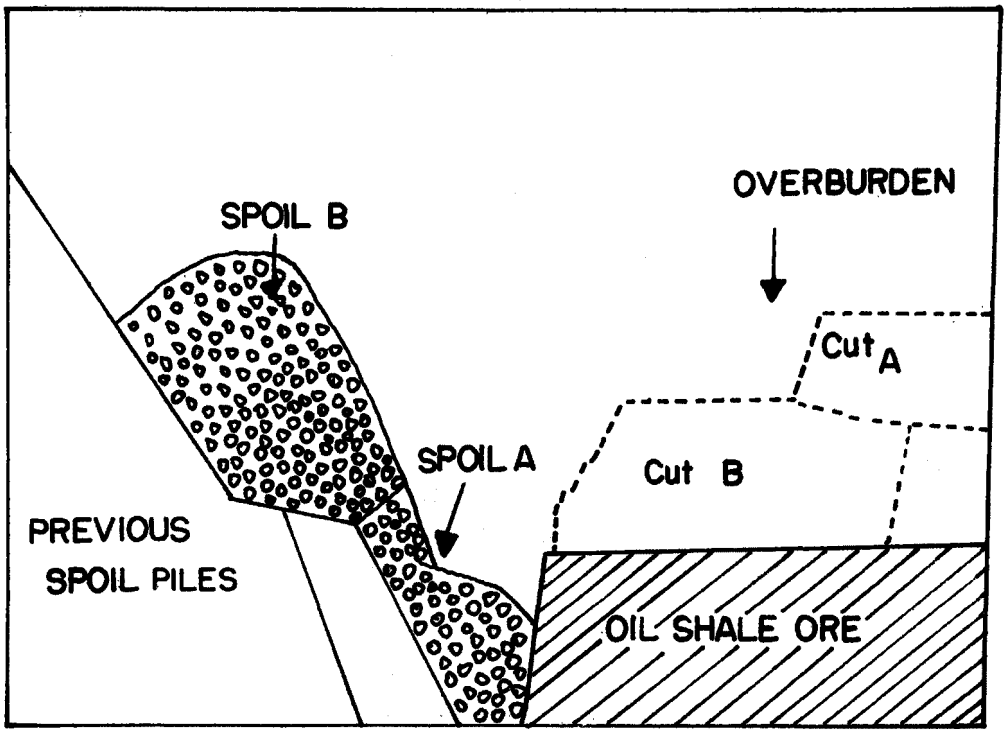


Figure 2-4. Typical strip mining operation (modified from U.S. ERDA, 1976a).

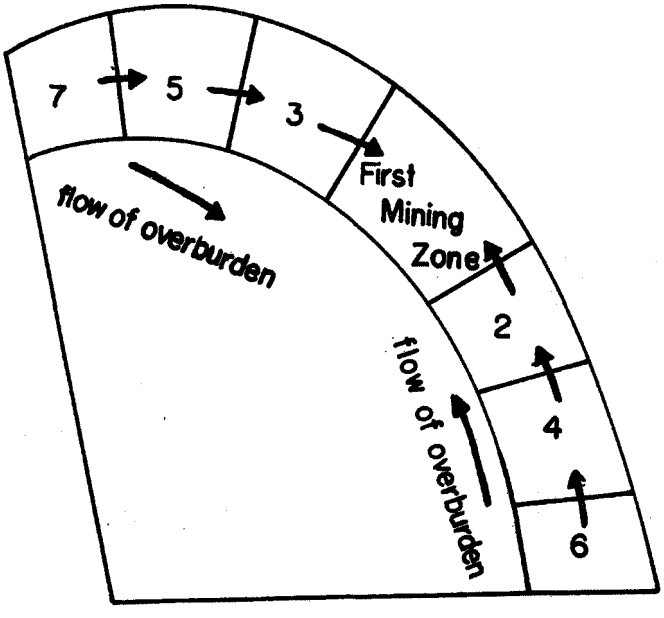
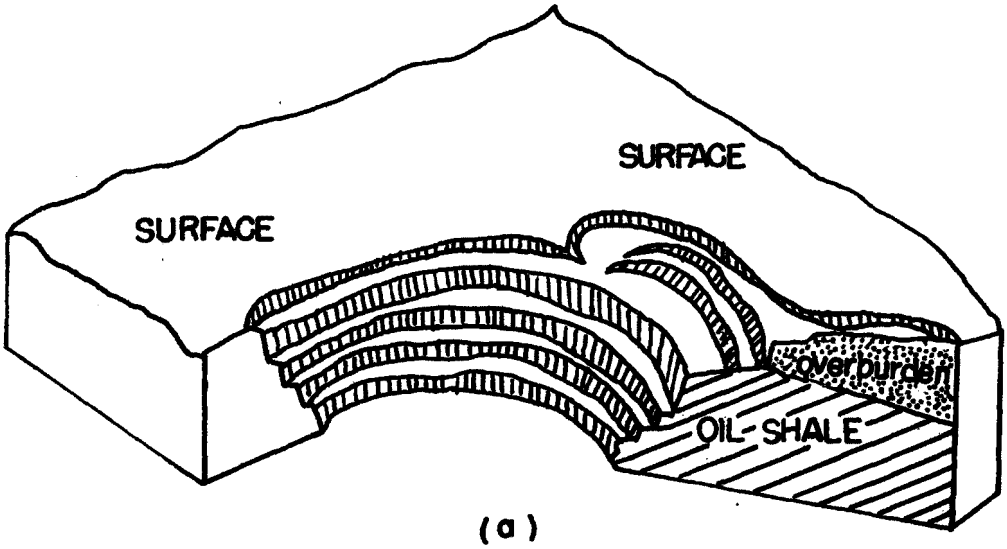
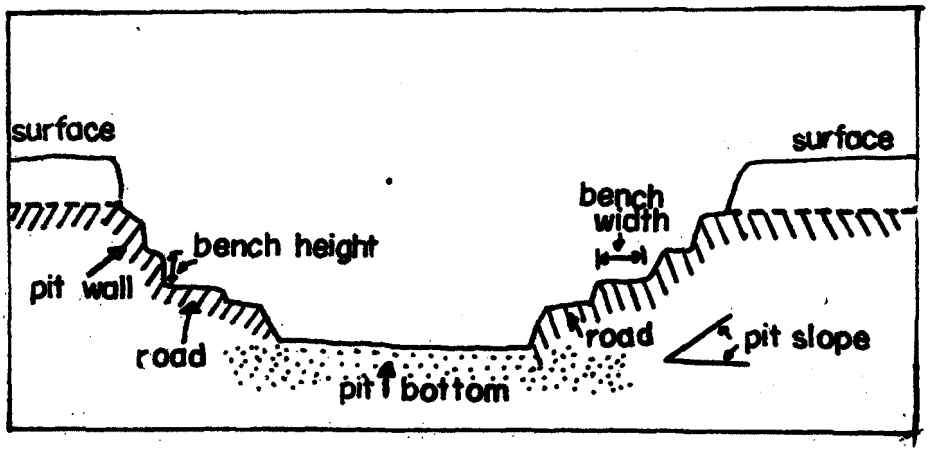


Figure 2-5. Block-and-cut modified strip mining concept.

In open-pit mining, the overburden is loosened using explosives implanted in drill holes. The ore is removed by power shovels and trucks. As the pit is deepend, a series of benches is produced, which provide stability for the sides of the pit (Figure 2-6). When the desired shale deposit is reached, it is then loosened by blasting, loaded into trucks, and conveyed to crushers and other process areas.



(a)



(b)

Figure 2-6. Open-pit mining operation: (a) isometric [modified from Steele, 1976] and (b) section [modified from U.S. ERDA, 1976a].

In open-pit mining, as in strip mining, large amounts of overburden are generated. A suitable site for storage must be located. About 80 percent of all mined oil shale material is discarded as shale residue. The overburden and residue must be stored away from the mine site initially until pit disposal is feasible.

Theoretically, open-pit mining can optimally recover 85 percent or more of the available resource. However, because of the area required for disposal (including in-pit disposal of overburden and spent shale), this figure may not be achievable in practice (White River Shale Project, 1976).

One important concept of open-pit mining is that the waste or capping directly over the ore not only must be removed but removed beyond the limits of the ore body at the edge of the pit. The purpose is to permit the mining of boundary ore and prevent the sides from sliding into the pit. Thus, as the depth increases, the pit must also be widened. If the stripping ratio becomes too high (about 2.5) and haulage distance increases too much as the pit is expanded, open-pit recovery will become uneconomical. Any remaining ore would then be recovered using alternative recovery techniques, such as underground mining.

A recent study by the Department of Interior (Prien, 1976) envisages a very large unitized open-pit operation in the Piceance Creek Basin, with a pit as deep as 610 meters (2,000 feet). Under this condition, both lower grade oil shales and associated saline materials may be recovered economically. This operation could eventually be a combination of open-pit mining and underground mining. The pit would subsequently be filled and revegetated, and the entire disturbed area restored (Prien, 1976). To date, however, open-pit mining of oil shale deposits has not been undertaken in the United States.

IN SITU MINING

In the in situ operation, both mining and retorting of oil shale are processed underground. There are two techniques, namely, "modified" and "true" in situ processes.

Modified In Situ Method

In this method, mining of sufficient shale deposits (approximately 15 to 20 percent) takes place at the upper and/or lower layer of the shale. This provides the desired porosity when the shale is fractured by explosives and collapsed into a room and is done by drilling vertical longholes from the mine-out room into the shale layer. An explosive agent is implanted in the holes for blasting. Blasting on vertical free faces can also be included in the retort development process. Finally, retorting is operated in a vertical gas combustion mode. This process is shown in Figure 2-7.

Occidental Research and Development is currently developing a commercial-size modified in situ process in Colorado. The first commercial-size retort (Retort No. 4) with a 36.6- x 36.6-meter (120- x 120-foot) cross section and 76-meter (250-foot) height, containing rubblized shale, was ignited in December 1975 (TRW and Denver Research Institute, 1976). A total of 4,300 m^3 (27,000

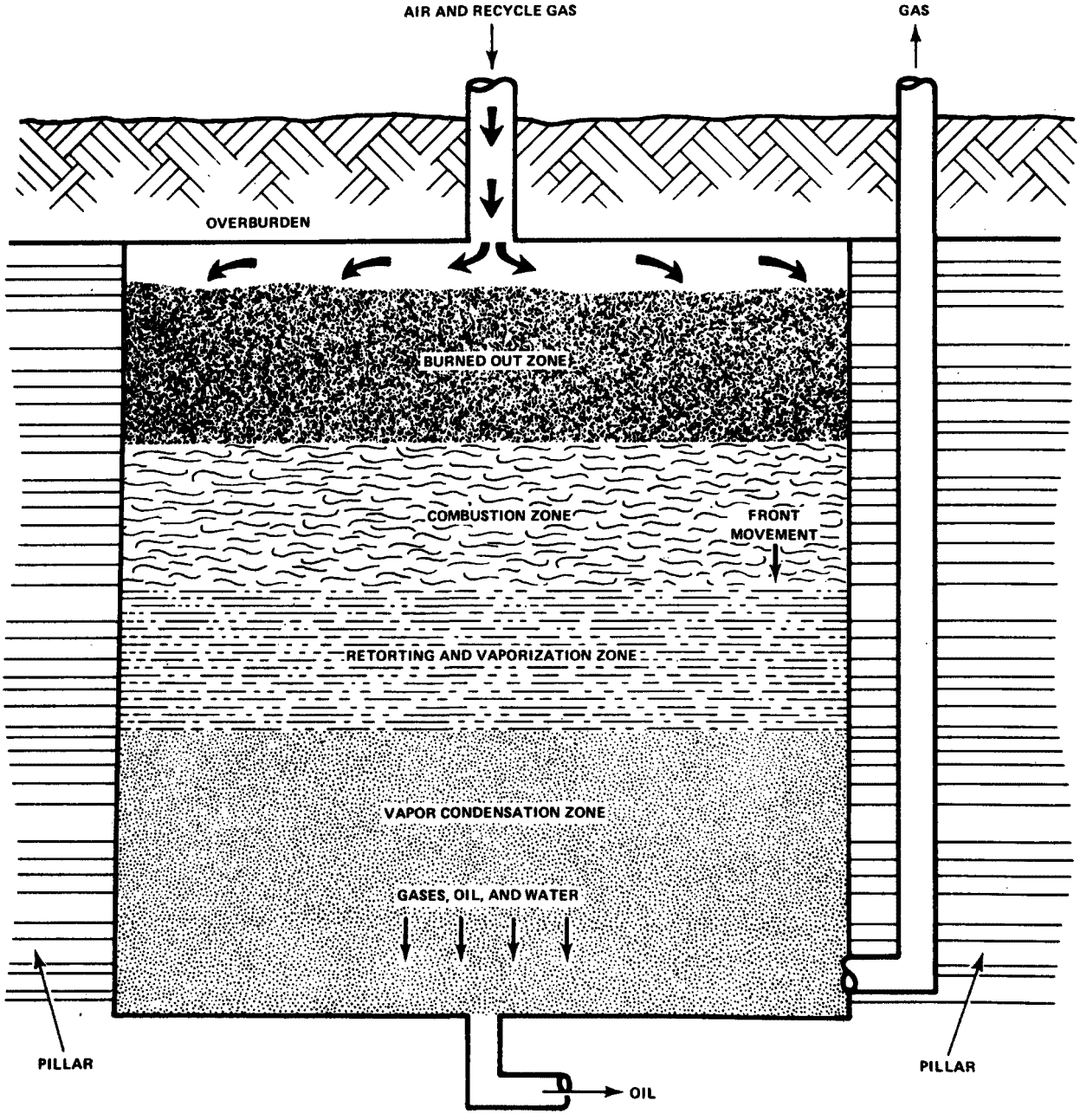


Figure 2-7. Flame-front movement in the Occidental modified in situ process (McCarthy and Cha, 1975).

bbl) of oil has been recovered and production rates of 80 m^3 (500 bbl) per day have been realized. Production from a similar sized retort (Retort No. 5) has also been completed by Occidental.

True In Situ Methods

The usual approach to this method is to drill a pattern of wells into the shale deposit, consisting of a central injection well surrounded by a series of production wells. The shale between the wells may be fractured by using hydraulic pressure, chemical explosives, or steam. Use of nuclear explosives has also been discussed, but has been dismissed as not being a realistic alternative. The fractured oil shale is then ignited by injecting heated compressed air or hot natural gas into the injection well. Product recovery from the underground combustion and pyrolysis is through the surrounding production wells (Figure 2-8).

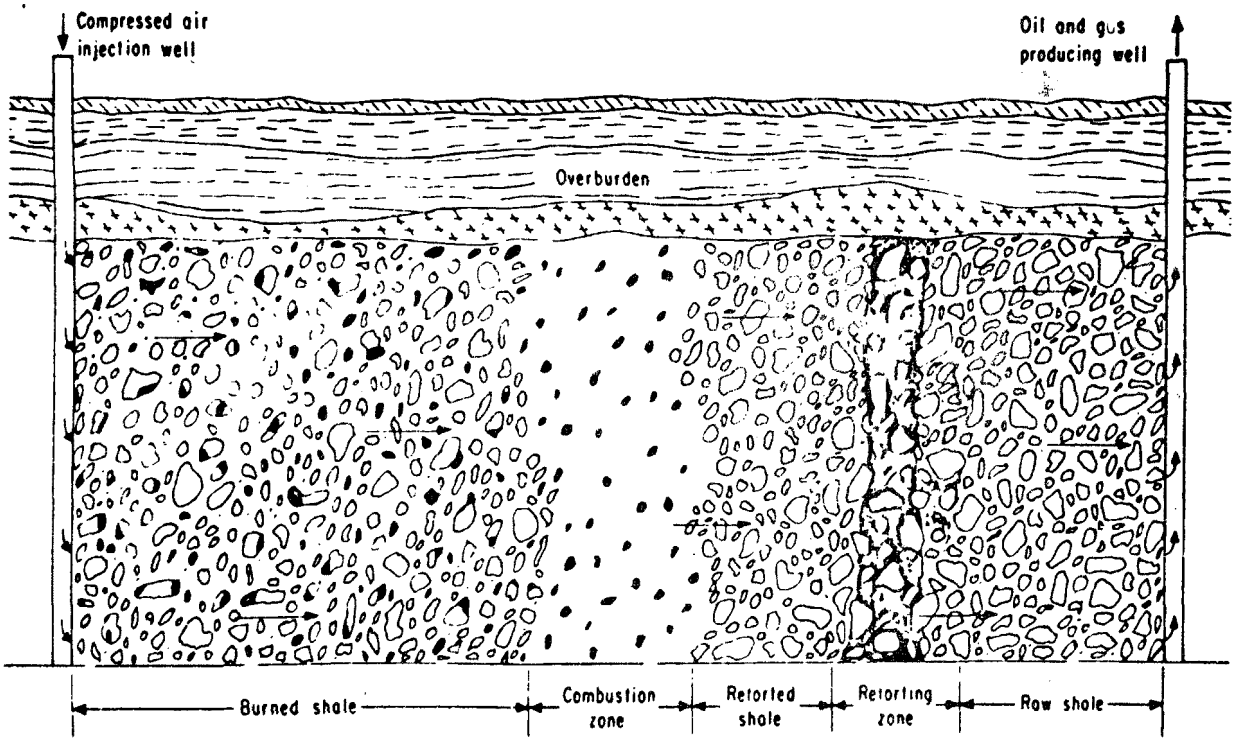


Figure 2-8. Horizontal in situ oil shale retorting process (Duvall and Jensen, 1975).

A critical point for this process is that the fracturing techniques must produce sufficient heat-transfer surfaces for successful operation. A research project is in progress, sponsored by the U.S. Department of Energy, to test this method near Rock Springs, Wyoming. In field experiments, several methods of fracturing, including hydraulic pressure, chemical explosives, and electricity, have been used for tests on an oil shale bed of 6- to 12-meter (20- to 40-foot) thickness, with 15 to 122 meters (50 to 400 feet) of overburden. Horizontal fractures were produced by using hydraulic pressure over a 10.7-meter (35-foot) vertical interval at a depth of 122 meters (400 feet). Fractures extending at least 61 meters (200 feet) from the injection well were reported. Chemical explosives and the combination of hydraulic pressure with liquid chemical explosives have also been used. Explosives in liquid form may be introduced into natural or artificial fractures while those in solid form are put in well bores. Tests were able to produce small quantities of oil. Larger underground recovery tests are planned (U.S. ERDA, 1976).

The U.S. Energy Research and Development Administration (ERDA) has also undertaken extensive experimentation involving laboratory studies, pilot scale simulations of underground operations and field experiments. Eight experiments utilizing various fracturing and recovery methods were conducted at a depth of 25 meters (82 feet). Additionally, two fracturing experiments were performed at a depth of 120 meters (394 feet) (Dinneen, 1976). Experiments with such fracturing techniques as electricity, chemical explosives and hydraulics have been conducted (Burwell et al., 1970; Campbell et al., 1970; Carpenter et al., 1972; Melton and Cross, 1967; Miller and Howell, 1967; Wise et al., 1976). These trials have demonstrated that underground combustion can be initiated after site preparation, and oil can be produced from in situ processing (Carpenter et al., 1977).

Fracturing Methods Using Chemical Explosives—

Chemicals, such as ANFO and nitroglycerine, have been used as fracturing agents. Explosive fracturing following hydraulic fracturing improves permeability while also creating additional fractures. Fracturing shale by chemical explosives has been limited to depths of 10 to 100 meters (about 30 to 300 feet). However, for a vertical, downward-moving combustion zone processing, the rubblized zone must be overlain by a relatively unbroken, impermeable zone in order to control the gas flow. Chemical explosives may not be suitable for this kind of breakage because of damage to overburden integrity and subsequent difficulty of controlling the burn.

Hydraulic and Steam Fracturing—

Hydraulic injection can be utilized to leach out the soluble minerals from oil shale formations. Hot water (66° to 149°C [150° to 300°F]) produces a higher leaching rate than cold water. As leaching progresses, the oil shale formation becomes more permeable and may also begin to rubble. Steam at 329°C (625°F) and 102 atm (1,500 psi) or hot gases may be injected for pyrolysis and shale oil recovery. At a temperature of about 315°C (600°F), the organic material in oil shale, kerogen, is converted to oil (U.S. House of Representatives Hearings, 1974). Equity Oil Company began an in situ program near Rio Blanco, Colorado, in 1965. Hot methane gas was injected into a naturally

fractured oil shale zone, and a low pour point oil was produced. Modifications of the procedures have since been made to utilize steam as the heat carrier in place of methane (Hendrickson, 1975).

Nuclear Explosive Fracturing—

Detonation of nuclear explosives has been proposed for oil shale recovery. A cavity that is approximately spherical would be formed underground by the explosion. Roof collapse would lead to formation of a vertical rubble pile or chimney. The chimney would be surrounded by relatively unbroken rocks of low permeability. Hot gas would then be injected into the rubble zone for combustion and retorting processes (Lewis, 1974).

Although the use of nuclear devices has been proposed for numerous peaceful and constructive programs, at least two major obstacles will prevent their use for some time. The method has not undergone field demonstration which would entail exhaustive studies on its feasibility and environmental impacts. Also, the public sector still largely opposes the introduction of nuclear detonations into public and private enterprises. These problems suggest that nuclear detonations will not be used in mining operations for many years.

OIL SHALE PREPARATION

Oil shale consists of solid organic materials intimately associated with large amounts of solid minerals. The size requirement of the crushed shale depends on the retorting process adopted. Since more retorting processes require shale rock to be from 5.1 centimeters (2 inches) or 7.6 centimeters (3 inches) to no smaller than 0.32 centimeters (0.125 inches), mined shale needs to be crushed and sized before retorting. Mined shales from trucks or conveyors are introduced into a feed surge control hopper. The ore is then conveyed to "grizzlies" above the primary crushers. Grizzlies are designed to screen out ore that will clog the entry to the primary crusher. The primary crusher reduces the ore to a size that will fit the entry to the secondary crusher. The primary crushed output is screened, and the oversize portion is returned to the primary crusher feed. The primary crusher product is transported to a raw shale stockpile. Materials from this stockpile are then transported to the secondary crusher feed bins. Grizzlies are not required on the secondary crushers, since the materials are already sized to fit. After crushing and screening, the secondary crusher output is ready as retort feed. The surface storage capacity required for reliable feed for retorting is considered to be a minimum of a 30-day supply.

Alternative crushing systems that may be employed include jaw crushers, gyratory crushers, roller crushers, and impact mills. However, it has not yet been determined which units are most efficient.

Transfer of the shales between different parts of the mining area can be achieved by a number of methods. The most efficient means appears to be truck or belt haulage from the mine, with subsequent transfer by continuously moving belts.

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SECTION 3

KEROGEN RECOVERY PROCESSES

TYPES OF RETORTING

Commercial recovery of oil from oil shale is based on thermal decomposition of its solid organic materials. The major portion of the organic material in oil shale is the insoluble kerogen. The term retorting, as applied to oil shale, signifies the process of adding heat to decompose the shale into kerogen products and by-products. The two basic categories of oil shale retorting are in situ and aboveground processes.

In the in situ process, thermal decomposition takes place underground. Extensive experimental work on this type of recovery process has been conducted by the Laramie Energy Research Center (LERC) (Burwell et al., 1969 and 1970; Carpenter et al., 1972) and by the Occidental Petroleum Corporation (Garrett, 1972; McCarthy and Cha, 1976). The LERC in situ program addresses recovery from fractured oil shale retorted between injection and recovery wells. This combustion-type, true in situ retort is of the forward burning type where gas plus oil move in the same direction. The Occidental modified in situ retorting involves underground mining of a portion of the oil shale deposit and explosively fracturing shale into this cavity to create a rubblized chimney of oil shale for retorting. Lawrence Livermore Laboratory is also working on a modified in situ process (Braun and Rothman, 1975; Industrial Research, 1975). This concept, Rubble In Situ Extraction (RISE) has not been field tested.

In the aboveground retorting processes, retorting is performed in large vessels (retorts) in which the heat is applied to crushed oil shale. Retorting processes may be categorized according to the mode of heating: directly heated or indirectly heated.

Until recent years, virtually all efforts to develop oil shale technology were directed toward aboveground retorting. Hundreds of U.S. patents have been issued concerning the retorting of shale (Klosky, 1959; Hendrickson, 1975; Perrini, 1975). Some of the most developed retorting processes are:

- Directly Heated Retort

  Paraho DH Process (Bartick et al., 1975; White River Shale Project, 1976)

  Union Oil Type "A" Process (Berg, 1951; Irish and Deerling, 1964)

N.T.U. Gas Combustion Process (Harak et al., 1971; Ruark et al., 1956)

Indirectly Heated Retort

TOSCO II Process (Whitcombe and Vawter, 1976; Hall and Yardumian, 1968)

Paraho IH Process (Bartick et al., 1975; White River Shale Project, 1976)

Union Oil Type "B" Process (Berg, 1951; Irish and Deerling, 1964)

Lurgi Process (Rammier, 1968; Dinneen, 1976)

Petrosix Process (Bruni, 1968; Chemical Engineering, 1974)

The major retorting processes considered in this section are Paraho and TOSCO II.

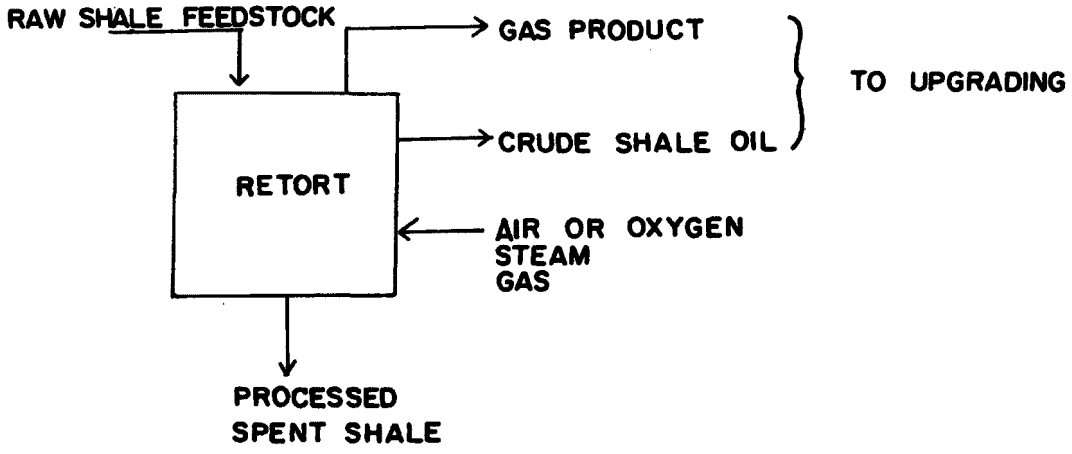
Directly Heated Retort

A directly heated (DH) retort is one in which the heat of retorting is supplied by the burning of carbonaceous-processed shale residue and a portion of the retorted gas and oil. The combustion heats the shale, causing oil and gas to be released and the products to flow out of the retort (Figure 3-1a). Because combustion air is admitted into the retorting vessel, the product gases are diluted with nitrogen and, therefore, have relatively low heating values on the order of $3x10^6$ to $3.7x10^6$ joules per standard m^3 (800 to 100 Btu per standard ft^3).

Indirectly Heated Retort

An indirectly heated (IH) retort is one in which the heat of retorting is supplied by an externally heated carrier (Figure 3-1b). A heat carrier (either a gas or a solid) circulates continuously through the retort to heat the shale, the heat being supplied to the carrier by the burning of fuel in an external heater. As the shale is heated, oil and product gas are released and are recovered from the retort. The product gases from an indirectly heated retort, such as the TOSCO type, are composed of undiluted components produced during oil shale pyrolisis and, therefore, have a higher heating value (on the order of $30x10^6$ joules per standard m^3 [800 Btu per standard ft^3]) than product gases from directly heated retorts. In addition, the oil product from an IH retort tends to have a slightly higher API gravity and a lower pour point than shale oil from a DH process.

(A) DIRECTLY HEATED (DH) RETORT



(B) INDIRECTLY HEATED (IH) RETORT

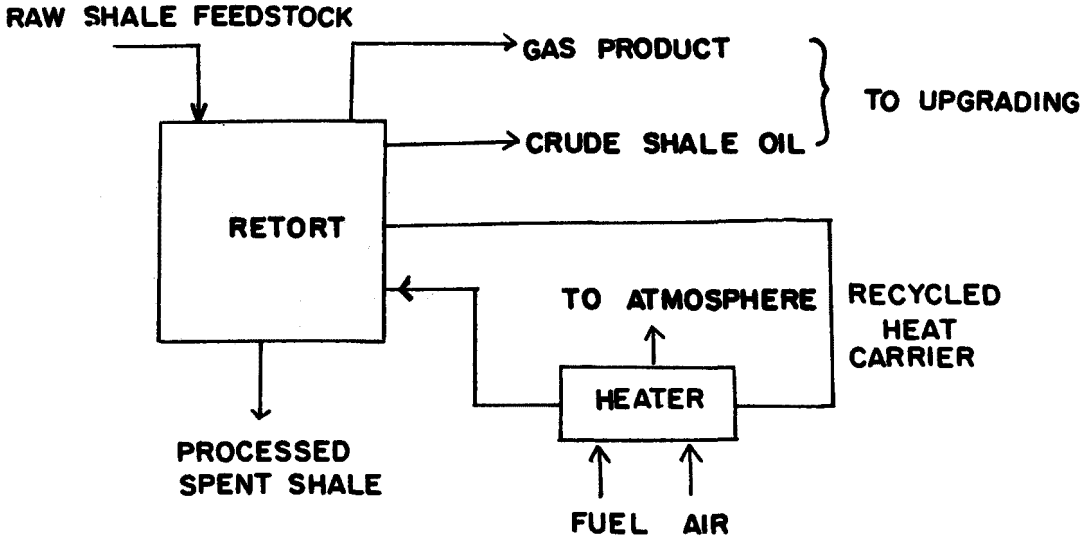


Figure 3-1. Two types of oil shale heating processes (modified from White River Shale Project, 1976).

PARAHO RETORTING PROCESS

Mechanical Description

A general layout of the Paraho DH-type retort located at Anvil Points, Colorado, is shown in Figure 3-2. The size of this semiworks retort unit is 3.2 meters (10.5 feet) O.D., 2.6 meters (8.5 feet) I.D., and 23 meters (75 feet) high. The term "semiworks" refers to a facility that is larger than a pilot plant but still smaller than commercial scale. The Paraho IH retort is essentially the same except for the addition of an external heater for recycle gas. Besides the retort unit, process equipment includes raw shale crushers, condensers for oil vapor and product gas, a precipitator, and blowers for air, recycle gas, and product gas (Figure 3-3).

The air-gas distributors near the middle of the retort consist of two pipes with small orifices of various sizes for the distribution of air and recycle gas. Oxygen in the air reacts with residual carbon to produce hot gases. This gas rises through the retorting zone where the raw shale is heated in excess of 900°F (482°C), causing thermal decomposition of the kerogen in the shale. Feedstock is distributed at the top of the retort by a revolving distributor with four legs that maintain an even feed rate over the whole cross section. The process gases are collected by two inverted U-shaped pipes near the top of the retort.

The linear grate mechanism at the bottom of the retort provides for controlled, uniform, and continuous rate of solids descent. Recycle-gas distribution channels are incorporated into these grates, allowing contact between gas and solids in the cooling zone of the retort.

Process Description

In the Paraho process, the retorting of crude shale oil from the oil shale is accomplished in vertical, refractory-lined vessels equipped with shale and gas distribution systems. Raw shale from the feed bin in a size range of approximately 1.3 to 7.6 centimeters (0.5 inch to 3 inches) moves downward through a combined mist formation and cooling zone where the oil shale particles are preheated to about 70°C (160°F) by gas and oil mist ascending from the retorting zone. The shale proceeds downward into the retorting zone and contacts the recycle gas that has been heated by the burning of residual carbon in the processed shale (DH mode), or heated to about 593°C (1,100°F) in an external heater (IH mode). In this zone, the raw shale reaches temperatures high enough to pyrolyze the kerogen into oil vapor and gas.

A carbon residue from the pyrolysis reaction remains in the retorted spent shale. The retorting temperatures also cause decomposition of mineral carbonates, principally calcite and dolomite. The spent shale moves downward from the hot zone to the cooling zone where the heat of the retorted shale is transferred to the rising stream of recycle gas. The cooled shale is then discharged from the retort through a grate mechanism at the bottom of the retort.

The recycle gas is injected at the bottom of the retort and rises through the retorting shale in the cooling zone in the DH retort. This zone acts as a

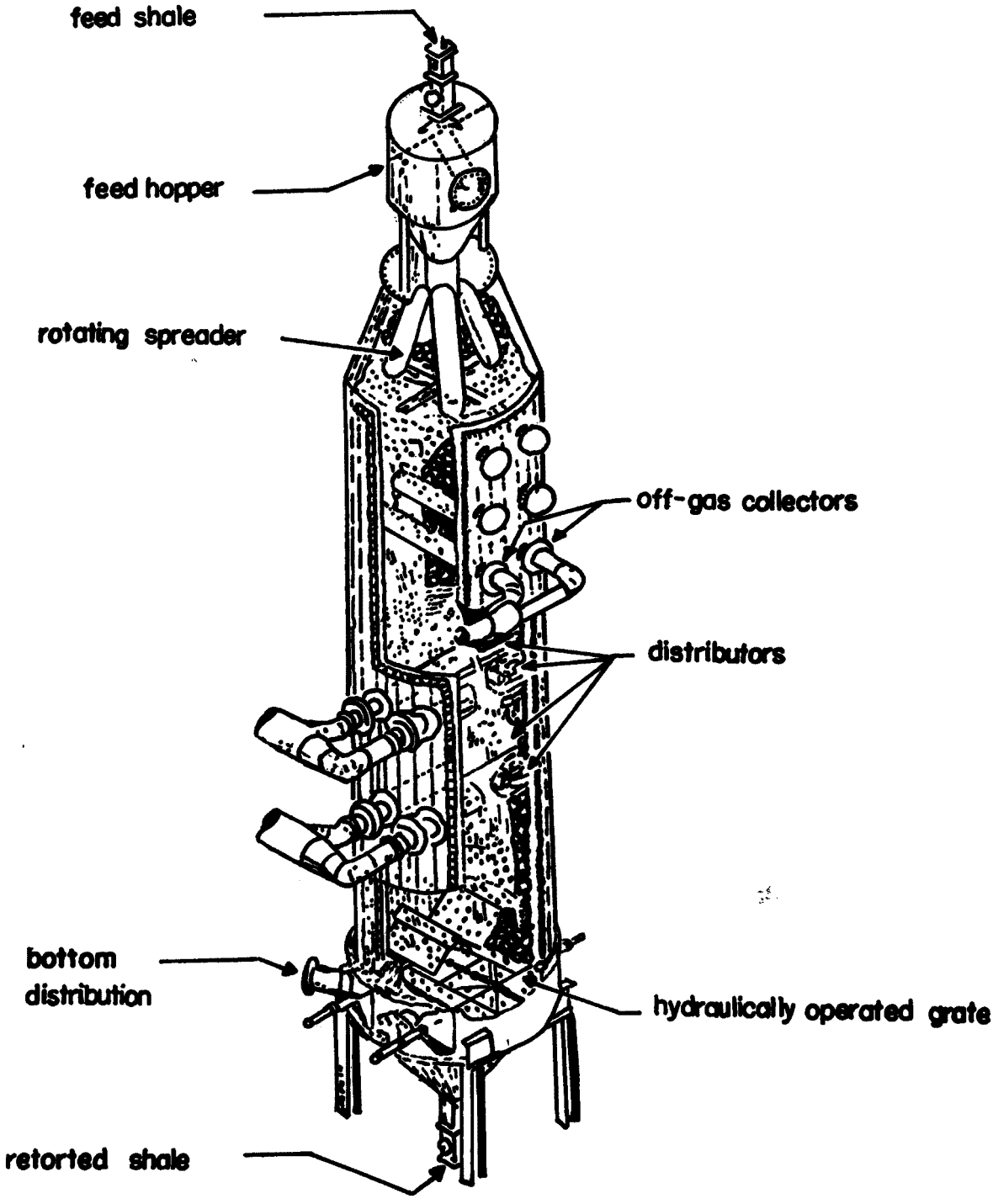


Figure 3-2. Paraho DH-type retort unit (Jones, 1976).

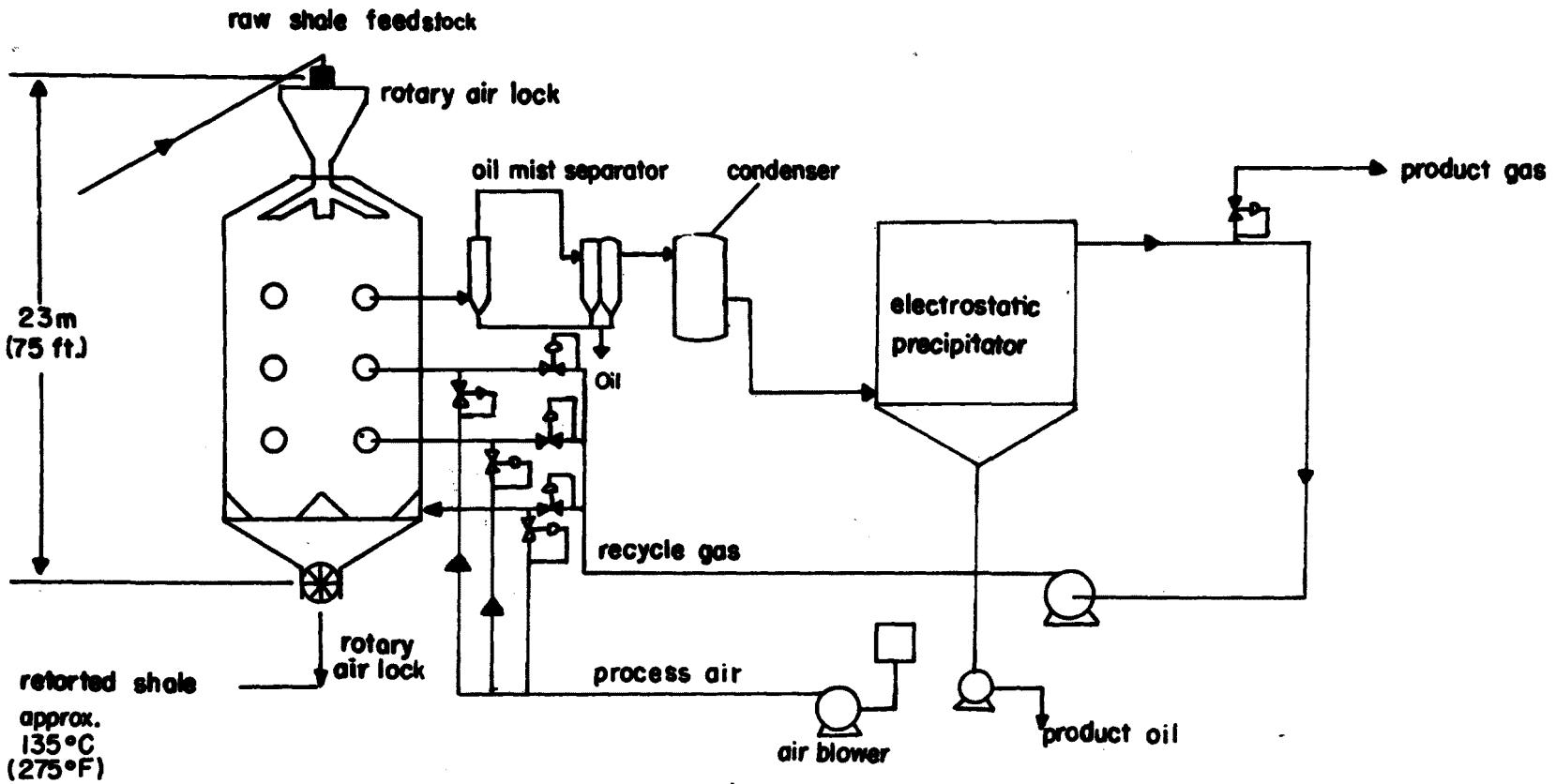


Figure 3-3. Semiworks retort for Paraho process (modified from Bartick et al., 1975).

simple countercurrent solid-to-gas heat exchanger. Air, diluted with retort recycle gas, is injected through air-gas distributors located at two levels near the center of the retort unit. The hot gas ascends through the raw shale in the retorting zone where the solid oil shale is heated to over 482°C (900°F) to cause thermal decomposition of the kerogen in the shale. In an IH retort, the heated gases are injected into the retorting zone.

The retort product gas and the oil mist are passed through an electrostatic precipitator where the shale oil is recovered (Figure 3-3). Recovered product oil flows to an oil tank, from which it is pumped either directly to downstream processing or to storage. The product gas, after leaving the electrostatic precipitator, enters a blower where it is pressurized and is then diverted to either the recycle gas system or to the net product gas system.

The spent shale discharged from the retort is conveyed to rotary moisturizing drum coolers that cool the spent shale and suppress dust. After cooling and dust suppression, the spent shale, with a moisture content of 5 to 10 percent by weight, passes on conveyors to the disposal area.

Flow Diagram

Figure 3-4 is a flow diagram of the Paraho process. The water requirements shown are based on the full commercial operation scale planned by White River Shale Project (1976). This diagram includes secondary crushing, spent shale disposal, and air processing. Approximate overall quantities of raw materials and products are indicated.

Material Balance

Assuming an average oil shale grade of 125 liters per tonne (30 gallons per ton) and a recovery efficiency of 85 percent (Fischer assay), the manufacture of 13,600 m^3 (85,000 bbl) per day of crude shale oil would require a feed rate of 122,400 tonnes (135,605 tons) per day of oil shale and 79.9 million standard m^3 (2,797 million standard ft^3) per day of combined air and recycle gas. The raw water requirement for this operation would be 9.78 million liters (2,570,400 gallons) per day. At this production rate, 96.9 million kilograms (107,355 tons) per day of spent shale and 31.79 million standard m^3 (1,122 million standard ft^3) per day of product gas would be generated (Table 3-1).

Products/Effluents Characterization

The composition of the crude shale oil produced from the 2.59-meter (8.5-foot) Paraho DH retort is presented in Table 3-2. The product gas composition is estimated for the vertical-type DH and IH retorts in Table 3-3.

The comparison of hydrogen-to-carbon ratios among petroleum crude (H/C = 2.4), oil shale syncrudes (H/C = 2.0), and coal syncrudes (H/C = 1.4) is encouraging. The similarity in hydrogen content of oil shale syncrudes and petroleum crude indicates that needed refining processes may be closely related to current petroleum refining technology. Consequently, the fuels

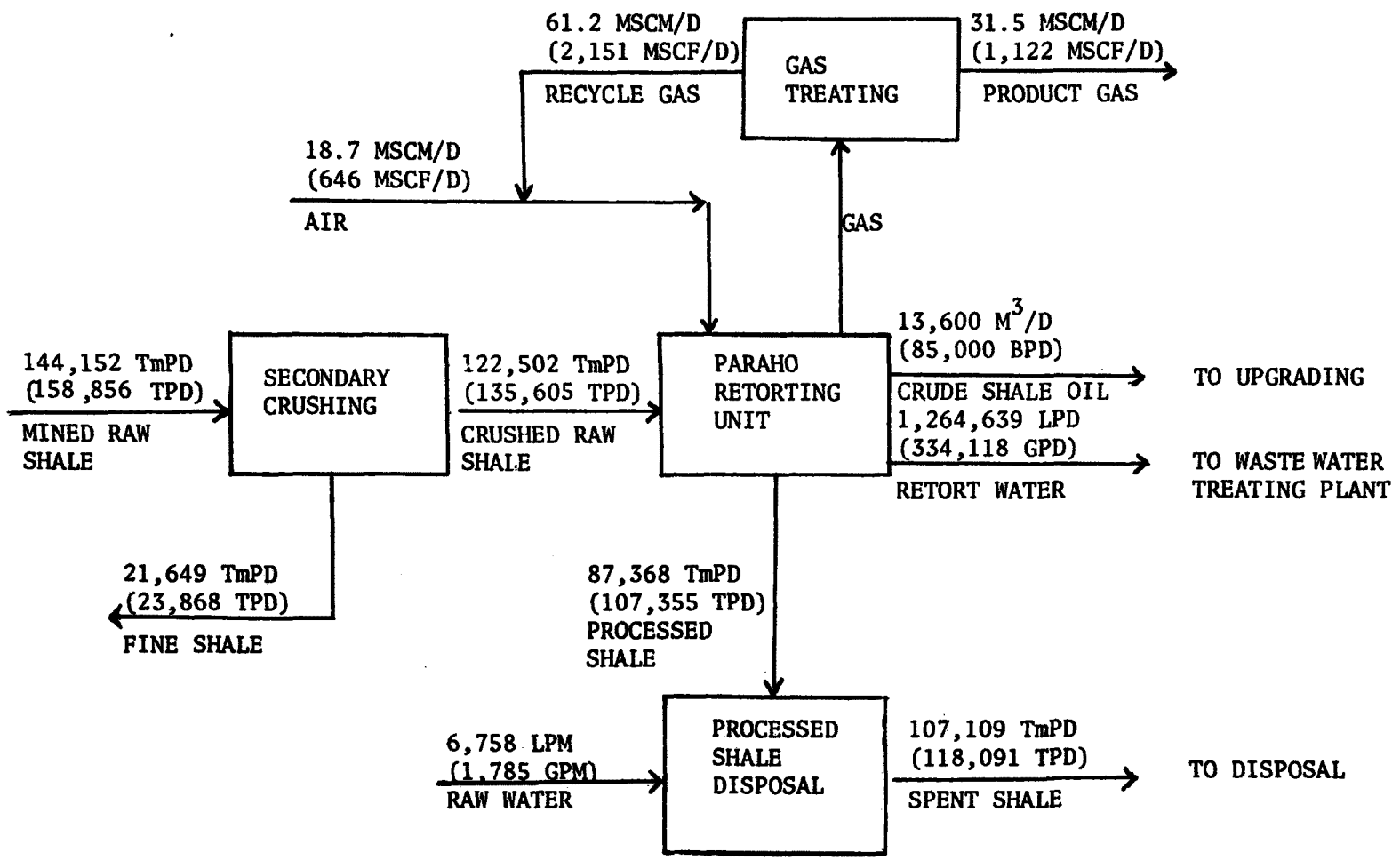


Figure 3-4. Flow diagram of the Paraho process.

TABLE 3-1. MATERIAL BALANCE OF THE PARAHO RETORTING PROCESS (BASED ON 13,600 m^3 [85,000 bbl) CRUDE SHALE OIL PER DAY)

Material	Tonnes	Tons	m^3	bbl	Std m^3 (millions)	Std ft^3 (millions)
Amount in:						
Crushed raw shale feed[a]	122,502	135,065	-	-	-	-
Recycle gas	64,371	70,967	-	-	61.2	2,161
Process air	22,381	24,676	-	-	18.7	646
Total in:	209,254	230,708	-	-	-	-
Amount out:						
Off-gas[b]	97,946	107,993	-	-	-	-
Crude shale oil[c]	12,674	13,974	13,600	85,000	92.7	3,273
Retort water[d]	1,267	1,394	-	-	-	-
Processed shale[e]	97,368	107,355	-	-	-	-
Total out:	209,255	230,716	-	-	-	-

[a] Starting from 144,194 tonnes (158,976 tons) of mined oil shale, 15 percent consisting of fine crude shale (size 0.5 in.).

[b] Recycle plus product gas.

[c] °API 19.3.

[d] Retort water assumed here to be about 10 percent of crude shale oil.

[e] Process water needed for wetting spent shale is about 9.733 million liters (2.570 million gallons) per day.

TABLE 3-2. COMPOSITION OF CRUDE SHALE OILS (FROM PARAHO AND TOSCO II PROCESSES), PETROLEUM CRUDE, AND COAL SYNCRUDE

Parameter	Paraho retort[c]	TOSCO II retort[e]	Petroleum crude[f]	Coal syncrude[h]
Physical Properties				
Gravity (°API)	19.3	21.2	15-44	-
Spec. Gravity (60/60°F)	0.938	0.927	-	-
Pour Point (°F)	85	80	0	95
Viscosity (Centistokes)	20.15 at 140°F	22	-	-
Viscosity (SUS)	47.1 at 210°F	106 at 100°F	31-1025 at 100°F	-
Total Acid No. (mg KOH/gm)	·	-	-	-
Oil Properties				
Oil (wt%)	96.0[d]	-	-	26[i]
Resin (wt%)	2.8[d]	-	-	48[i]
Asphaltene (wt%)	1.0[d]	-	-	15[i]
Carbene and Carboid (wt%)	0.2[d]	-	-	11[i]
Ultimate Analysis				
Carbon (wt%)	84.90	85.1	86.4%	82.5
Hydrogen (wt%)	11.50	11.6	11.7[g]	9.3
Oxygen (wt%)	1.40	0.8	0.16[g]	7.2
Nitrogen (wt%)	2.19	1.9	1.14[g]	0.8
Sulfur (wt%)	0.61	0.9	0.1[g]	0.3
Selected Metal Concentration				
Arsenic (ppm)[a]	19.6	-	0-0.03	-
Nickel (ppm)[b]	2.5	-	0.03-45	-
Iron (ppm)[b]	71.2	-	-	-
Vanadium (ppm)[b]	0.37	-	0.002-348	-

[a]Determined by atomic absorption.

[b]Determined by γ-ray fluorescence.

[c]Data modified from Bartick et al. (1975); data are for directly heated Paraho retort.

[d]Data from Wen and Yen (unpublished data).

[e]Data modified from Hall and Yardumian (1968).

[f]Data modified from Dunstan et al. (1938).

[g]Data from Nelson (1958).

[h]Data from Jones (1966).

[i]Data from Yen and Schwager (1976).

TABLE 3-3. GAS COMPOSITION OF DH AND IH RETORTS

Gas composition	Vertical type DH[e] Vol%	Vertical type IH[e] Vol%	TOSCO II IH[f] Vol%
N_2[a]	61.0	1.8	-
O_2[b]	0.1	-	-
H_2[c]	4.9	36.6	22.4
CO	2.9	7.3	3.6
CO_2[d]	22.8	21.2	21.4
H_2S	0.1	2.0	4.3
C_1	2.1	20.5	15.2
C_2'S	1.1	6.5	15.7
C_3'S	0.6	1.2	7.7
C_4'S	0.3	0.6	4.3
C_5+	-	-	5.4
H_2O[d]	4.1	2.3	-
Total:	100.0	100.0	100.0

[a]Determinations made by Dohrmann method. For samples with end points of 343°C (649°F), nitrogen is determined by the Kjeldahl method.

[b]Determined by pyrolyzing the sample in He and CO_2 determined by thermal conductivity.

[c]Determined by oxidizing the sample in an oxygen stream.

[d]Determined by thermal conductivity.

[e]Data from Bartick et al. (1975).

[f]Data from Hall and Yardumian (1968).

produced are likely to be much like those in use today, minimizing impacts on combustion system design.

The results of the true boiling point data for various distillation fractions are presented in Table 3-4. Levels of the various heterocyclic atoms (nitrogen, sulfur, and oxygen) in various distillation fractions are also provided, along with analyses of the organic properties and levels of selected metals.

RETORTING PROCESS—TOSCO II

The Oil Shale Corporation (TOSCO) developed this IH retorting process in 1957, building a 22 tonne (24 ton) per day pilot plant in Denver. In 1964, the "Oil Shale Venture" was formed by TOSCO, SOHIO, and Cleveland Cliffs Iron Company for the purpose of demonstrating the process on a semiworks scale. Field operations reached a capacity of 910 tonnes (1,000 tons) per day using a 17-story semiworks plant built at Parachute Creek, Colorado. The semiworks plant was shut down in 1972.

Mechanical Description

The TOSCO II retorting process (Whitcombe and Vawter, 1976; Hall and Yardumian, 1968) features the use of heated ceramic balls as a heat-transferring medium. The retorting vessel is a rotating drum in which raw oil shale is heated by contact with the heated ceramic balls (Figure 3-5).

Process Description

In the TOSCO II process, crushed oil shale is heated to approximately 482°C (900°F) by direct contact with heated ceramic balls (Rammier, 1968). Raw oil shale is crushed to a size of 1.27 centimeter (cm) (0.5 inch) or smaller and is first preheated by ball-heater flue gas before it is deliverd into the pyrolysis drum. The 1.27-cm (0.5-inch) diameter ceramic balls are heated to about 593°C (1,100°F) and then fed to the rotating retort drum where the thermal decomposition reaction takes place (Figure 3-5). The rotation of the pyrolysis drum mixes the crushed shale and ceramic balls, providing a high rate of heat transfer and pyrolysis.

The pyrolysis drum discharges directly into the accumulator where retorted shale and balls are separated on a cylindrical trommel screen. Spent shale passes through the screen openings and into a surge hopper. The ceramic balls pass from the accumulator to a ball elevator for transfer to the ball heater where they are reheated by direct contact with flue gas. The ceramic balls are then recycled through the retort.

The processed (spent) shale discharged from the pyrolysis drum at 482°C (900°F) is cooled by being the heat source for a rotating high-pressure steam generator. It then is discharged to another rotating vessel in which it is further cooled by direct quenching with water. The water flow is controlled to obtain about 12 percent (by weight) moisture in the spent shale discharged from the vessel (Whitcombe and Vawter, 1976). The moisture is added to control dust emission and to make the spent shale suitable for compacting in the disposal area.

TABLE 3-4. COMPOSITION ANALYSES OF DISTILLATION FRACTIONS FROM PARAHO CRUDE SHALE OIL[a]

Characteristic	Gas	IBP-165	165-380	380-480	480-520	520-600	600-650	650-700	700-750	750-800	800-843	843
Physical properties												
Gravity (°API)	—	85.0	39.5	34.2	30.3	28.6	23.7	22.0	20.2	19.7	17.7	12.0
Specific gravity	—	0.65	0.8275	0.8540	0.8745	0.8838	0.9117	0.9218	0.9328	0.9358	0.9484	0.9861
Pour point (°F)	—	—	—	-35	-10	+15	+45	+60	+80	+100	+100	—
Smoke point (°F)	—	—	—	11.5	—	—	—	—	—	—	—	—
wt% of cut on crude shale oil	0.13	0.32	0.70	4.95	3.10	9.47	6.46	6.08	6.13	7.55	15.57	39.54
Ultimate analysis												
Sulfur (wt%)	—	0.93	1.15	0.75	0.84	0.67	0.69	0.68	0.63	0.55	0.53	0.52
Nitrogen (wt%)	—	0.138	1.33	1.34	1.47	1.76	1.74	1.82	2.33	2.07	1.99	2.60
Oxygen (wt%)	—	3.19	0.52	0.66	0.72	0.98	0.48	0.77	0.32	0.67	1.96	0.82
Carbon (wt%)	—	84.36	83.84	84.16	83.29	83.98	84.05	84.92	84.39	85.05	85.72	—
Hydrogen (wt%)	—	13.42	12.63	12.54	12.31	12.26	11.39	11.78	11.44	11.34	11.65	—
C/H	—	6.29	6.64	6.71	6.77	6.85	7.05	7.21	7.38	7.50	7.36	—
Oil properties[b]												
Paraffins	—	—	—	36.7	32.1	30.6	34.3	19.8	28.9	11.3	—	—
Olefins	—	—	—	3.1	4.6	—	—	2.0	2.0	2.0	—	—
Naphthenes	—	—	—	33.3	28.6	18.9	9.3	15.7	8.2	21.9	—	—
Aromatics	—	—	—	26.9	34.7	50.5	56.4	64.5	62.9	66.8	—	—
Selected metal concentrations												
Nickel (ppm)	—	—	1.86	0.51	0.49	0.19	0.17	0.23	0.27	0.38	0.71	1.57
Vanadium (ppm)	—	—	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.11
Iron (ppm)	—	—	7.0	10.7	32.2	4.68	3.8	5.9	8.8	6.3	10.8	36.2
Arsenic (ppm)	—	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17.2

[a]Data modified from Bartick et al. (1975).

[b]Olefin content determined by fluorescence indicator absorbence (FIA); paraffin, naphthene, and aromatics determined by mass spectrometry.

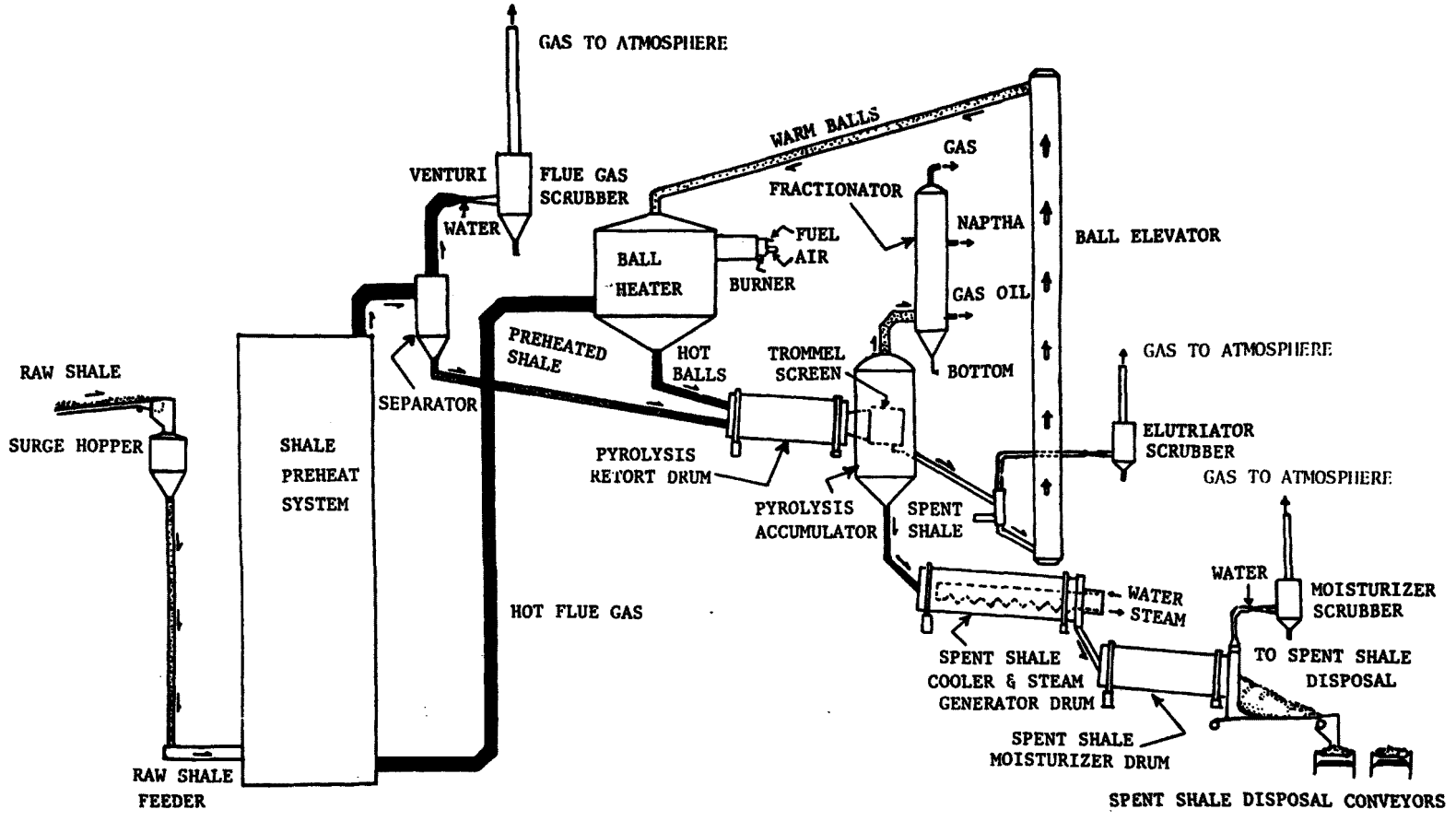


Figure 3-5. Pyrolysis unit, TOSCO II process (modified from Whitcombe and Vawter, 1976).

Vaporized product shale oil and gas at the top of the pyrolysis accumulator flow through a cyclonic separator to remove entrained solids and into a fractionation system. In the fractionator, the oil vapor is cooled to produce heavy oil, distillate oils, naphtha, and light gases. Hot vapors are further cooled to recover additional oil before the gas is compressed and conveyed to downstream hydrogen sulfide treatment.

Flow Diagram

Figure 3-6 is a general flow diagram showing the TOSCO II process. The water requirements presented are based on calculations for the White River Shale Project. In this diagram, the fuel requirement of the plant is supplied by combustion of gas formed in the retorting process after scrubbing the gas to remove hydrogen sulfide. Sulfur is recovered as the by-product of this process. Other by-products include ammonia and petroleum gas.

Material Balance

A representative balance for the TOSCO II process for the production of 2,400 m^3 (15,000 bbl) per day of crude shale oil is shown in Table 3-5. After mining and crushing, the shale is fed to the retorting unit, which consists of two 8,182 tonne (9,000 ton) TOSCO II retorting trains operating parallel to each other. Sulfur is recovered at a 30-tonne (33-ton) per day rate as the by-product.

Products/Effluents Characterization

Composition data on a typical TOSCO II oil is presented in Table 3-2. Elemental analyses of the feedstock and products are given in Table 3-6. Note that the primary product, shale oil, contains about 0.83 percent sulfur and 1.82 percent nitrogen (Table 3-2). The high content of nitrogen and sulfur in crude shale oil necessitates special HDNS (Hydrogen Denitrogenation, Desulfurization) processing. Table 3-7 shows a typical analysis of C_8 and lighter components produced in the TOSCO II retort. Because air is excluded from the TOSCO II retort, the gas is substantially free of nitrogen and contains the amount of carbon oxides produced by pyrolysis as well as hydrogen sulfide and other sulfur compounds.

A chemical analysis of spent shale from the TOSCO II retorting process in Colorado is listed in Table 3-8. The dissolved salts reported in the leachate from spent shale are listed in Table 3-9.

SUPPORTING PROCESSES

Processed Shale Cooling

The processed shale from retorting represents 80 to 90 percent of the raw material fed to the retorts. The treated retort water used to moisten the spent shale contains inorganic and organic compounds that could be the products of oil shale retorting or residues in the spent shale. The approximate concentrations of contaminants expected in the water are reported in Table 3-10. There are three basic approaches for cooling processed shale from the high temperatures

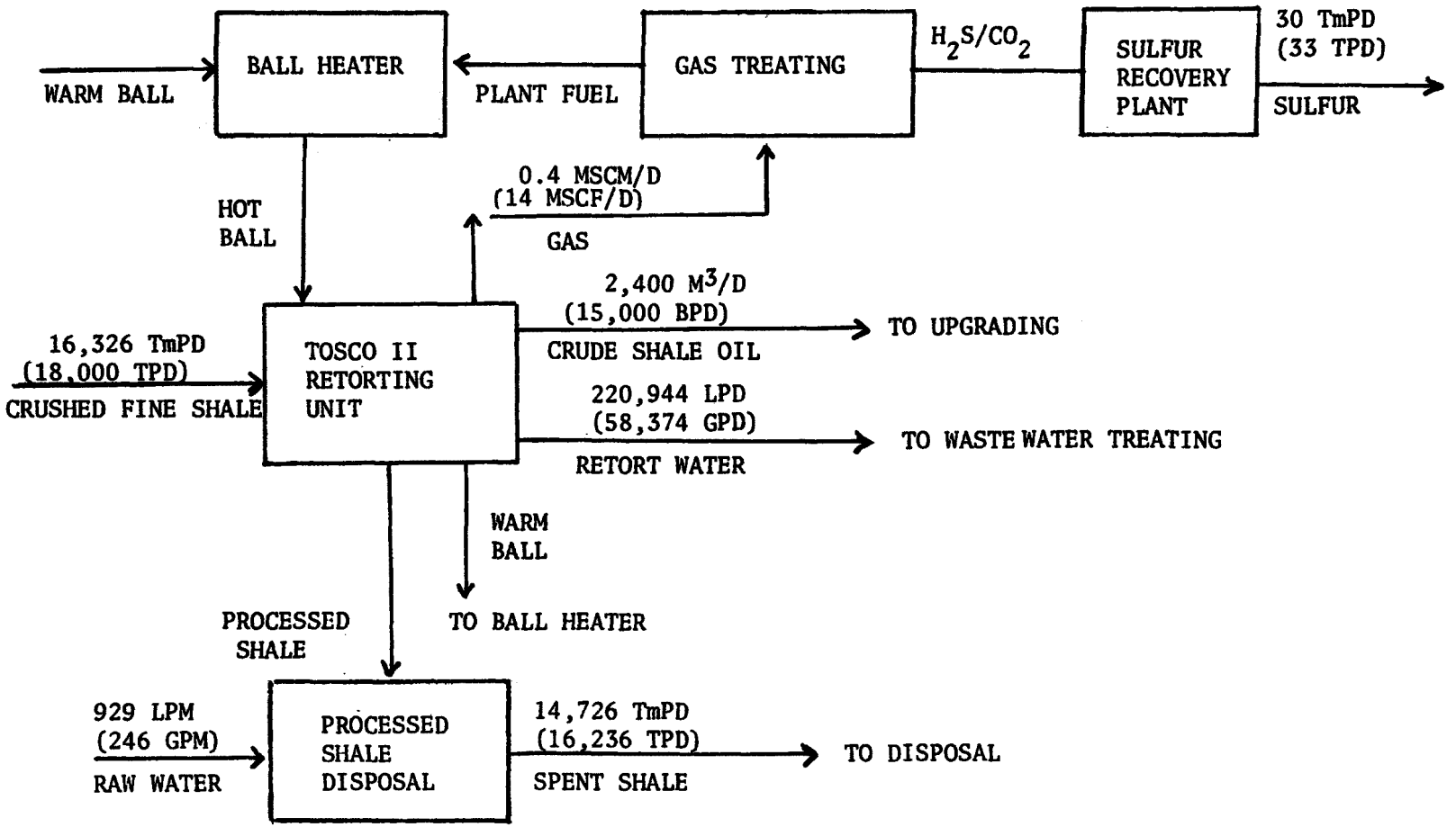


Figure 3-6. Flow diagram for the TOSCO II process.

TABLE 3-5. MATERIAL BALANCE OF THE TOSCO II PROCESS (BASED ON 2,400 m^3 [15,000 bbl) CRUDE SHALE OIL PER DAY)

Material	Tonnes	Tons	m^3	bbl	Std m^3 (millions)	Std ft^3 (millions)
Amount in:						
Crushed raw shale feed	16,326	18,000	-	-	-	-
Total in:	16,326	18,000	-	-	-	-
Amount out:						
Off-gas[a]	440	485	-	-	0.4	14
Crude shale oil[b]	2,210	2,437	2,400	15,000	-	-
Retort water[c]	221	244	-	-	-	-
Processed shale[d]	13,387	14,760	-	-	-	-
Total out:	16,258	17,926	-	-	-	-

[a]Based on retort gas production of 923 std ft^3 per barrel of oil (Hendrickson, 1975).

[b]°API 212.

[c]Retort water assumed here to be about 10 percent of crude shale oil.

[d]Spent shale approximately 80 percent of raw shale feed.

TABLE 3-6. ELEMENTAL ANALYSES OF RAW SHALE AND RETORT PRODUCTS OF TOSCO II PROCESS[a]

	Organic carbon (wt%)	Sulfur (wt%)	Nitrogen (wt%)	Hydrogen (wt%)
Raw shale feedstock[b]	16.53	0.75	0.46	2.15
Retort product				
Spent shale	4.94	0.62	0.28	0.27
Crude shale oil	84.68	0.83	1.82	11.27
Gas	48.87	4.37	nil	9.86
Water	nil	0.43	1.30	11.30

[a]Data from Atwood (1973).

[b]33 gallons per ton of raw shale.

TABLE 3-7. LIGHTER COMPONENT PRODUCTS FROM THE TOSCO II SEMIWORKS PLANT PROCESS

Component product	Yield per 100 pounds Fischer assay oil (pounds)
H_2	0.41
CO	0.91
C_1	2.22
C_2	2.84
C_2-	1.37
C_3	1.62
C_3-	1.41
Subtotal	10.78
iC_4	0.13
nC_4	0.68
C_4-	1.38
C_5^-	1.67
C_6	1.17
C_7	0.76
C_8	0.36
Fischer assay oil	99.59
Subtotal	105.74
Total	116.52
CO_2	8.58
H_2S	1.34
Grand total	126.44

[a]Data modified from Hall and Yardumian (1968).

TABLE 3-8. CHEMICAL ANALYSIS OF SPENT SHALE FROM TOSCO II PROCESS AND FISCHER ASSAYS

Constituent	TOSCO II[a] wt (%)	Fischer assays[b] wt (%)
Total carbon	9.82[c]	8.16[d]
SO_3	2.63	2.02
SiO_2	33.07	40.22
Al_2O_3	9.14	11.20
Fe_2O_3	3.24	4.24
CaO	17.56	20.31
MgO	7.74	8.54
Na_2O	0.77	3.11
K_2O	1.39	2.20
Others	14.64	-
Total	100.00	100.00

[a]Data modified from Nevens et al. (1961).

[b]Average values from oil shale grade 17.8 gallons/ton to 51.8 gallons/ton.

[c]Inorganic carbon 4.41 percent; organic carbon 5.41 percent.

[d]Inorganic carbon 5.43 percent; organic carbon 2.73 percent.

TABLE 3-9. SOLUBLE SALTS IN SPENT SHALE LEACHATE OF TOSCO II PROCESS[a]

Incremental volume of leachate sample (ml)	Cumulative total volume leachate (ml)	Conductance (mmhos/cm at 25°C)	Concentration (mg/l) of sample				
			Na^+	Ca^{++}	Mg^{++}	$SO_4^=$	Cl^-
254	254	78,100	35,200	3,150	4,720	90,000	3,080
340	594	61,600	26,700	2,145	3,725	70,000	1,900
316	910	43,800	14,900	1,560	2,650	42,500	913
150	1,060	25,100	6,900	900	1,450	21,500	370
260	1,320	13,550	2,530	560	500	8,200	250
125	1,445	9,200	1,210	569	579	5,900	138
155	1,600	7,350	735	585	468	4,520	138
250	1,850	6,825	502	609	536	4,450	80
650	2,500	5,700	–	–	–	–	–
650	3,150	4,800	–	–	–	–	–
650	3,800	4,250	–	–	–	–	–
760	4,560	3,850	–	–	–	–	–

[a]Data from Hendrickson (1975).

TABLE 3-10. COMPOSITION OF WASTEWATER USED IN SPENT SHALE MOISTURIZING[a,b]

Constituent	Concentration (ppm)
Amines	1900
Organic acids	1000
Carbonates	520
Sulfates	510
Chlorides	330
Chromates	130
Thiosulfates	60
Phenol	60
Cyanides	50
Ammonia	30
Hydroxides	30
Phosphates	15
Chelates	3
Arsenic	0.03

[a]Data from Colony Development Operation (1974).

[b]Processed water after ammonia stripping and other pretreatment or primary treatment.

at the retort outlet sufficiently to allow safe and reliable transport and disposal. These are discussed below.

Spraying with Water on Conveyors—

In this system, cooling water is sprayed on the spent shale as it travels on a conveyor belt leading from the retort unit (Figure 3-7). The entire system is enclosed and the dust-laden steam is collected and treated using a wet scrubber system with heat rejection to the atmosphere. Belt-conveyor slopes are limited to a maximum slope of about 30 degrees, and a more preferred slope is generally in the 18-to-20-degree range. The belt-conveyor system requires less equipment than some other types of processed shale cooling systems and subsequently has a lower cost and greater reliability. However, the system is enclosed and transmits dust-laden steam, which could make it difficult to cool and wet the processed shale adequately and also to suppress dust efficiently.

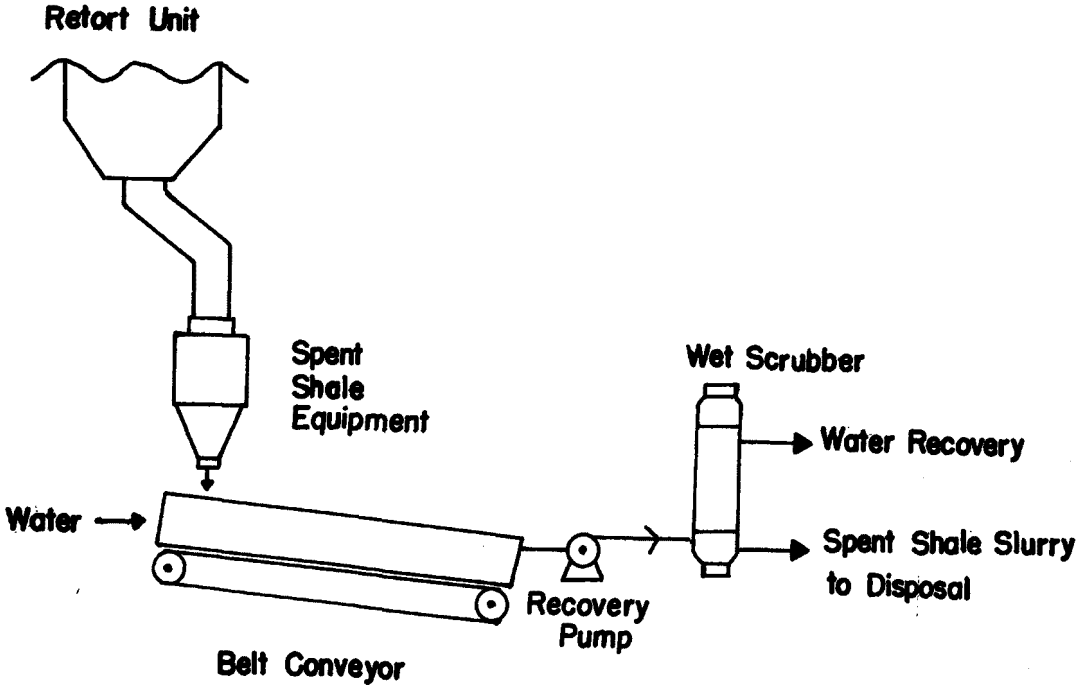


Figure 3-7. Spent-shale closed disposal system with water spraying on conveyor (modified from Hendrickson, 1975).

Air Cooling on Moving Grates—

The moving-grate mechanism at the bottom of the Paraho retort spreads processed shales from the retorting zone which are cooled by air blown upward on them. The dust-laden cooling air is contained in a totally enclosed system and moved to scrubber equipment. After cooling, the processed shale is moisturized to suppress dust and passed on conveyors to the disposal area.

This system uses mainly air, thus minimizing the water requirement. However, equipment needs are greater and, consequently, the system costs more and is less reliable.

Rotary-Drum Cooler—

Rotary-drum coolers have been successfully applied to a wide range of chemical industries. In this system, processed shale, after leaving the retorting unit, is conveyed to rotary moisturizing drum coolers where its temperature is reduced by tumbling and water sprays. The intimate mixing of water and processed shale could be guaranteed in this system. Dust-laden steam and moist air produced are passed to scrubbers that condense steam and remove dust. The advantages of this system are that it ensures that a reasonable temperature can be achieved for the disposal of processed shale. In addition, shorter distances are required to ensure cooling of processed shale in comparison with other cooling systems. Its disadvantages are the higher cost of equipment, maintenance, and operating expenses.

Raw Shale Feeding and Crushing

Raw shale for retorting processes must be crushed. The size of the crushed raw shale that can be processed varies from one type of retort to another. The Paraho process requires shale particles between 1.3 centimeters (0.5 inch) and 7.6 centimeters (3 inches) in size, while the TOSCO II process handles crushed shale smaller than approximately 1.3 centimeters (0.5 inch). Various retorting processes have different needs depending on how the shale is heated and how it is transported, among other factors.

Among the reasons for limiting the maximum particle size are time requirements for particle heating and kerogen diffusion. In retorting, heat must be conducted to the center of the particle in order to attain maximum efficiency of conversion from solid organic matter to oil vapor, gas, and residue. Then, the oil vapor and gas must be diffused from the particles to the surrounding gas space. Heating and diffusion time increase with particle size.

Figure 3-8 shows a raw shale feed crushing system of the Paraho retorting process. Raw shale from the mine is charged to the primary crusher feed hopper and passed through a jaw crusher where oversize pieces are either broken down to allow passage or discarded. After the first stage of reduction by the jaw crusher, the shale is carried by a belt conveyor from the primary crusher to the primary screen. The oversize shale goes to the secondary crusher, and the undersize shale is conveyed to the fine shale storage pile or discarded. The particles retained on the (lower) screen are of the desired product size for the Paraho retort system and are conveyed by the product conveyor to storage bins. Before retorting, the crushed shales of desired size are passed down a polishing screen to remove dust and then conveyed to the retort unit. Raw shales in a size range of approximately 1.3 to 7.6 centimeters (0.5 to 3 inches) are fed to the retort.

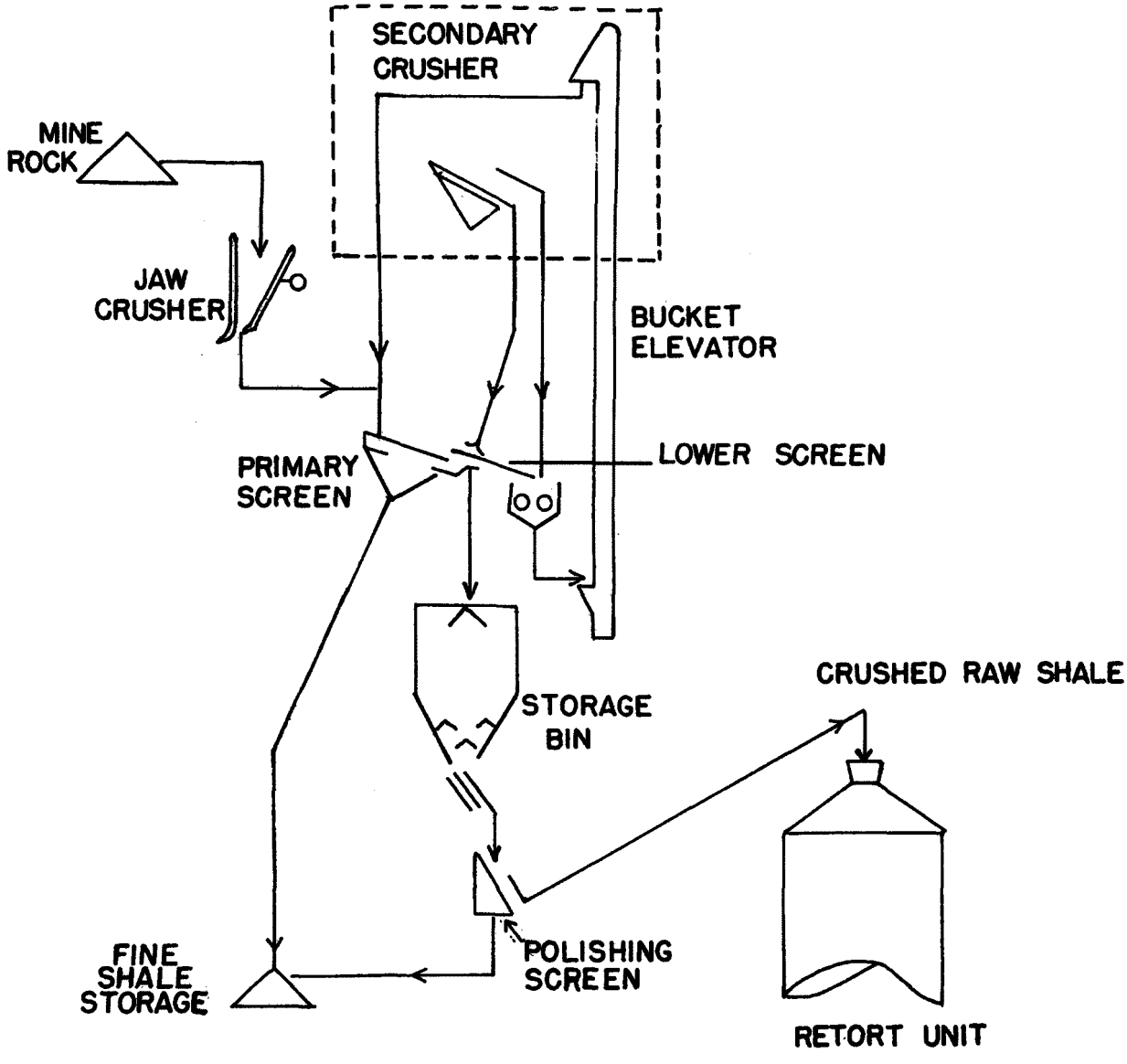


Figure 3-8. Raw shale feed crushing system (modified from Bartick et al., 1975).

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SECTION 4

HYDROGENATION (UPGRADING) PROCESS

GENERAL PROCESS DESCRIPTION

Oil shale retorting yields a viscous, waxy, high-nitrogen, and moderate level-sulfur liquid product that is undesirable for transportation or storage. For this reason, development plans usually include an upgrading or hydrotreating process to treat shale oils before they are shipped to petroleum refineries. The upgrading involves heating, hydrogenation, and possibly some cracking of the crude shale oil. The upgrading alternatives can be categorized according to the desired final product (Table 4-1).

Visbreaking, categorized as a mild thermal cracking process, lowers the molecular weights of the shale oil hydrocarbons only slightly. If the visbreaking is accomplished in the presence of hydrogen, the hydrogen helps to stabilize the reduced pour point of crude shale oil products obtained by combining visbroken and hydrogenated oils. The resulting combination of crude shale oils is a product with a reduced pour point which is suitable for storage and transportation without becoming too viscous to be handled.

Delayed coking is a semicontinuous thermal cracking process. It produces a lower molecular weight distillate and a solid residue (coke). The distillate is a cracked shale oil with lowered pour point and viscosity.

In the heavy-oil cracking process, both lower molecular weight distillate and a coke residue are produced. The properties of cracked shale oil are similar to those of the shale oil produced by the delayed coking process described above.

During hydrotreating, the crude shale oil is treated with hydrogen in the presence of a catalyst to remove the components of sulfur, nitrogen, and oxygen from the crude oil. The product resulting from the hydrotreating process has a low viscosity and a low pour point, and the concentrations of sulfur, nitrogen, and oxygen in the bulk of crude shale oil are reduced greatly. The upgraded shale oil produced from a severe upgrading process, as shown in Table 4-1, is suitable for pipeline transport and further processing in petroleum refineries.

TABLE 4-1. UPGRADING ALTERNATIVES FOR CRUDE SHALE OIL[a]

Upgrading alternatives	Processing choices	Product quality
I. None	→	Crude shale oil not readily transported by pipeline
II. Mild	→ Visbreaking → Delayed coking → Heavy-oil cracking → Hydrostabilization	A cracked shale oil more suitable for transport by pipeline
III. Moderate	→ Moderate hydrogenation	Suitable as boiler fuel or refinery feedstock
IV. Severe	→ Delayed coking → Hydrogenation → Severe hydrogenation → Heavy-oil cracking → Hydrogenation	High-quality refinery feedstock similar to sweet crude oil

[a] From White River Shale Project (1976).

HYDROGENATION

Mechanical Description

Shale oil hydrogenation includes hydrotreating the crude shale oil to reduce levels of sulfur and nitrogen, and hydrocracking of the naphtha to reduce product viscosity for piping purposes.

The crude Paraho processed shale oil has been refined by using the Gary Western facility at Fruita, Colorado (Bartick et al., 1975). The hydrotreating unit consists of a denitrogenation/desulfurization reactor, a fractionating tower, and a naphtha hydrotreater with separators. Under contract to the U.S. Navy, the Gary Western facilities have been used to convert Paraho crude shale oil into military fuels including NATO gasoline, JP-4, JP-5/Jet A, DFM/DF-2, and heavy fuel oil. The components of a typical hydrogenation scheme are illustrated in Figure 4-1. Because of reactor size limitations, multiple reactors might be required.

Two types of hydrotreating units have been proposed for TOSCO II crude shale oil refining (Whitcombe and Vawter, 1975). One is a distillate hydrotreater for processing the 400° to 950°F oil component from retorting plus similar boiling-point range components formed in the coker. The other type processes C_5 to 400°F naphtha formed in the retort, coker, and distillate hydrotreater. The process is designed by Atlantic Richfield Company, which conducted pilot plant studies using TOSCO II crude oil.

Process Description

The hydrogenation process (Figure 4-1) includes a crude shale oil hydrotreater and a naphtha hydrotreater. The crude shale oil hydrotreater unit consists of a multistage hydrogen denitrogenation, desulfurization reactor (HDNS) with a separator, a gas stripper, a fractionating tower, and a stabilizer. The naphtha hydrotreater consists of a heater, a denitrogenation reactor, a separator, and a gas stripper.

In the crude shale oil hydrotreating process, the oil and hydrogen are premixed and heated. This mixture then enters the HDNS reactor, which contains catalysts with high selectivity for hydrogenation of nitrogen and sulfur compounds. The output stream from this reactor is mixed with water and enters a separator. The excess hydrogen is removed and recycled back to the HDNS reactor. Water, ammonia, and hydrogen sulfide are removed from the separator. The desired denitrification and desulfurization of the C_4 and light material are accomplished in the HDNS unit. The "heavy" hydrocarbon (C_5 and up) fractions are then distilled in a fractionating column to yield the desired distillation fractions. The naphtha fraction produced is stabilized and separated and then further treated by the naphtha hydrotreater unit for additional denitrification.

Ammonia and hydrogen sulfide are removed from the crude shale oil hydrotreating unit by water-washing the recycle gas in the separator. Sour wash water is sent to the wastewater treating plant. The stripped water, after the removal of hydrogen sulfide and ammonia, can be recycled to the hydrotreating units.

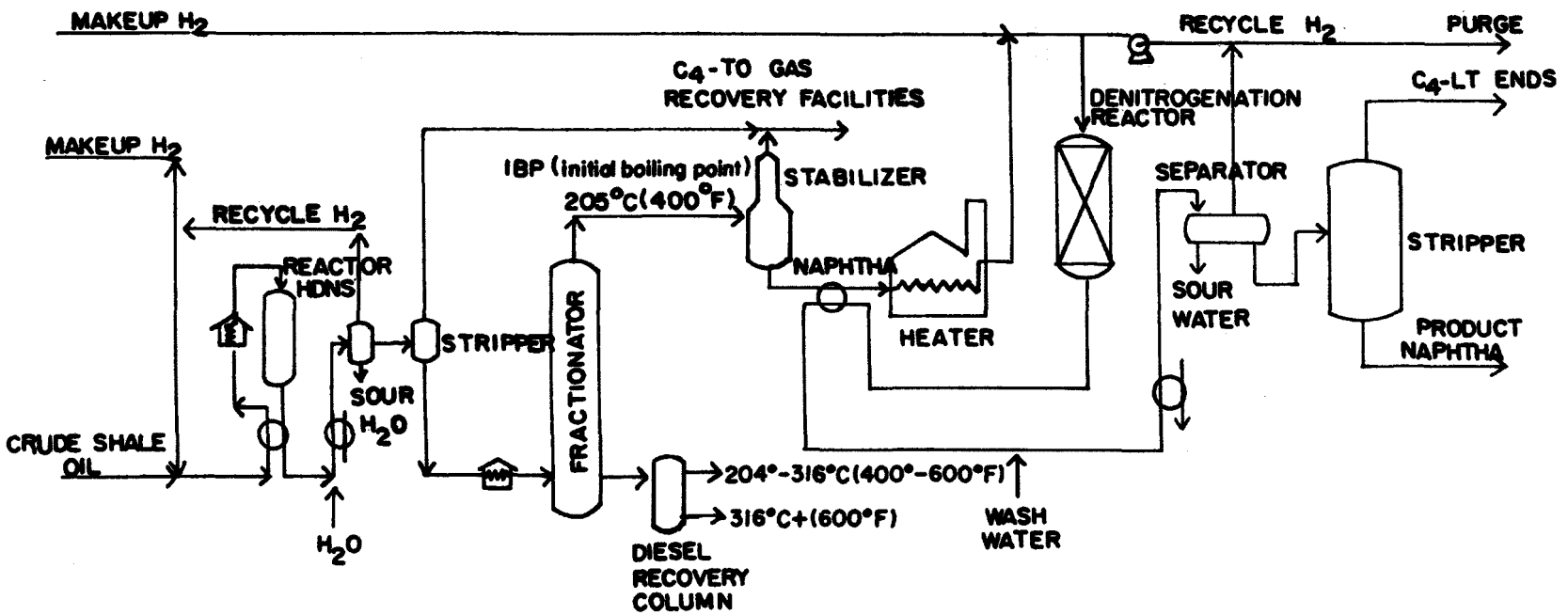

Figure 4-1. Typical hydrotreater for crude shale oil (modified from White River Shale Project, 1976).

The slip-stream fraction (bottom material of 205°C [400°F] and up which is separated from the fractionator) is fed to a recovery column to recover the diesel fuel (204° to 316°C [400° to 600°F] fraction and the resulting bottom fraction (316°C [600°F] and up). The bottom fraction of 316°C (600°F) and up is used as fuel oil for process heaters and the utility plant.

The naphtha fraction recovered from each crude shale oil hydrotreating unit and C_5 to 205°C (400°F) fraction recovered from the light ends (gases) compression facilities are processed in a conventional naphtha hydrotreating unit (see Figure 4-1) to reduce the nitrogen content from 3,000 ppm to about 1 ppm. The C_4 and light ends separated from the stripper in the naphtha hydrotreater unit are combined with the light fraction from the HDNS reactor and sent to the amine absorber treating unit to remove acid gases (hydrogen sulfide and carbon dioxide) and some trace heavier material. After amine treating, the C_4 and light ends fraction can be used for hydrogen plant feed.

Flow Diagram

A flow diagram for a generalized full-scale shale oil upgrading plant is shown in Figure 4-2. The diagram presents all the supporting processes including amine treating, hydrogen plant, low-Btu gas treating, sulfur recovery and tail gas treating, wastewater treating, and sour water stripper. These supporting processes are discussed in a later subsection. Additional details on hydrogenation, denitrogenation, and desulfurization may be found in Thomas (1970), Schuit and Gates (1973), Cottingham and Nickerson (1975), Satterfield et al. (1975), Silver et al. (1976), and Frost et al. (1976).

Material Balance

An overall material balance for crude shale oil upgrading and product recovery is shown in Table 4-2. Each processing component of hydrotreating inputs and outputs is listed.

Product Characterization

Table 4-3 gives the properties of the output from the crude shale oil hydrogenation and naphtha hydrotreater. A comparison between crude shale oil and upgraded product shows a great decrease in pour point from 30° to 10°C (85° to 50°F) and a decrease of viscosity from 20 centistokes at 60°C (140°F) to 4 centistokes at 38°C (100°F). The sulfur content of 0.61 weight percent in crude shale oil is reduced to 0.025 weight percent after upgrading. Similarly, after denitrogenation, nitrogen content is decreased from an original 2.19 weight percent to 0.034 weight percent.

Table 4-4 presents the overall yields from crude shale oil after completing the hydrogenation of crude shale oil. The combined yield of products from hydrogenation is about 76.8 percent by weight of the crude shale oil.

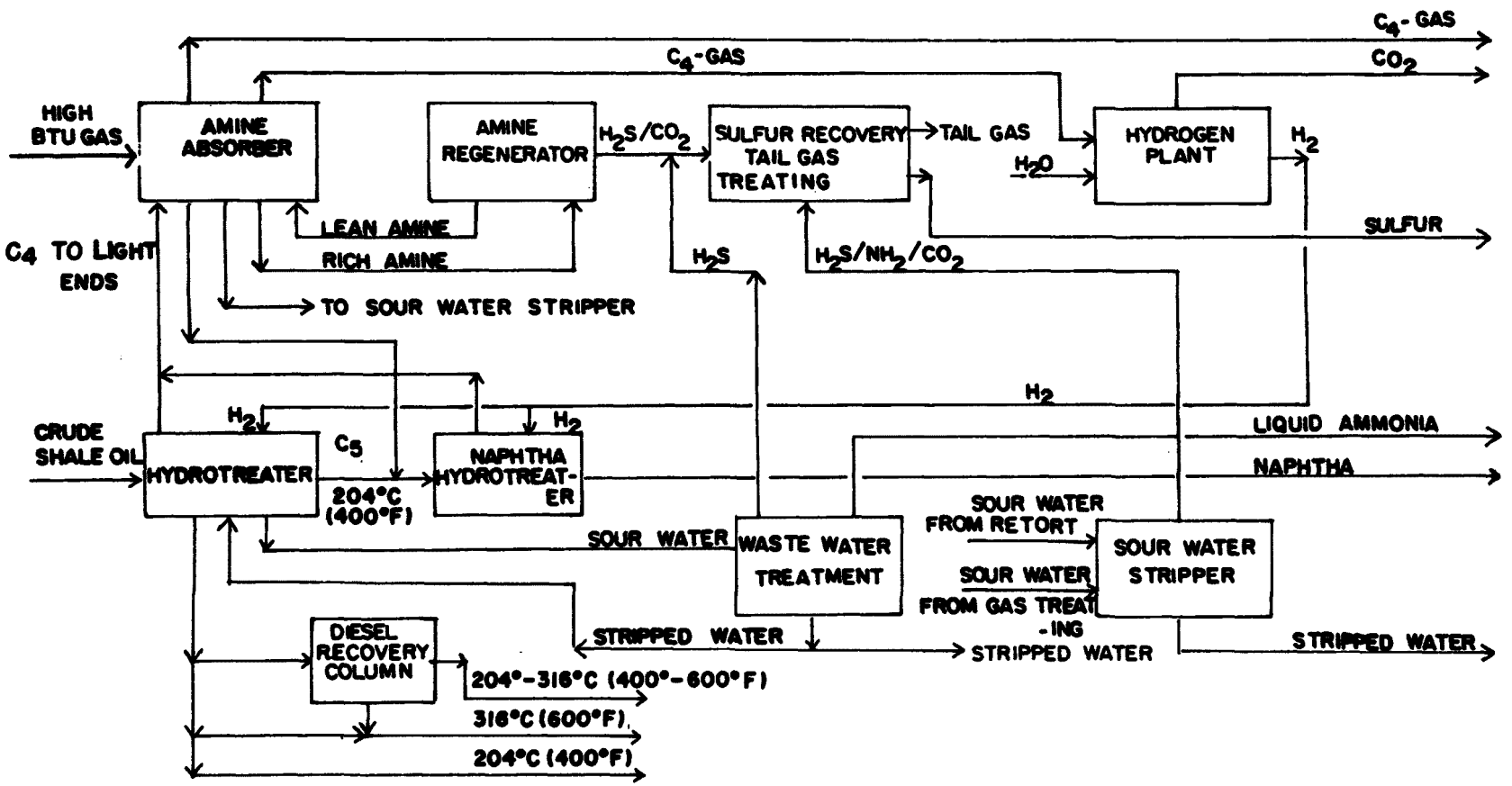

Figure 4-2. Flow diagram for upgrading operation of crude shale oil (modified from White River Shale Project, 1976).

TABLE 4-2. MATERIAL BALANCE OF UPGRADING PROCESS (BASED ON 1,600 m^3 [10,000 bbl] CRUDE SHALE OIL CAPACITY PER DAY)[a]

Material	Tonnes	Tons	m^3	bbl	Std m^3 (Millions)	Std ft^3 (Millions)
Amount in:						
Crude shale oil[b]	1,491	1,644	1,600	10,000	-	-
Gas-to-amine treating plant	116	128	-	-	0.1	3.5
Water-to-hydrogen plant	209	230	-	-	-	-
Air-to-sulfur plant	33	36	-	-	0.03	0.9
Total in:	1,849	2,038				
Amount out:						
Off-gas	16	17	-	-	0.01	0.4
CO_2 from hydrogen plant	257	283	-	-	-	-
Naphtha	268	295	364	2,270	-	-
Gas oil	1,153	1,271	1,367	8,549	-	-
Sulfur	15	17	-	-	-	-
Ammonia	37	41	-	-	-	-
Water produced	25	28	-	-	-	-
Sulfur plant tail gas	78	86	-	-	-	-
Total out:	1,849	2,038	-	-	-	-

[a]Data modified from White River Shale Project (1976).

[b]API 19.3.

TABLE 4-3. INSPECTIONS OF HYDROTREATED PRODUCTS FROM PARAHO CRUDE SHALE OIL[a]

Characteristic/ constituent	Crude oil	Products			Upgraded shale oil
		IBP-204°C (IBP-400°F)	204°-316°C (400°-600°F)	316°-371°C (600°-700°F)	
Gravity (°API)	19.3	61.1	40.8	31.6	40
Specific Gravity (16°/16°C; 60°/60°F)	0.938	0.735	0.821	0.868	---
Pour Point	30°C (85°F)	---	---	---	10°C (50°F)
Viscosity (cSt)	20 (60°C; 140°F)	---	---	---	4 (38°C; 100°F)
Flash Point	---	---	21°C (75°F)	---	---
Freeze Point	---	---	-18°C(1°F)	---	---
Molecular weight	---	---	208	---	---
Nitrogen (wt%)	2.19	24 ppm	0.288	0.63	0.034
Sulfur (wt%)	0.61	30 ppm	0.006	0.01	0.025
Oxygen (wt%)	1.40	0.29	0.23	0.18	---
Carbon (wt%)	84.90	85.51	86.40	86.19	---
Hydrogen (wt%)	11.50	47.70	13.69	12.54	---
C/H	0.62	0.49	0.53	0.57	---
Olefins (vol%)	---	0.8	1.0	---	---

[a] Data modified from White River Shale Project (1976) and Bartick et al. (1975).

TABLE 4-4. OVERALL YIELD OF HYDROGENATION PRODUCTS FROM PARAHO CRUDE SHALE OIL[a]

Outputs	wt%
Gas	10.1
IBP-204°C (IBP-400°F) Product	10.4
204°-316°C (400°-600°F) Product	24.3
316°-371°C (600°-700°F) Product	23.6
371°-454°C (700°-850°F) Untreated	18.5
Coke	12.0
NH_3	0.9
H_2S	0.4
H_2O	0.9
TOTAL	101.1

[a]Data modified from Bartick et al. (1975).

Coke yield is approximately 12 percent by weight of crude shale oil, and total gas generated is about 10.1 percent by weight. Total net hydrogen input utilized amounts to 1.3 weight percent of the crude shale oil. This is equivalent to approximately 790 standard ft^3 of hydrogen used per barrel of shale oil; since 100 percent efficiency cannot be attained, gross process input of hydrogen is on the order of 2,000 standard ft^3 per barrel of oil.

Catalysts and Additives

Hydrogenation catalysts may be classified as follows:

- Free metals (e.g., platinum, palladium, and nickel) or supported metals (e.g., cobalt-molybdenum on aluminum oxide [Nalcoma 471], nickel-tungsten on aluminum oxide [Harshal Ni-430]), which are useful for low temperature operation with clean, nonpoison-containing feedstocks. The principal application is for olefin and aromatic saturation. Since these compounds do not contain nitrogen, oxygen, or sulfur additions, they do not poison the catalyst.

- Metal oxides and sulfides or a combination of the two, supported on nonacidic materials such as alumina, magnesia, or kieselguhr. These types of catalysts are used largely for saturative hydrogenations in the presence of potential poisons.

- Metal oxides and sulfides, or combinations of the two, supported on acidic materials such as silica-alumina, silica-magnesia,

activated clay, or acidified alumina. This class is used largely in hydrocracking.

A series of catalysts has been studied for single-stage hydrorefining of the coke distillate from a shale oil (Benson and Berg, 1966). Twelve different catalysts were investigated as potential denitrogenation catalysts (Table 4-5). At pressures up to 70 atmospheres, a hydrofluoric acid-treated cobalt oxide-molybdenum oxide-alumina was found as best in the 12 studies. The tabulation of the efficiency values is given in Table 4-6. Nitrogen conversion with the HF-activated cobalt molybdate catalyst was 89.5 percent of total denitrogenation, whereas for the best catalyst, the Peter Spence cobalt molybdate catalyst, the conversion was 71.1 percent.

One other study has favored hydrorefining the shale oil-coke distillate in a two-stage treatment (Montgomery, 1968). In the first stage, conditions were mild in order to saturate the olefins, give a reduction in oxygen compounds, and allow removal of some sulfur. Conditions in the first stage were 245°C (473°F), 35 atmospheres, space velocity of 0.89 volume of oil per volume of catalyst per hour, with hydrogen circulation of about 2.3 moles per mole of distillate. The catalyst was presulfided (reacted with hydrogen sulfide prior to use) commercial cobalt oxide-molybdenum oxide-alumina, and hydrogen consumption was 0.8 moles per mole of feed. Conditions in the second stage were 435°C (815°F), 100 atmospheres, space velocity of one volume of oil per volume of catalyst per hour, with hydrogen circulation of about 11 moles per mole of feed. The catalyst was presulfided commercial nickel tungsten alumina, and hydrogen consumption was about 3.3 moles per mole of feed. Table 4-7 summarizes the results of this hydrogenation procedure. With a total hydrogen consumption of 4.1 moles per mole of coke distillate, some aromatic rings, as well as the olefins, were saturated.

Recently, in situ crude shale oil, produced by the underground combustion retorting method, has been hydrocracked over a nickel-molybdena catalyst at 427°C (800°F) and 103 atmospheres (Cottingham and Nickerson, 1975). The yield of diesel fuels was 51.6 percent (by volume) of the in situ crude shale oil, and the yield of No. 4 fuel oil was 21.5 percent (by volume). In conclusion, a total of 73.1 percent (by volume) of the in situ crude shale oil could be hydrocracked into low-sulfur, high-cetane-index diesel fuels or No. 1 through No. 4 burner fuels.

The denitrification of shale oil gas has also been studied in the comparison of cobalt-molybdenum and nickel-tungsten catalysts (Silver et al., 1976; Frost et al., 1976). The metallic components of the catalysts did show differences in effecting the denitrification reaction. Cobalt-molybdenum had the greatest effect, presulfided nickel-tungsten the next, and nonpresulfided nickel-tungsten the smallest. This demonstrates that presulfiding did increase the activity of the nickel-tungsten metallic components.

The spent catalysts contain metal oxides or sulfides, as well as the carbonaceous deposits. In all the cracking catalyst regenerations, the catalyst is first purged with steam or inert gas. Regeneration is carried out in air diluted with steam or inert gas, so the oxygen content is 0.5 to 1 percent and preferably at 2 to 10 atmospheres pressure. Burning begins at

TABLE 4-5. COMPOSITION OF CATALYST USED FOR HYDROTREATING OF SHALE OIL[a]

Catalyst	Composition	Identification code	Catalyst source
Cobalt molybdate I	9.5% MoO_3, 3.0% CoO 5.0% SiO_2, 2.0% graphite 80.5% Al_2O_3	Co-Mo-0201-T-1/16 in.	Harshaw Chemical Company
Cobalt molybdate II	Same as above	Co-Mo-0201-T-1/8 in.	Harshaw Chemical Company
Cobalt molybdate III	$CoMoO_4$-Al_2O_3 Large pore	#2127-2	Humble Oil and Refining Company
Cobalt molybdate IV	2.5% CoO 14.0% MoO_3 Graphite base	Graphite-type pellets, 5/32 in. diameter	Peter Spence and Sons, Ltd.
Cobalt molybdate V	-	3/16 in. diameter pellets	Union Oil Company
Molybdenum oxide I	16% MoO_3 79% Al_2O_3 5% SiO_3	Mo-0203-T-1/8 in.	Harshaw Chemical Company
Molybdenum oxide II	Same as above	Mo-0203-T-1/8 in. promoted with indium	Harshaw Chemical Company
Oronite hydroforming catalyst	-	-	Esso Research
HF-activated cobalt molybdate	-	-	Esso Research
Platinum (type 1000)	-	-	Esso Research
MnO_3 deposited on DA-1 cracking catalyst	86% DA-1 13.5% MnO_3	#9816	Esso Research
Molybdenum sulfide	-	-	Esso Research

[a]From Benson and Berg, 1966.

TABLE 4-6. CATALYST ACTIVITY USED FOR HYDROTREATING OF SHALE OIL[a]

Catalyst[c]	Activity at operating condition[b] No. 1	No. 2
HF-activated cobalt molybdate	1.30	2.70
Cobalt molybdate IV	1.00	1.00
Cobalt molybdate I	0.78	-
Cobalt molybdate III	0.71	0.82
Molybdenum oxide I	0.70	1.00
Cobalt molybdate IV	0.70	0.59
Oronite hydroforming catalyst	0.66	0.75
Molybdenum sulfide	0.59	-
Platinum (type 100)	0.59	0.51
MnO_3 deposited on DA-1 cracking catalyst	0.50	0.37
Union Oil cobalt molybdate 3/16-in. pellets	0.43	0.33
Molybdenum oxide II	0.36	0.49

Operating variable	Condition No. 1	No. 2
Catalyst bed temperature (°C)	440	510
Reactor pressure (psig)	1,000	1,000
Space velocity (g/g-hr)	1.0	1.0
Gas rate (std ft^3/bbl)	2,500	4,000
Gas composition, % H_2	100	100

[a] From Benson and Berg (1966).

[b] Activity = $\frac{\text{wt\% nitrogen of cobalt molybdate IV}}{\text{wt\% nitrogen of catalyst}}$

[c] Catalyst composition corresponding to Table 4-5.

TABLE 4-7. HYDROREFINING OF CRUDE SHALE OIL[a]

	Original coke distillate (wt%)	After first stage (wt%)	After second stage (ppm)
Sulfur	0.54	0.49	60
Nitrogen	2.0	2.0	917
Oxygen	1.2	0.83	-

[a]From Montgomery (1968).

30° to 350°C (86° to 662°F), and the characteristic "hot spot," or burning, zone passes through the entire catalyst bed in the direction of flow. When the burning zone has passed through the entire catalyst bed, the oxygen concentration can be increased, keeping the above restriction at the maximum temperature until air itself is being used. Then it is cooled to the operating temperature, or presulfiding temperature, and purged with inert gas or steam. Frequently, idle time on a commercial unit is so costly that the deactivated catalyst can be replaced by fresh catalysts much faster, and thus more cheaply, than they can be regenerated. The spent catalyst is removed and regenerated ex situ, or custom regenerated. The regenerated catalyst is then ready for the next replacement.

Certain deficiencies of crude oil can be corrected by supplying certain chemical additive agents. The kind of additive agent to be used depends on the desired quality to be imparted or accentuated in the oil. Some of the agents may be beneficial under one set of conditions and harmful under another. The additive agents consist of oxidation inhibitors, oiliness carriers, viscosity index improvers, fluorescence improvers, and pour point depressants.

Agents for improving the viscosity index usually consist of high molecular weight polymers of unsaturated hydrocarbons. The lack of fluidity in crude shale oil at moderately low temperatures (high pour point) is explained by the presence of bituminous materials, including resin, asphaltene, carbene, carboid, and/or wax, which congeal when the shale oil is cooled. The fluidity of oil containing bituminous substances depends not only on the quantity but also on the type of crystals dispersed in the crude shale oil. Certain chemicals can modify the structure of the crystals and alter the fluidity of the oil. Such pour-point depressants may be present in the oil itself or may be added to it.

Several synthetic compounds have been found which, when added in small proportions to an oil, reduce the pour point (Kalichevsky and Stagner, 1942; Wunderlich and Frankovich, 1970). These compounds are high molecular weight condensation products. One type of pour-point reducing agent is made by condensing phenol and chlorinated wax by means of aluminum chloride, and further condensing this reaction product with phthalyl chloride. Another type is a synthetic hydrocarbon used for reducing the pour point by condensing a high boiling monochloroparaffin with naphthalene by means of anhydrous aluminum chloride.

An oil can be exposed to oxidation through exposure to the air. When a shale oil breaks down in service as a result of oxidation, it may form more heavy end products (resin, asphaltene, carbene, and carboid) or corrosive or noncorrosive acids, or it may increase in viscosity. Oxidation, once started, can proceed as a chain reaction that may take place in storage tanks, refinery lines, and the fuel injection systems of engines. Oxidation in shale oil can be delayed or prevented by the addition of small amounts of inhibitors. These usually consist of hydroxy compounds, such as phenolic derivatives and naphthols; nitrogen compounds, such as naphthylamines, aniline, and its derivatives; and sulfur compounds, represented by elemental sulfur, disulfides, etc.

Oiliness is the ability of the oil to form a hydrodynamic film between two relatively moving surfaces and to support the load between them. Oiliness agents are polar compounds. Shale oil refining processes may reduce the oiliness property through the removal of naturally occurring polar-film-forming compounds. Addition agents for improving oiliness usually include fatty oils, such as sperm oil, lard oil and tallow; fatty acids, such as oleic acid; and synthetic esters of fatty acids.

Usually, the addition of fluorescent agents in oils has no relation to their performance in engines. However, the refiner is sometimes obliged to refine the oils to meet the demand of the usually light-colored oils. In service, oils tend to develop black carbonaceous material, which remains at least partially suspended in them. If the oil is fluorescent and is examined in reflected light, these black particles are concealed, and the oil appears relatively unchanged. Several dyes have been developed for imparting the desired fluorescence to oils. However, the addition of fluorescent agents may not be necessary, since the production of shale oil with oil shale clay minerals at elevated temperatures during retorting might create the fluorescent property inherently.

SUPPORTING PROCESSES

Hydrogen Manufacturing Plant

The shale oil produced by Paraho or TOSCO II retorting is generally too high in its pour point, too viscous to be piped, and too high in nitrogen and sulfur to be used as normal refinery feedstock. As a result, a refinery upgrading process is necessary for crude shale oil, normally hydrogenation. Generally, an auxiliary hydrogen plant is needed and constructed onsite.

Gases produced by the retort and the hydrotreating unit of crude shale oil are first treated to remove sulfur compounds and saturate the olefins before the gases and light ends are used in hydrogen plant feed. Activated carbon, or CoMo—ZnO, beds are usually used to catalyze the removal of trace quantities of sulfur compounds. Typically, a conventional steam-hydrocarbon reforming hydrogen plant is used to provide hydrogen for the hydrotreating units (Figure 4-3). Natural gas, propane, butane, and/or naphtha are used as general feed gases. In catalytic steam-hydrocarbon reforming, volatile hydrocarbons are reacted with steam over a nickel catalyst at 700° to 1,000°C (1,292° to 1,832°F) to produce carbon oxides and hydrogen. The carbon monoxide formed, as indicated in the following equation, uses propane as a typical hydrocarbon:

$$C_3H_8 + 3H_2O \longrightarrow 3CO + 7\ H_2$$

It is converted to carbon dioxide according to the water-gas shift reaction shown in the following equation:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

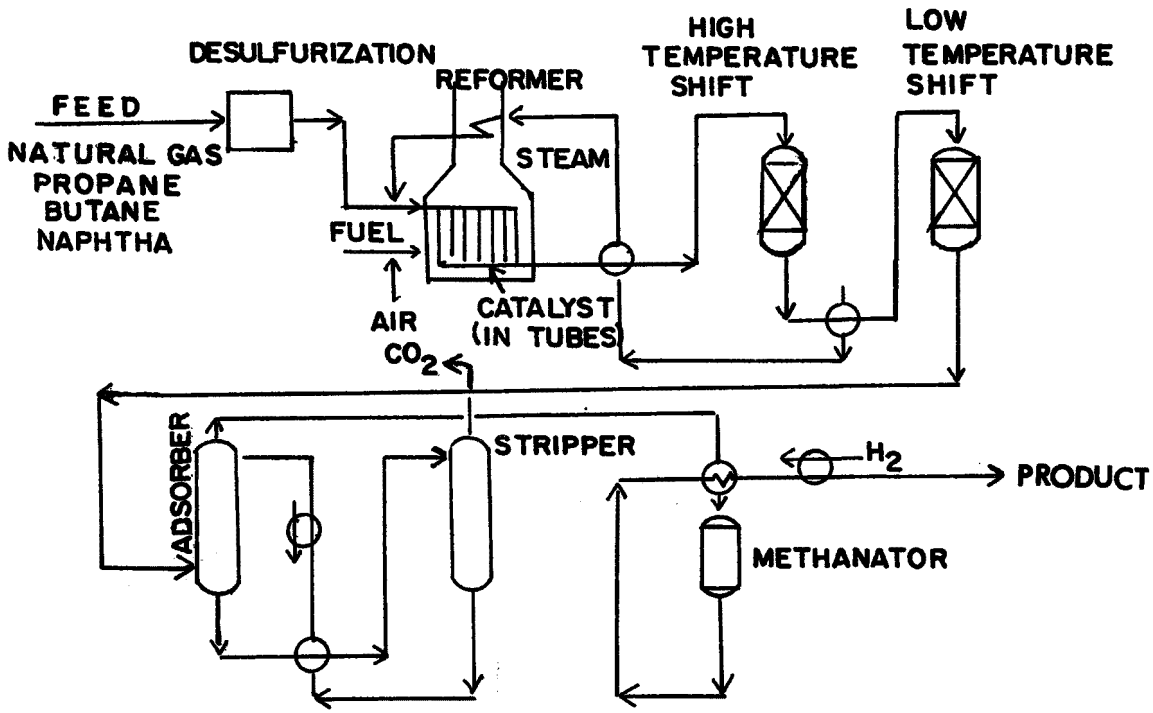

Figure 4-3. Flow diagram of a typical steam-hydrocarbon reforming hydrogen plant.

The latter conversion takes place at 250°C (482°F) over an iron oxide catalyst. The gas leaving the reformer contains carbon monoxide and hydrogen. The carbon monoxide is shifted to carbon dioxide, which can be readily adsorbed and stripped from the system.

The total amount of hydrogen required for the hydrotreating unit is about 5.5 million standard m^3 (200 million standard ft^3) per day (White River Shale Project, 1976) based on a production rate of 16,000 m^3 (100,000 barrels) per day of crude shale oil. A portion of the hydrogen (about 10 percent) can be recovered from the hydrotreating unit and produced in the retorting plant (available in the high-Btu gas). The hydrogen plant must be started a few days before oil shale retorting to insure maximum hydrogen production.

Amine Treating

The purpose of amine (or acid gas) treatment is to separate sulfur compounds for processing in a sulfur recovery plant and to separate a clean CO_2 stream that can be rejected to the atmosphere. In the case of hot carbonate scrubbing, a relatively concentrated H_2S stream can be separated for processing in a Claus plant for sulfur recovery.

Gases and light ends produced by retorting and by hydrotreating crude shale oil contain acid gases (hydrogen sulfide and carbon dioxide) as impurities, A recirculating stream of diethanolamine (DEA) is used to remove these impurities by the following reactions:

$$RNH_2 + H_2S \rightleftharpoons RNH_3HS \qquad (1)$$

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3HCO_3 \qquad (2)$$

Adsorption of hydrogen sulfide occurs at 38°C (100°F) or lower temperature in the adsorber and rejection of hydrogen sulfide from the decomposition of amine salts in the stripper is active at 116°C (240°F). Higher temperatures are required for carbon dioxide both for adsorption (at 49°C [120°F]) and rejection (149°C [300°F]). A solution strength of 20 to 30 percent DEA is used. Monoethanolamine, triethanolamine, and methyldiethanolamine have all been used to adsorb hydrogen sulfide in amine treating.

A simplified schematic diagram of the equipment for recovery and amine treating of the light ends is shown in Figure 4-4. The gas phase enters an adsorber where it contacts the amine solution to form salts that then pass to the stripper as rich amine. In the stripper, heat is applied to decompose the salts and regenerate the lean amine, which is returned to the adsorber. The major portion of the treated gas leaving the adsorber is combined with the hydrotreating unit light ends and compressed to hydrogen plant feed pressure. The gas then passes to the hydrogen plant where it undergoes further treatment for hydrogen sulfide removal and final desulfurization.

Low-Btu Gas Treating

Low-Btu gas is generated by the Paraho direct heating process. Usually it contains small quantities of hydrogen sulfide and ammonia and thus requires

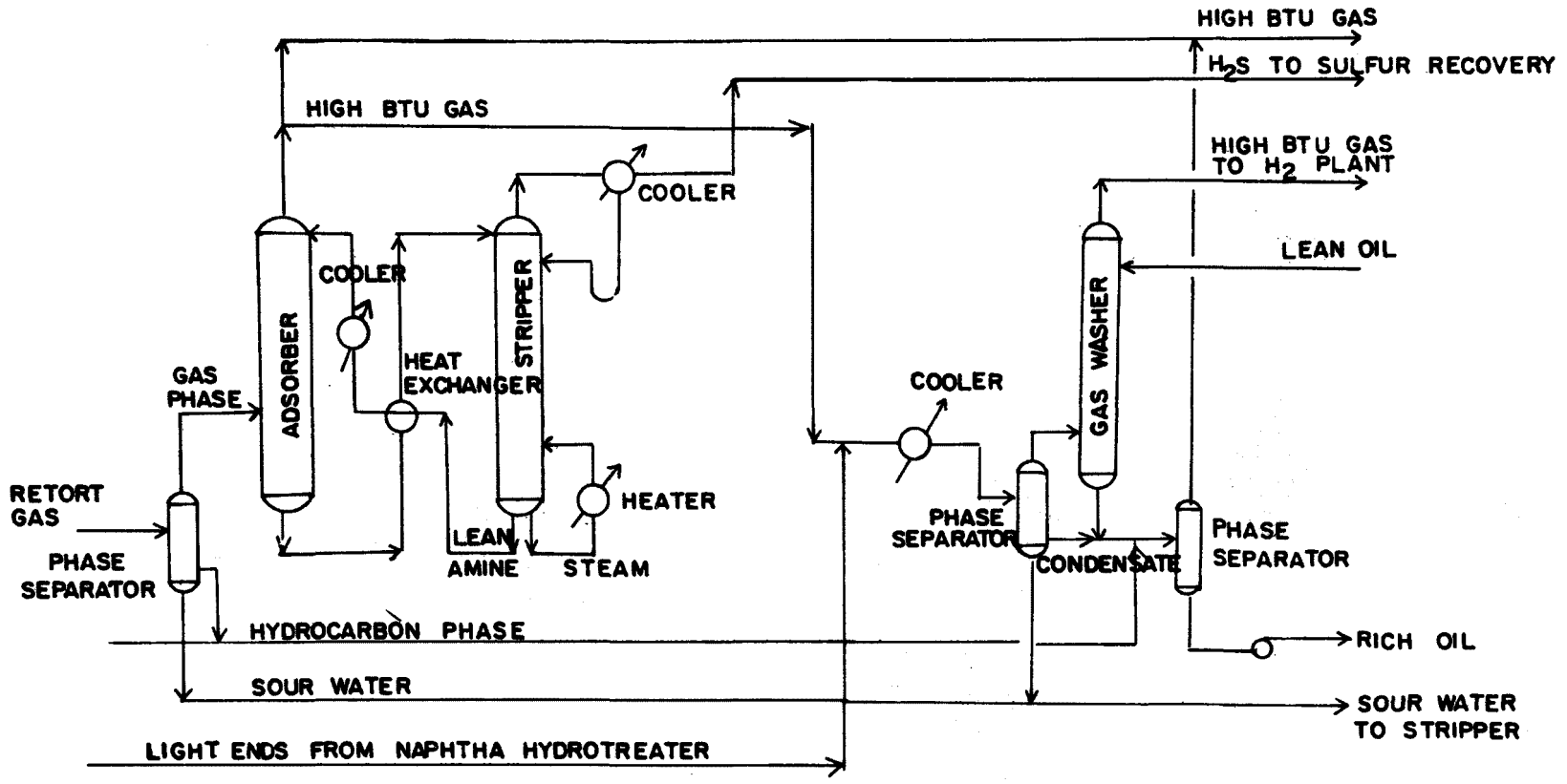

Figure 4-4. Flow diagram for amine treating and recovery of shale oil light ends.

treatment before it can be used for fuel gas. Amine treating is not efficient for removing ammonia. The gas can be water-washed to remove ammonia prior to sulfur removal. The high content of ammonia and carbon dioxide in the washing tower bottom material is treated in the sour water stripper.

Hydrogen sulfide in the washed low-Btu gas may be removed by any of a number of wet or dry processes, such as absorption in liquid scrubbing systems or on dry solids (dolomite or iron oxide). The use of hot carbonate scrubbing requires that the gases be cooled to 120°C (250°F), while hot ferric oxide, for example, can be used on a solid absorbent if the gases are cooled to below 537°C (1000°F). The purified low-Btu gas can be fed as the fuel gas for the retorting unit.

Tail Gas Treating and Sulfur Recovery

The purpose of tail gas treating is to separate sulfur compounds for processing in a sulfur recovery plant and to separate a clean CO_2 stream that can be eliminated in the atmosphere. The tail gas treating unit handles the waste flue gas from the sulfur recovery plant, the amine absorber treating unit, the wastewater treating plant, and the sour water stripper unit. The exhaust gases of these treating units contain high levels of hydrogen sulfide, ammonia, and carbon dioxide.

The following two consecutive reactions show the Claus process (Seglin, 1976) for sulfur recovery:

$$H_2S + 3/2\ O_2 \longrightarrow H_2O + SO_2 \qquad (3)$$

$$2H_2S + SO_2 \xrightarrow[\text{Catalyst}]{\text{Bauxite}} 2H_2O + 3S \qquad (4)$$

Carbonyl sulfide (COS) undergoes reactions similar to these to form sulfur plus carbon dioxide. In the Claus operation, one-third of the recovered sulfur is burned in a waste heat boiler to form the necessary SO_2 for reaction 4. This process reduces the hydrogen sulfide emission in the tail gas to a very low level.

The hydrogen sulfide produced in the tail gas can also be recovered as elemental sulfur using the Stretford process in which the gas is washed with an aqueous alkaline solution containing sodium carbonate, sodium vanadate, and anthraquinone disulfonic acid. The hydrogen sulfide dissolves in the alkaline solution, reacts with the 5-valent state vanadium, and is oxidized to elemental sulfur. The liquor is regenerated by air-blowing. The hydrogen sulfide can be removed to any desired level via this process.

Wastewater Treatment

Processed water from the hydrotreating units is transferred in the wastewater treating plant to recover hydrogen sulfide (sulfur recovery plant feed), anhydrous liquid ammonia as a net product, and stripped water (which is recycled to the hydrotreating processes).

Various methods are available for cleaning the hydrotreating wastewater for reuse. The Claus process can be used to remove H_2S, then a sour water stripper can be used for ammonia removal. Other cleanup steps may also be needed—for example, filtration to remove suspended solids and lime to remove inorganic ions (e.g., ammonium, carbonates). In order to further reduce the level of soluble organics, biological oxidation (biox) may be provided. Biox can be effective on organics, nitrogen, phosphorus, and sulfur compounds, though additional nutrients may have to be added to provide the proper balance. Biox does not, however, satisfactorily clean up refractory compounds such as alkylated benzene and naphthalene that may be present. Final treatment with an electrolytic process (Wen and Yen, 1977) or activated carbon may be needed.

Sour Water Stripper

The condensate formed by cooling the hydrotreating unit contains water from unreacted steam, together with oil, coke, and contaminants from crude shale oil decomposition. The types of compounds present in this condensate, or sour water, include sulfur compounds (such as hydrogen sulfide, thiophene, carbonyl sulfide, etc.), oxygen compounds (such as phenols, fatty acids, etc.), nitrogen compounds (such as ammonia, amines, etc.), carbon dioxide, chlorides, and other contaminants. There are also complexes resulting from the interaction of these compounds, e.g., thiocyanates, ammonium polysulfides, etc.

The major constituent of the sour water is ammonia. The system for removing ammonia from sour water is an ammonia stripping process (Culp and Culp, 1971; Snow and Wnek, 1968). In sour water, either ammonium ions, NH_4^+, or dissolved ammonia gas, NH_3, or both, may be present. At pH 7 only ammonium ions in solution are present. At pH 12 only dissolved ammonia gas is present, and this gas can be liberated from wastewater under proper conditions. The equilibrium is represented by the equation: $NH_4^+ \rightleftharpoons NH_3 + H^+$. As the pH is increased above 7, the reaction proceeds to the right. Two major factors affect the rate of transfer of ammonia gas from water to the atmosphere: (1) surface tension at the air-water interface; and (2) difference in concentration of ammonia in the water and the air. Surface tension decreases to the minimum in water droplets when the surface film is formed, and ammonia release is greatest at this point. Little additional gas transfer takes place once a water droplet is completely formed. Therefore, repeated droplet formation of the water assists ammonia stripping. To minimize ammonia concentration in the ambient air, rapid circulation of air is beneficial. Air agitation of the droplets may also speed up ammonia release. The ammonia stripping process, then, consists of: (1) adjusting the pH of the water to values in the range of 10.8 to 11.5; (2) formation and reformation of water droplets in a stripping tower; and (3) providing air-water contact and droplet agitation by circulation of large quantities of air through the tower (Figure 4-5).

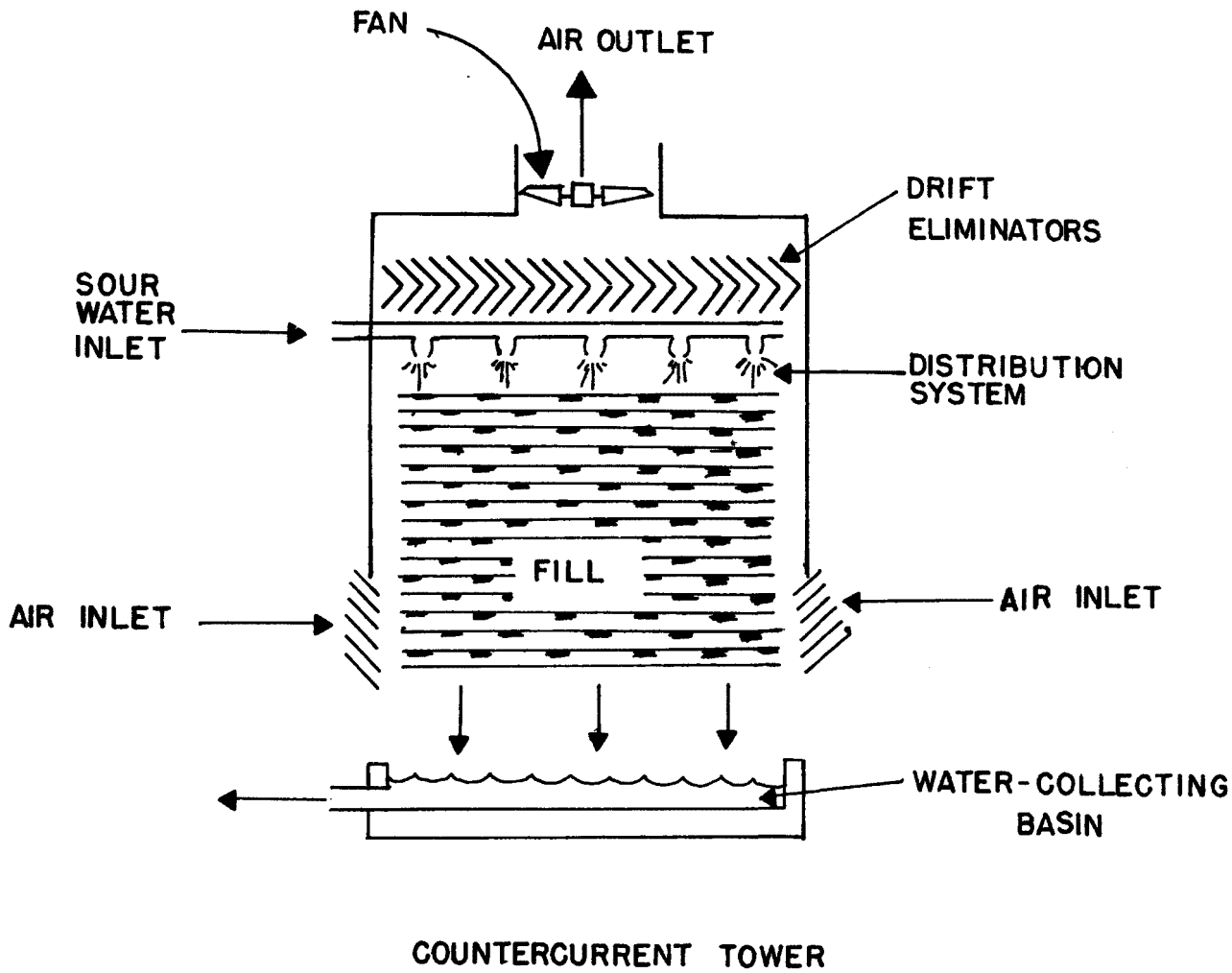

Figure 4-5. Typical ammonia stripper tower.

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SECTION 5

ORGANIC CONTAMINANTS

Because of the known and unknown consequences of oil shale exploitation, actions seeking to stimulate its commercialization must be balanced by concerns for environmental, social, and economic impacts that might be caused by oil shale development. Perhaps the major environmental health problem associated with oil shale technology is the potential release of carcinogenic organic compounds, such as the polynuclear aromatic hydrocarbons, and their nitrogenous derivatives. In this section, potential pollutants are first categorized by the origins of their production. These potential pollutants are then discussed in relation to possible health and environmental problems. In the characterization and measurement of organics, there are two extremes: one can view organics as a lumped constituent and determine total organic carbon (TOC) or similar measurements, or one can address specific compounds. The level of organic compound identification for this discussion is somewhere in between, restricted largely by the incomplete state of knowledge concerning organics in oil shale processing. An attempt will be made to identify the classes of organic compounds that may be present in oil shale.

SOURCE OF POLLUTANTS

Many of the pollution effects associated with oil shale are similar to those of other mining or refining operations. However, shale retorting results in the production of unique gaseous and liquid effluents, plus solid residues, which contain potentially hazardous organic and inorganic pollutants. Pollutants may differ in type and quantity, depending on the type of recovery, retorting, upgrading, and disposal methods used. A generalized oil shale fuel production cycle is shown in Figure 5-1.

Mining Processes

Oil shale extraction and handling result in generation of particulates, noise, runoff, and many pollutants similar to those encountered in other mining operations. Many of the pollutants from mining and crushing are inorganic; these are discussed in Section 6. The major sources of organic pollutants from mining are the mining and crushing machinery that contribute to air pollution.

In both the conventional and the in situ processes, chemical explosives are used in the fracturing step and might prove to be a significant source of organic pollutants (Miller and Johnsen, 1976). For example, picryl chloride has been tentatively identified from the X-ray diffraction pattern (Figure 5-2) of the acid fraction in retort water (Kwan and Yen, unpublished data).

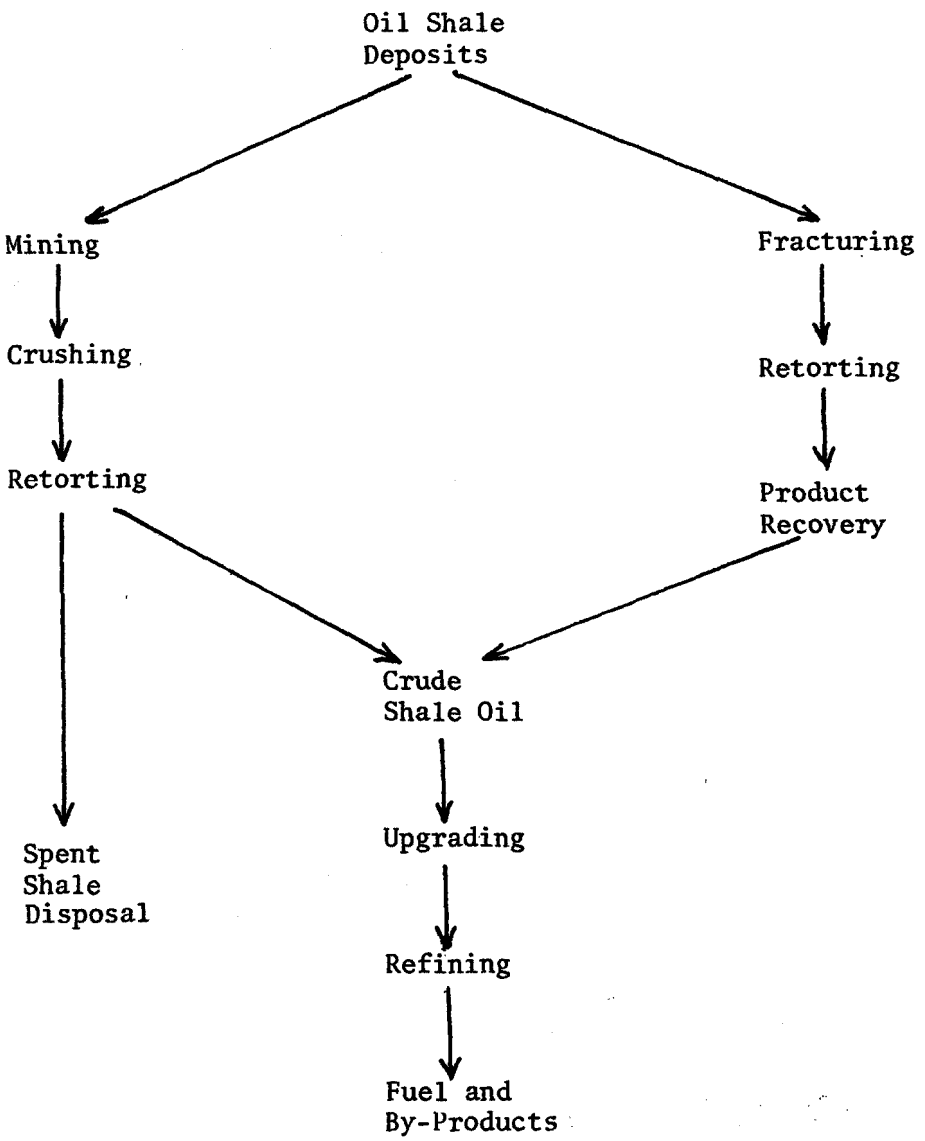


Figure 5-1. Oil shale fuel production cycle.

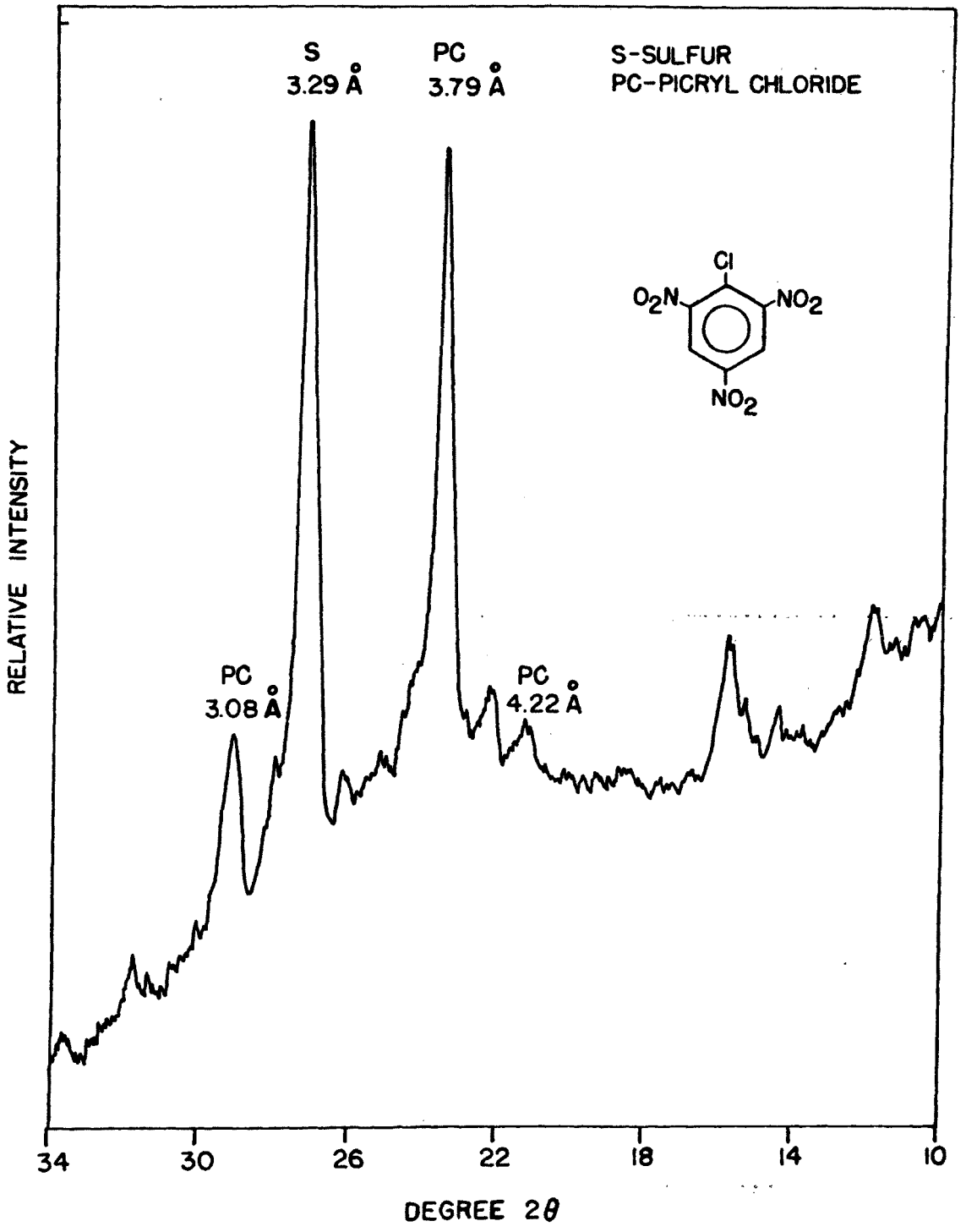
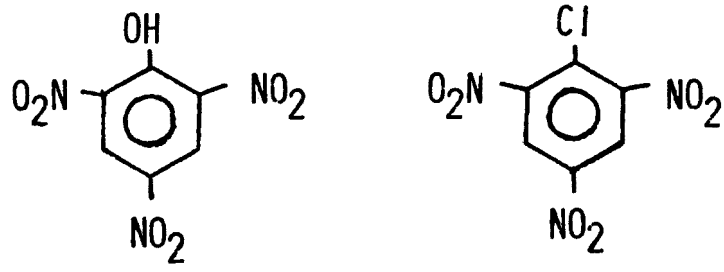


Figure 5-2. X-ray diffraction pattern of acid fraction in retort water (Kwan and Yen, unpublished data).

Picryl chloride (2-, 4-, 6-trinitrochlorobenzene) could be derived from TNT (2-, 4-, 6-trinitrotoluene) during the retorting process (Figure 5-3).



TNT Picryl Chloride

Figure 5-3. Derivation of picryl chloride from TNT.

Retorting Processes

Retorting of oil shale results in the production of unique gaseous and liquid effluents containing potentially hazardous inorganic and organic pollutants. In the Paraho and the TOSCO II retorting processes, the oil vapors are collected and condensed into liquid shale oil. The uncondensable fraction of oil vapor is a low-Btu gas that is used as internal fuel, as shown in Figure 5-4. The heating value of these gases is about 83 Btu/standard ft^3 for the Paraho DH process, 100 Btu/standard ft^3 for the Paraho IH process, and 923 Btu/standard ft^3 for the TOSCO process. Water is also produced during the pyrolysis of the oil shale, and this water may be treated for use and/or used for moisturizing the spent shale prior to disposal. These gaseous and liquid waste streams are discussed in more detail subsequently.

In the in situ process after shale has been retorted from a portion of a wet shale formation, the residue and surrounding strata are cooled by conduction and seepage of water into the region. Migration of groundwater through the burned-out region as the result of hydraulic gradients may cause leaching of chemicals from the residue. An in situ rubblized zone may include areas with only spent shale and areas with partially burned shales in varying states. There may be regions that contain condensed tars because of incomplete pyrolysis. Thus, the water migrating through a burned-out zone may come into contact with anything from spent shale to unaffected shale. Therefore, a wide variety of both organic and inorganic compounds may be extracted by these processes.

Upgrading Processes

Upgrading of crude shale oil results in pollutants common to petroleum refinery operations. The sources of wastes originating from refinery operations can be divided into five categories (Rice et al., 1969; McPhee and Smith, 1961).

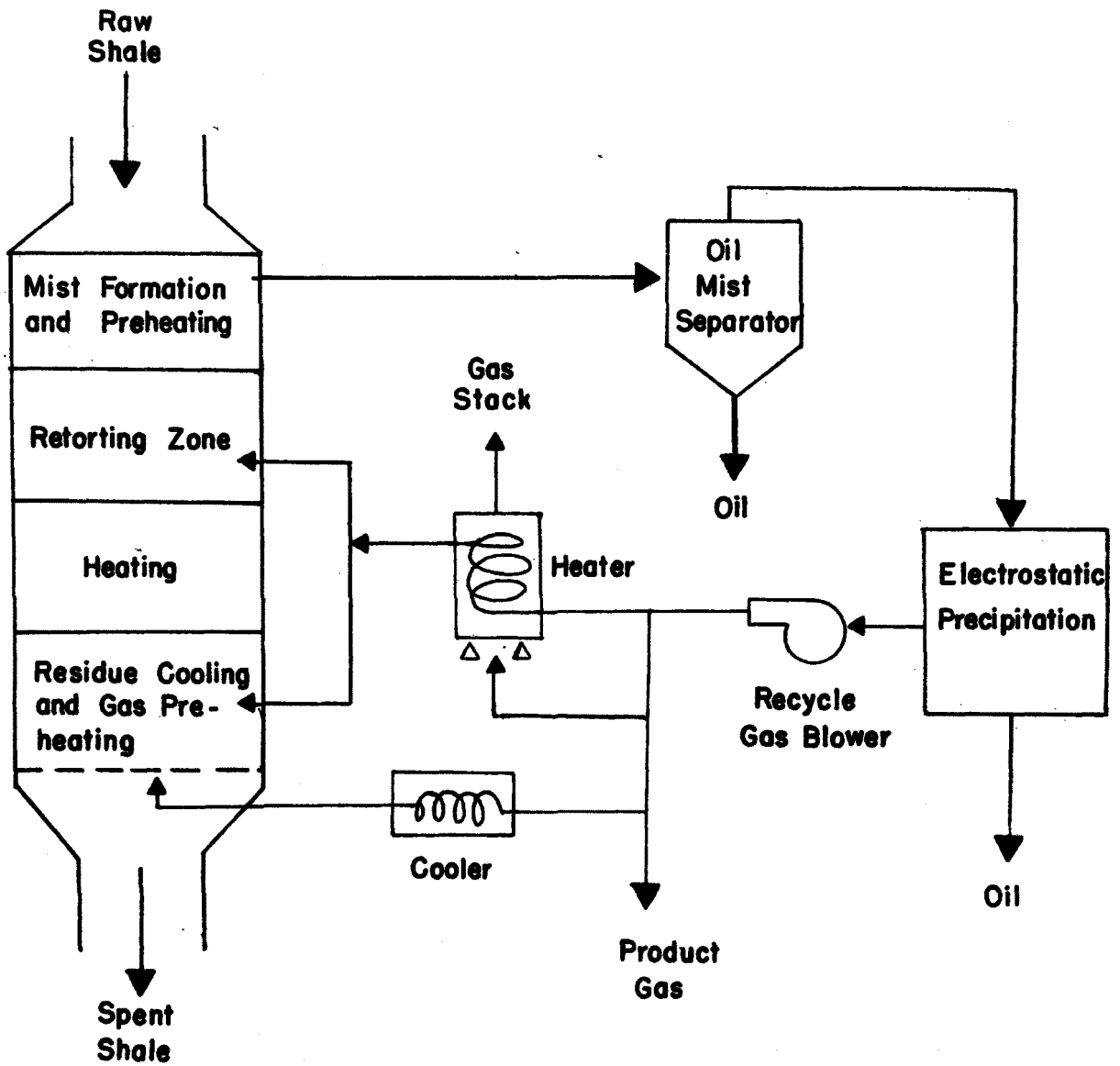


Figure 5-4. Paraho process—indirect heating mode flow diagram.

1. Wastes containing a principal raw material, or product, resulting from the stripping of the product from solution

2. By-products produced during reactions

3. Vessel cleanouts, slab washdown, spills, sample point overflows, etc.

4. Cooling tower and boiler blowdown, steam condensate, water treatment wastes, and general washing water

5. Storm waters, the degree of contamination depending on the nature of the drainage area.

The characteristics of wastes discharged from refinery complexes depend on the nature and source of the crude oil processed, the design and type of production facilities, the age of the facilities, the cooling water requirements, and housekeeping and control practices employed.

Waste Disposal

Disposal and stabilization of large volumes of potentially toxic spent shale from aboveground retorting are significant waste management concerns. To supply the raw material for a projected 8,000 m^3 (50,000 bbl) per day operation, 66,850 tonnes (73,700 tons) per day of raw shale (averaging 114 liters [30 gallons] of shale oil per ton) must be mined. The mining and retorting will generate about 54,420 tonnes (60,000 tons) of spent shale to be disposed of each day. The 16,000 m^3 (100,000 bbl) per day U-a and U-b operation in Utah will ultimately require about 900 hectares (2,300 acres) for spent-shale disposal (WRSP, 1976). The leaching of such disposal piles could be a serious problem. Erosion of spent-shale piles may be eliminated to a certain extent through physical, chemical, and vegetative methods of stabilization (Dean et al., 1968). The tailings can be covered with topsoil removed from underneath the shale residue piles. Studies by Schmehl and McCaslin (1969) indicated that 10 centimeters (4 inches) or more of topsoil cover may be required for vegetative stabilization. Chemical stabilization may be achieved by reacting the spent shale with chemicals to form an air and water impermeable layer that prevents erosion and groundwater leaching. Compaction aids to decrease infiltration of water into the processed-shale pile, thus mitigating formation of leachate. Compaction also aids in reducing erosion and hence helps stabilize the disposal pile. Sloping and contouring to control runoff and erosion also aids stabilization.

A conceptual spent-shale disposal operation of a type represented by commercial developments was presented by Parker (1976) (Figure 5-5). In this design, an upstream flood control reservoir will divert any water that might flow down the canyon around or under the spent-shale pile to reduce leaching problems. Runoff water from the spent-shale embankment goes into a containment pond. The runoff water is returned to the plant and reused to moisturize more spent shale (Parker, 1976).

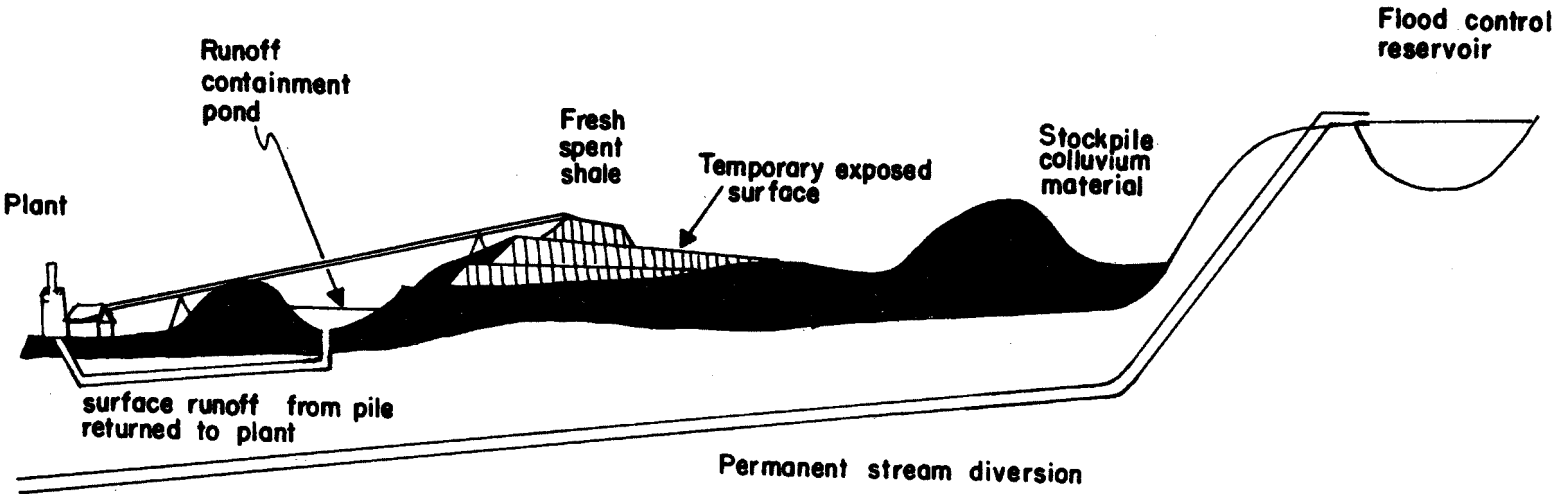


Figure 5-5. Disposal of spent shale from a commercial operation (Parker, 1976).

HEALTH AND ENVIRONMENTAL PROBLEMS

As summarized briefly in this discussion, a great deal of work has been and is being conducted to characterize oil shale products and by-products and to evaluate the potential effects (toxicity, carcinogenicity, etc.) of these materials. However, most of the effort to date has been somewhat qualitative since the likelihood that potentially hazardous materials may be present at levels high enough to present harm to organisms (including man) is not known.

Water Pollution

Management of spent shale requires considerable amounts of water for cooling, dust control, and compaction. Treatment and handling of the retort waters constitute another problem area.

The retort water or process water that comes from aboveground retorting processes may be separated from crude shale oil during storage (e.g., in the TOSCO II process) or broken up into aerosols (e.g., in the Paraho process). In order to identify the organic components in retort water, it is important to define what is collected as retort water. If fine oil particles are dispersed in the water, separation times can be lengthy. Therefore, consistent sampling techniques are very important in the organic analysis of retort water.

Crude shale oil has the highest nitrogen content relative to naturally occurring oils, as well as to other synthetic oils (Poulson et al., 1976; Bartick et al., 1975; Jensen et al., 1971; Dunstan et al., 1938). Crude shale oil contains twice as much nitrogen as high nitrogen petroleum crudes (Table 5-1). Retort waters contain high concentrations of ammonia-nitrogen (Table 5-2). Nitrogenous compounds are unique because they can assume either acidic, basic, neutral, or amphoteric properties and are recognized as good surface-active agents. Ammonium salt, nitrogen bases, amines with ester, or amide linkages are excellent cationic surface-active agents (Schwartz et al., 1970). Because of this characteristic, the nitrogen components in crude shale oil and the retort water result in the relatively high water content of crude shale oil and also the high total organic carbon (TOC) in both retort waters and the Black Trona water. Anionic detergency from carboxylic acids plays an important role, too, particularly for the latter type of water (Dana and Smith, 1973).

Many nitrogen-containing compounds are labeled as potential carcinogenic agents (Hueper and Conway, 1964); some of the known are shown in Figure 5-6. Many other compounds can cause a variety of physiological effects. The specific nitrogen compounds in the retort water have not been completely isolated and identified.

The aromatic hydrocarbon content in retort water is about 30 to 40 percent lower than the nitrogen compound content. Toxicity and bioaccumulation potential of the aromatics are very important. As a general rule, the very large polycondensed organic matter (POM) compounds, such as graphite, are quite inert and stable. It is the medium and small molecules that may be toxic. Also, in water treatment, removal efficiency is in inverse proportion to the molecular weight of the compound; the greater the number of rings, the more difficult is removal.

TABLE 5-1. PROPERTIES OF RAW SHALE OIL AND PETROLEUM CRUDES (Bartick et al., 1975; Jensen et al., 1971; Dunstan et al., 1938)

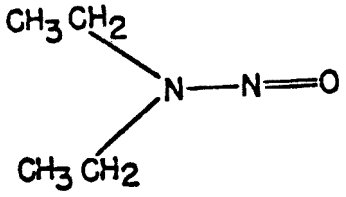
Properties	Petroleum crude	TOSCO II shale oil	LERC in situ shale oil	Paraho shale oil
Gravity °API	15 - 44	22	28	19.3
Sulfur wt%	0.04 - 4.1	0.9	0.7	0.61
Nitrogen wt%	0.01 - 0.65	1.9	1.4	2.19
Ni ppm	0.03 - 45	6	-	2.5
V ppm	0.002 - 348	3	-	0.37
As ppm	0 - 0.030	40	-	19.6
Viscosity SUS 38°C (100°F)	31 - 1025	106	78	46.8
Conradson Carbon wt%	0.1 - 11.4	4.6	1.7	1.4
Bromine Number	-	49.5	-	

TABLE 5-2. COMPOSITION OF RETORT WATER FROM DIFFERENT PROCESSES

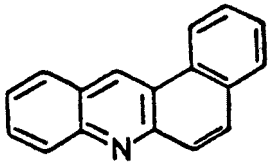
Constituents	LERC 10-ton in situ simulated[a]	Paraho direct mode[b]	Paraho indirect mode[b]
COD	20,000	19,400	17,100
BOD	5,500	12,000	4,850
TOC	3,182	29,200	9,800
NH_4-N	4,790	14,600	16,800
Organic-H	1,510	17,340	-
Phenol	169	46	42

[a]Yen and Findley, 1975.

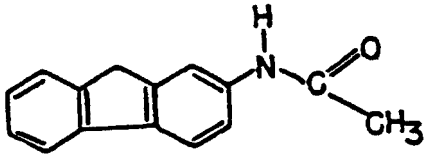
[b]Cotter et al., 1977.



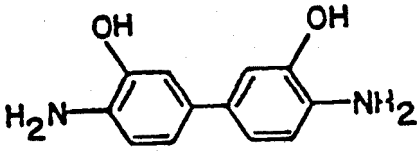
nitrosos (Basic)



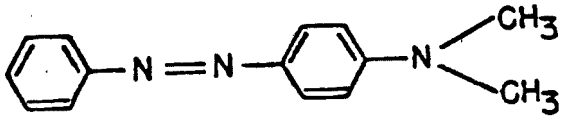
azabenzanthracenes (Neutral)



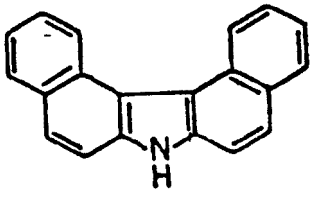
carbamic acid esters (Acidic)



aminobiphenyls (Acidic)



amino azobenzenes (Basic)



dibenzcarbazoles (Acidic)

Figure 5-6. Known nitrogenous carcinogenic compounds (Hueper and Conway, 1964).

A summary of the acute toxicity data (for fish) of the aromatic hydrocarbons is shown in Figure 5-7, with acute toxicity (48-hr LC_{50} plotted against molecular weight (Herbes et al., 1976). (The 48-hour LC_{50} here is the level of exposure resulting in 50 percent mortality of the test animals in 48 hours.) Figure 5-8 contains the same plot for arylamines. The data show a direct relationship between the acute toxicity and molecular weight. A 50-unit increase in molecular weight corresponds to a tenfold increase in toxicity. Unfortunately, there is generally a paucity of data available on the effects of these compounds, particularly with respect to long-term exposure, mutagenesis, teratogenesis, and carcinogenesis.

Another extremely important parameter in estimating the potential environmental impact of a contaminant is its bioaccumulation potential. Bioaccumulation is the process by which nonmetabolized materials are concentrated by passage through the food chain. Materials that are present in very low concentration in the abiotic regime can be concentrated in a stepwise manner until, at higher trophic levels, they may be present in sufficient levels to upset essential metabolic processes. Figure 5-9 shows potential bioaccumulation for polycyclic aromatic hydrocarbons (PAH) (Herbes et al., 1976). The higher the molecular weight of the compound, the greater the bioaccumulation potential. In addition, higher molecular weight compounds degrade more slowly and tend to persist in the environment for a longer time.

Air Pollution

Pollution resulting from extraction, processing, and retorting may alter the present good air quality of the resource region. Atmospheric emissions from demonstration plants and the transport and fate of organic compounds and other contaminants must be characterized and defined.

Atmospheric emissions of organics arise from several subprocesses during an oil shale operation (Table 5-3). Airborne particulates are of interest because the Aiken-type particulates (particles with diameter less than 0.1 micron), which may be organometallic, are released during the combustion of shale oil fuels. Because of the biocompatibility of organometallic compounds and fauna, the resulting particulates could be highly toxic, depending on the properties of the metal. Overall emission data for a fully developed oil shale processing facility have been estimated, and potential organic pollutants and particulates are summarized in Table 5-4 (Rio Blanco Oil Shale Project, 1976; Schmidt-Collerus et al., 1976). Vapors from the product storage tanks can contribute significantly to organic air pollution (Table 5-5).

Solid Wastes

Surface retorting results in considerable land disruption and requires the disposal of large amounts of spent shale. The health effects of spent shale and releated materials are of great concern. A very detailed study has been conducted by Schmidt-Collerus et al. (1976) on polycondensed (or polynuclear) aromatic compounds in the carbonaceous spent shale. A large number of polycyclic aromatic compounds including benzo(a)pyrene have been identified. They have been found to be easily leached out from carbonaceous shale and to migrate with the leaching water. Animal experiments with spent shale have

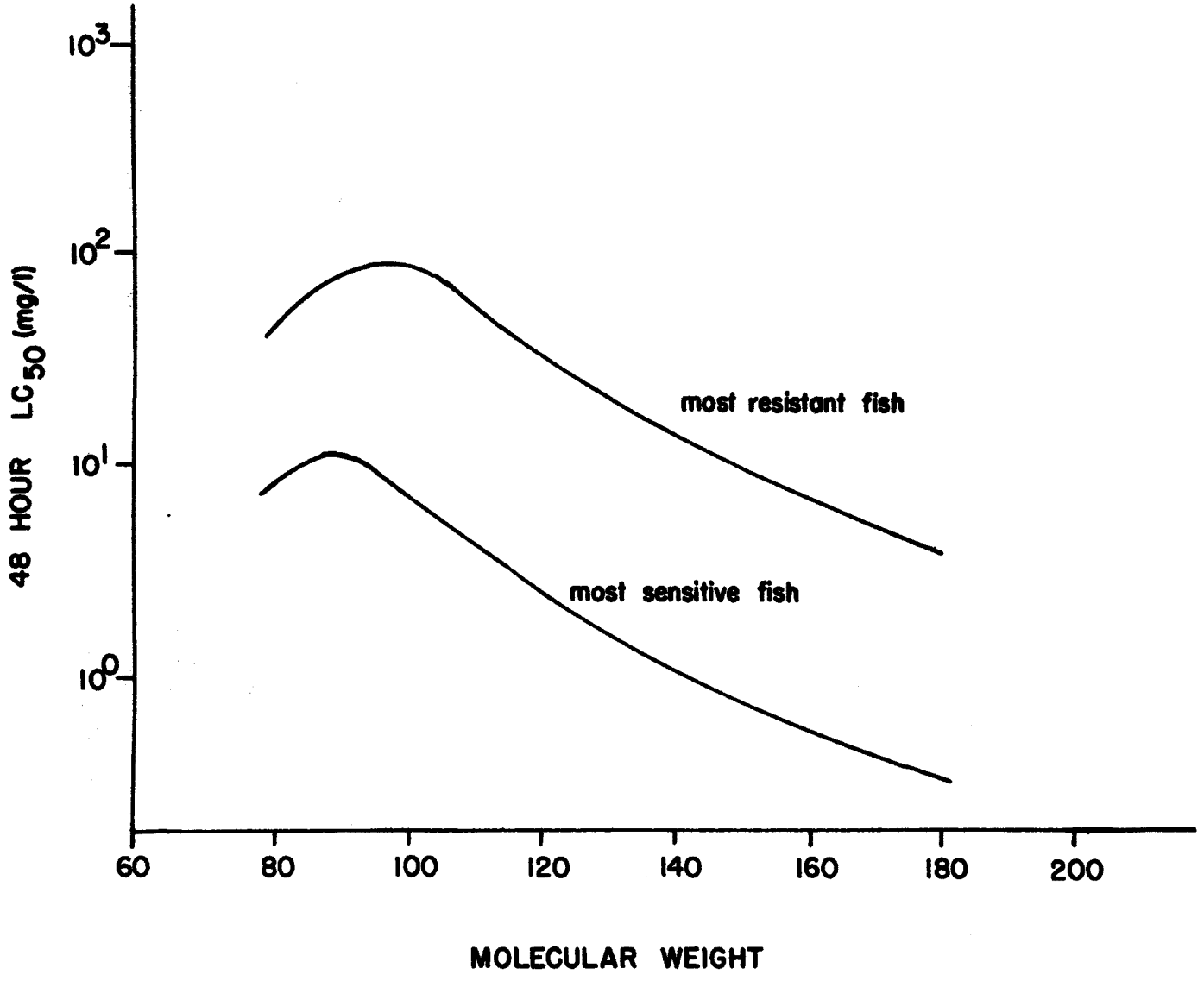


Figure 5-7. Acute toxicity data of aromatic hydrocarbon to fish (Herbes et al., 1976).

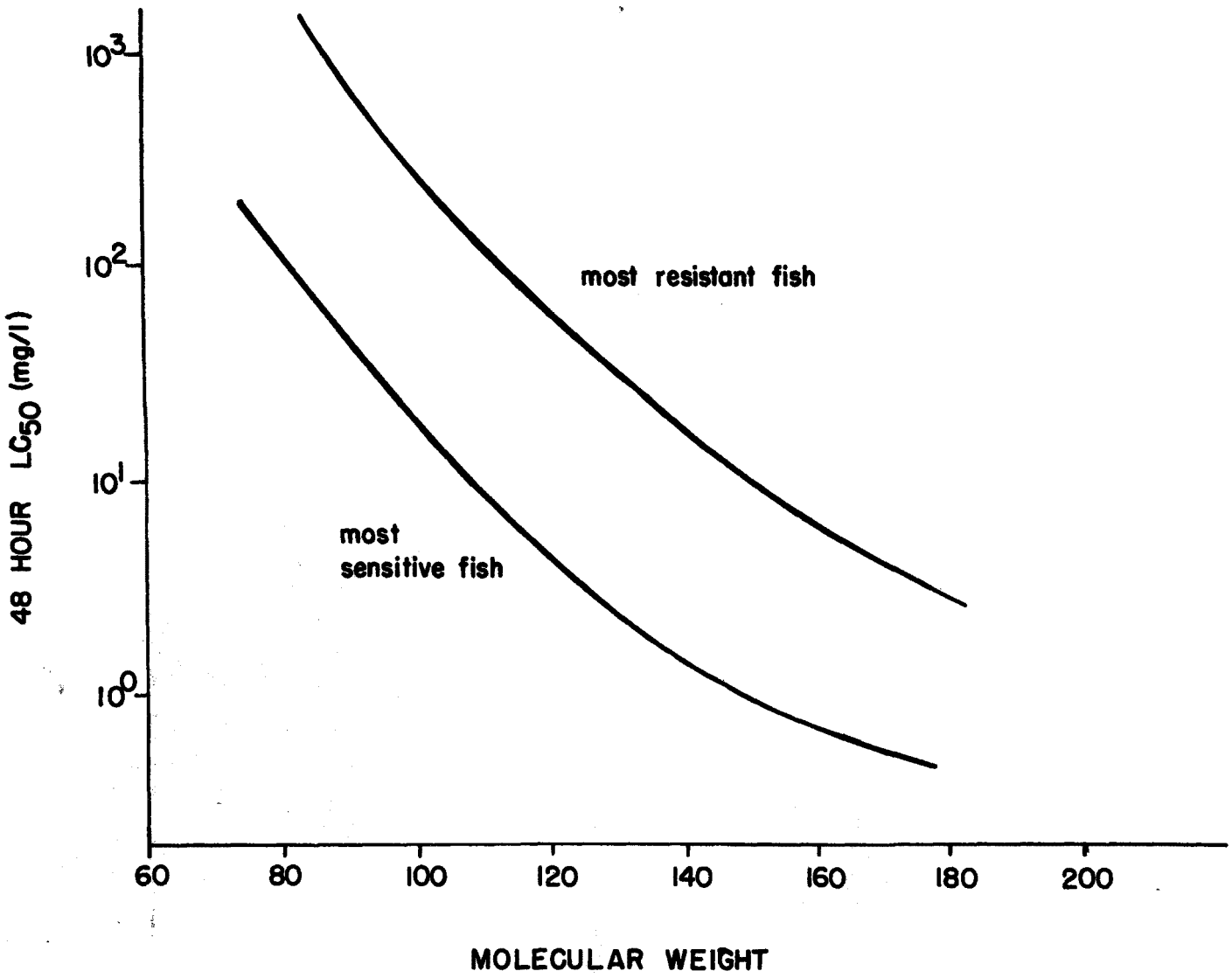


Figure 5-8. Acute toxicity data of arylamines to fish (Herbes et al., 1976).

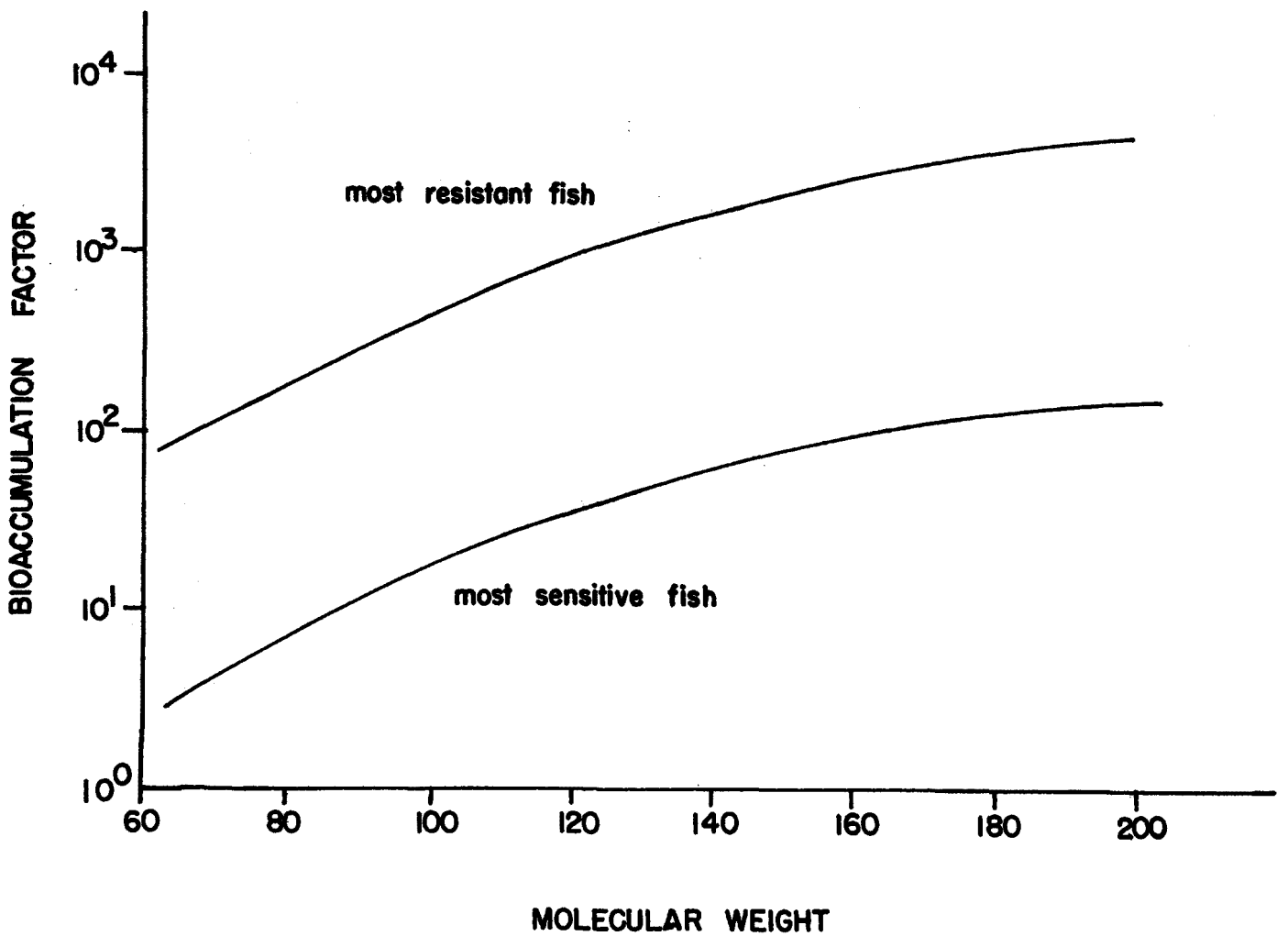


Figure 5-9. Bioaccumulation factor (concentration in organism vs. concentration in abiotic aquatic phase) for polycyclic aromatic hydrocarbons to fish (Herbes et al., 1976).

TABLE 5-3. PARTICULATES AND ORGANIC AIR POLLUTANTS FROM DIFFERENT SUBPROCESSES (Herbes et al., 1976)

Subprocess	Source of pollutants	Air pollutants	
		Particulate matter	Hydrocarbons
Extraction	Blasting	x	
	Mining equipment fuel use		x
Transportation	Equipment fuel use	x	x
Preparation	Crushing, screening, ore storage	x	
Retorting	Preheat fuel use	x	x
	Combustion of organic material	x	x
	Reheat carrier fuel use	x	x
Upgrading	Heater and furnaces fuel use	x	x
Product storage	Tank evaporation		x
Solid waste disposal	Spent shale transport	x	
	Coke, spent catalyst	x	

TABLE 5-4. AIR POLLUTION EMISSION INVENTORY ESTIMATED FOR OIL SHALE PROCESSES (Rio Blanco Oil Shale Project, 1976)

Emission source	Hydrocarbons (kg/hr)	(lb/hr)	Particulates (kg/hr)	(lb/hr)
Mining equipment (26,000 gal/day diesel fuel)	14.74	(32.5)	11.69	(25.8)
TOSCO II preheated system	130.2	(287)	107.85	(238)
TOSCO II steam superheater belt circulation	15.4	(34)	60.32	(133)
TOSCO II shale moisturization	-	-	31.82	(70)
Gas combustion process (Paraho) air heater	1.18	(2.6)	0.771	(1.7)
Gas combustion shale moisturizer scrubber	-	-	0.32	(0.7)
Coker feed heater	0.82	(1.8)	0.54	(1.2)
Gas oil hydrotreater heaters	1.54	(3.4)	1.04	(2.3)
Gas oil hydrotreater boiler	1.4	(3.1)	0.95	(2.1)
Naptha hydrotreater heaters	0.41	(0.9)	0.27	(0.6)
Glycol fired reboiler	1.27	(2.8)	0.86	(1.9)
Utility boilers	5.44	(12)	5.44	(12)

TABLE 5-5. VAPOR LOSSES FROM STORAGE TANK

Storage tank contents	Type of tank	Vapor pressure of contents, psi		Vapor loss	
		(10^{-3} kg/cm^2)		m^3/yr	(bbl/yr)
Raw shale oil	Floating roof	0.01	(0.703)	0.3	(2)
Raw shale oil residue	Cone roof	0.001	(0.070)	0.3	(2)
Raw naptha	Floating roof	1.8	(127)	14.2	(89)
Raw gas oil	Cone roof	0.01	(0.703)	9.4	(59)
Sponge oil	Cone roof	0.02	(1.406)	9.0	(56)
Hydrogen plant feed	Cone roof	0.001	(0.070)	0.02	(0.1)
Coker residue	Cone roof	0.001	(0.070)	0.05	(0.3)
Product naptha	Floating roof	2.2	(155)	19.5	(122)
Product gas oil	Cone roof	0.01	(0.703)	9.3	(58)
Product diesel	Floating roof	0.02	(1.406)	0.08	(0.5)

been conducted by TOSCO (Hueper, 1953). Hairless mice were kept in spent shale of various compositions and corncob bedding for the test of skin cancer. The result showed some susceptability to skin cancer; however, overall data from these and other experiments have been inconclusive as to the extent of potential carcinogenicity that may be associated with oil shale products.

In addition to spent shale, other solid wastes are also produced by different processing facilities. They include spent catalysts from hydrotreating, water-gas shift, naphthanation and sulfur recovery processes, sludge from water treatment, and spent ceramic balls, from the TOSCO process in particular (Table 5-6).

Regardless of the configuration of the in situ or modified in situ processes, the solid wastes generated are anticipated to be different from those from aboveground retorting. The quantitative and qualitative characters of organics may be expected to vary according to the severity of retorting conditions. The in situ process takes months to complete because of the slow cooling effect in the reaction site (Figure 5-10) (Kwan and Yen, unpublished data). The model was based on the assumption that the reaction cavity maintains a stable temperature for 5 months. The temperature outside the cavity depends on the thermal diffusivity and the thickness of the shale wall (Prates and O'Brien, 1975; Kwan and Yen, unpublished data). TOSCO II processed shale contains 4.5 percent (by weight) organic carbon (Whitcombe and Vawter, 1976); Paraho processed shale contains about 3 percent (Schmidt-Collerus et al., 1976). The amount of carbon, and also probably the composition of the organics, present in spent shale are expected to vary depending upon the retorting conditions (e.g., time and temperature of retorting; Figure 5-11).

Occupational Health

The potential carcinogenicity of oil shale was first reported in relation to a Scottish oil shale plant where 65 cases of skin cancer were identified during the period 1900-21 (Key, 1974). Mutagenicity may also be associated with industrial wastes (Mulling, 1972).

Early data from animal tests showed that shale oil has carcinogenic properties (Hueper, 1953). In Scotland, an experiment conducted to compare Scottish shale oil and raw shale showed that the shale oil exhibited carcinogenic properties (Berenblum and Schoental, 1943 and 1944), while the raw shale was inactive (Berenblum and Schoental, 1944). These results indicated that the carcinogenic compounds are formed during the pyrolysis or combustion of organic materials. Santer (1975) reported that workers involved in synthetic fuel operations such as coal or oil shale conversion have a 16- to 37-times higher-than-normal chance of contracting skin cancer. Among the carcinogenic agents in oil shale and its derivatives, benzo(a)pyrene has received the most attention (Schmidt-Collerus et al., 1976; Hueper and Cahnman, 1958; Colony Development Operation, 1974), largely because the analytical techniques for identifying benzo(a)pyrene are well established. However, as-yet-unidentified carcinogenic agents in the oil shale could be more hazardous. Health problems could stem from the potential carcinogenic, mutagenic, and teratogenic nature of some oil shale processing products.

TABLE 5-6. PROCESSING FACILITY SOLID WASTES FOR PHASE II OF PROCESSING PROJECTED FOR FEDERAL TRACTS U-a AND U-b (WRSP, 1976)

Process unit	Solid waste description	Approximate quantity[a]	
		kg/yr	lb/yr
Naptha hydrotreating	Spent hydrotreating catalyst	33,000	(73,000)
Naptha hydrotreating	Proprietary solid	65,500	(144,000)
Gas oil hydrotreating	Spent hydrotreating catalyst-1[b]	142,500	(314,000)
	Spent hydrotreating catalyst-2[b]	118,000	(260,000)
Gas oil hydrotreating	Proprietary solid	697,000	(1,536,000)
Hydrogen plant			
Shift conversion	Spent CO shift catalyst	36,500	(80,000)
Methanation unit	Spent CO methanation catalyst	4,500	(10,000)
Sulfur recovery			
Claus unit	Spent oxidation catalyst	36,500	(80,000)
Tail gas unit	Spent hydrogenation catalyst	22,500	(50,000)
Support facilities	Spent zeolites	2,385	(5,300)
Water treating	Lime sludge	6,500	(14,450)

[a]Averaged over catalyst life.

[b]Two different catalysts involved in gas oil hydrotreating.

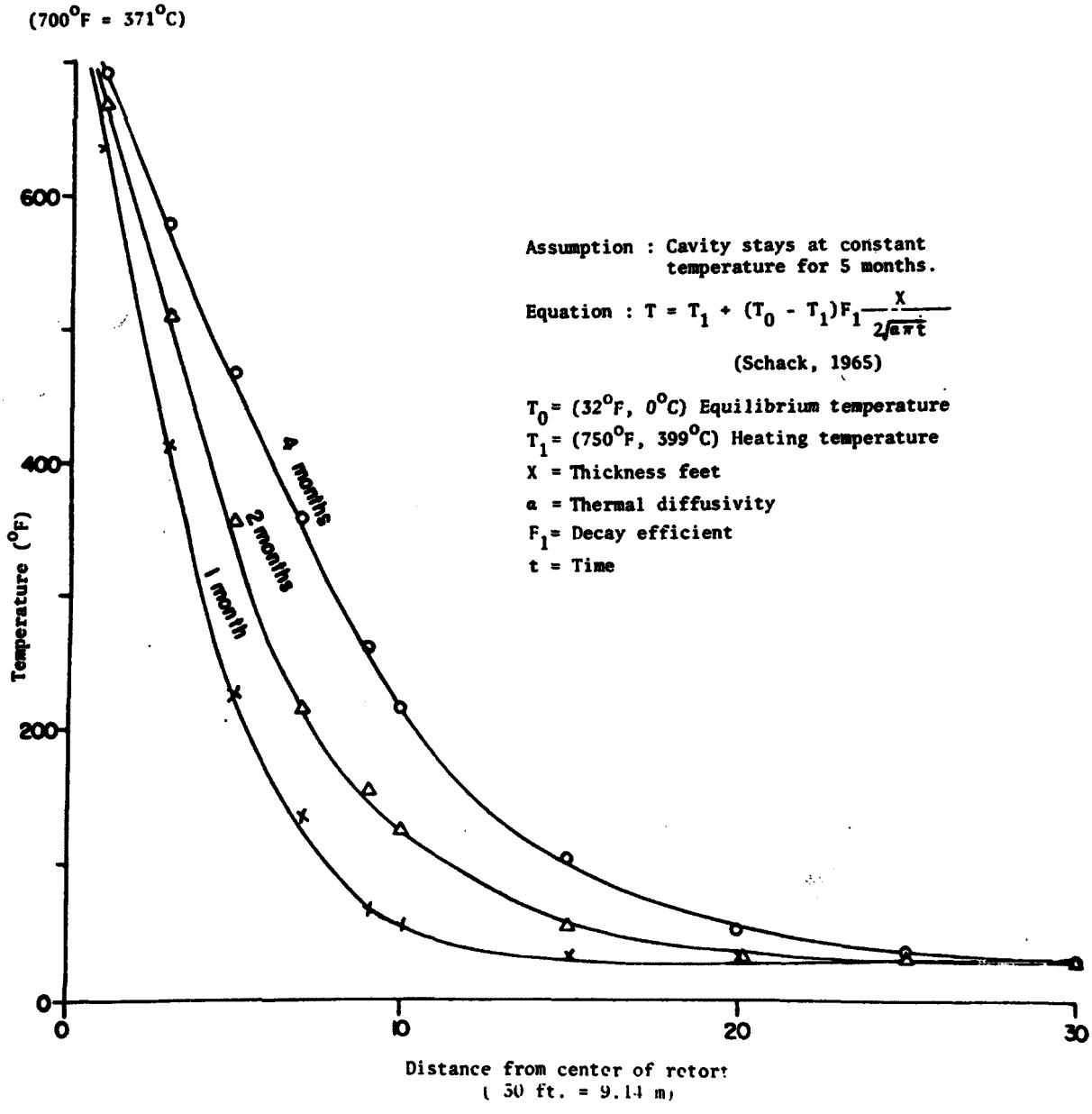


Figure 5-10. In situ retort cavity combustion temperatures before steady-state temperatures are reached.

Fig. a Temperature effect on benzene extract from spent shale derived from combustion (air) and pyrolysis (He)

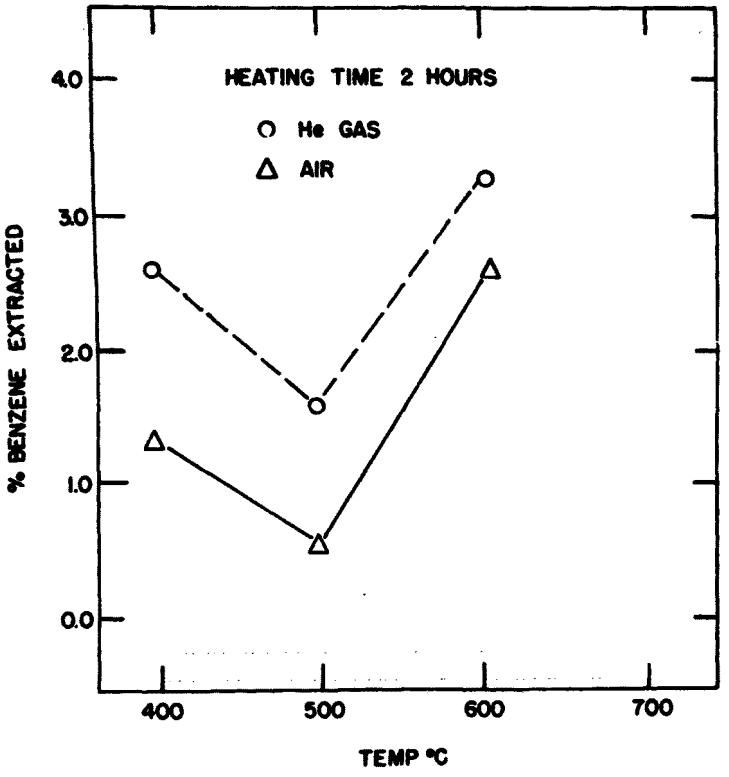


Fig. b Effect of heating time on benzene extract from spent shale derived from combustion (air) and pyrolysis (He)

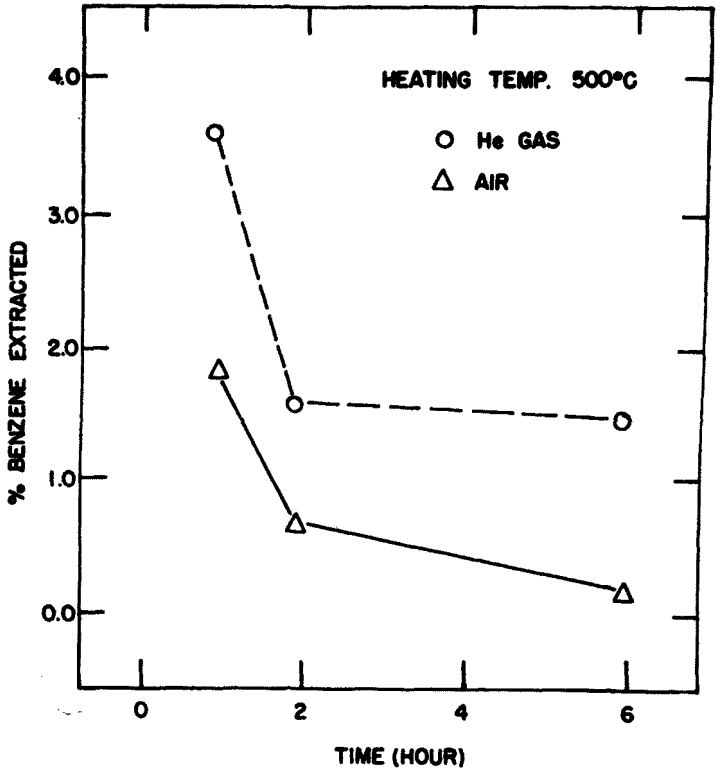


Figure 5-11. Effect of (a) temperature and (b) heating time on the proportion of organic carbon in spent shale extractable with benzene (percent benzene extracted). The spent shale was derived from combustion (air atmosphere) retorting, and pyrolysis (helium [He] atmosphere) (Kwan and Yen, unpublished data).

Some of the known human carcinogens are listed in Table 5-7. To date, these specific compounds have not been identified in oil shale process streams. Epidemiological data relating cancer to pollutants is still inconclusive. Exposure histories, particularly for humans, may be extremely complex and, in most cases, data do not exist for the several decades sometimes required for an effect to be realized. Also, many pollutant species have not been completely characterized. Another important factor is the carcinogen conglomerate, or the factors that affect the activity of a carcinogen. For example, the C_{12}-C_{28} n-alkanes can increase the carcinogenicity of benzo(a)pyrene a thousandfold.

TABLE 5-7. HUMAN CARCINOGENS[a]

Substance	Body parts affected
4-Aminobiphenyl	Urinary bladder
Benzidine	Urinary bladder
2-Naphthylamine	Urinary bladder
4-Nitrobiphenyl	Urinary bladder
Bis-(chloromethyl) ether	Lungs
Chloromethyl methyl ether	Lungs
Soots, tars, oils	Lungs
Cigarette smoke	Lungs, stomach, colon, urinary bladder
Asbestos	Bronchi, mesothelium
Coke oven fumes	Bronchi, kidneys
Nickel compounds	Bronchi
Chromate	Bronchi
Coal tar and pitch	Bronchi, skin
Melphalen	Blood
Cadmium	Prostate
Isopropyl oil	Nasal cavity
Vinyl chloride	Liver
Arsenic	Lungs, skin
Diphenylhydantion	Lymphoma
Chloroamphenicol	Blood
Cyclophosphamide	Blood

[a] From Hueper and Conway, 1964, and Sawicka, Eugene (EPA-RTP), 1978 personal communication.

Atwood and Coombs (1974) indicated that raw shale oil has a mild carcinogenic potential, comparable to some intermediate petroleum refinery products and product oils. Upgraded shale oil has a lower carcinogenic potential than raw shale oil. Most of the polycyclic aromatics are believed to be broken down by hydrogenation. The chemical character and ultimate fate of many of the materials used or created in oil shale processing are not clear and predictable at this time.

Product Combustion

Differences in emissions from the combustion of fuels refined from crude shale oil and those from combustion of conventional fuels are of interest because of the potential for widespread use of synthetic liquid fuels for transportation. The combustion of fuel products recovered from oil shale exposes occupational and general populations to various atmospheric pollutants. Health research is required to identify hazardous agents, to develop early indicators of stress and damage, and, most importantly, to determine the pathway and the fate of active agents.

The only significant differences between conventional petroleum fuel and oil-shale-derived fuel may lie in the trace elements, such as arsenic in shale fuel oil, and any unburned hydrocarbon emissions. An extensive program was conducted by the U.S. Navy Energy and Natural Resources Research and Development Office to determine the performance and emission characteristics of the shale-derived fuels in comparison with petroleum-based fuels (Denver Research Institute, 1976). In terms of combustion efficiencies, the two fuels showed no basic differences. Also, no appreciable differences were noted in unburned hydrocarbon emissions. In these tests, shale oil fuels demonstrated poor thermal and storage stability. These characteristics are attributed to its high olefin content (Jensen et al., 1971; Jackson et al., 1977).

High concentrations of high-melting-point wax were also noted in the Navy tests. Long chain paraffin compounds were found in shale oil asphaltene by Yen et al. (1977). The asphaltene was derived from a residue generated by processing Paraho syncrude through a delayed coker. Sharp bands at 3.70 and 4.15 Å from X-ray diffraction patterns (Figure 5-12) indicated the presence of these long-chain paraffins. Such crystalline peaks have also been found in petroleum-derived asphaltenes (Yen, 1971). The presence of long-chain paraffins in petroleum and shale oil asphaltene can be explained by the coprecipitation with asphaltene molecules during solvent separation.

Emissions from some combustion experiments using shale oil products have shown a rather high content of fuel-bound nitrogen. Upgraded shale oil is known to contain higher proportions of aromatics than do natural crudes (Goen and Rodden, 1974). The aromatic content of shale-oil-derived fuels will contribute to a high rate of emission of aromatics.

TYPES OF OIL SHALE AND PRODUCT ORGANIC COMPOUNDS

For research monitoring and identification of potential pollutants accompanying oil shale development, various analytical techniques have been utilized

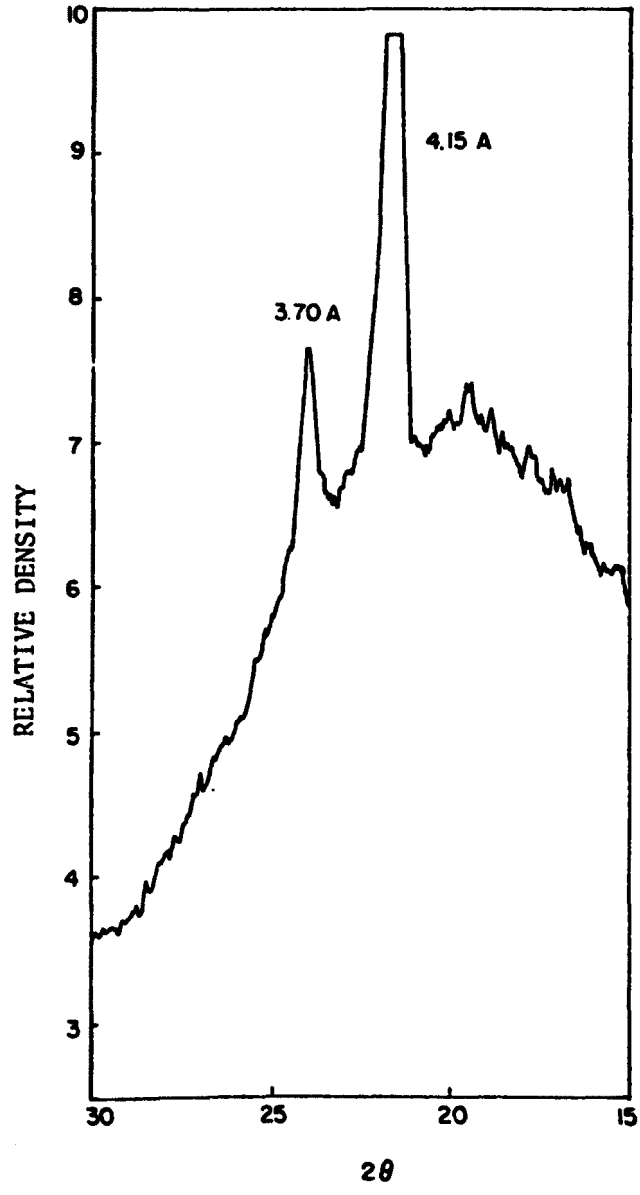


Figure 5-12. X-ray diffraction patterns of long-chain paraffins in petroleum-derived asphaltenes (Yen, 1971).

or proposed. Chemical separation, gas chromatography separation, and infrared spectrometer analysis are commonly used in environmental laboratories. Gas chromatography-mass spectrometry (GC/MS) has played a more important role in detection and identification of organic pollutants (Evans and Arnold, 1975). The recognition of high-pressure liquid chromatography (HPLC) in the field of organic analysis has had some impact. The new technique of liquid chromatography-mass spectrometry system (LC/MS) will broaden the analytical range which was previously limited by the gas chromatograph. The application of photoacoustic spectroscopy owes its potential mainly to its sensitivity and simplicity in operation (Krenzer, 1974; Krenzer and Patel, 1971; Krenzer et al., 1972; Golden and Goto, 1974; Dewey et al., 1973). Organic compounds found in oil shale products and by-products are categorized by type (nitrogenous, sulfur, oxygen, and aromatic hydrocarbon) and are described in the following subsections.

Selected compounds identified in shale oil include:

- Neutral compounds

N-alkanes	Branched alkenes
N-alkenes	Alkylfurans
Cyclohexane	Alkylthiophenes
Alkylcyclohexanes	Pristane
Branched alkanes	Phytane

- Aromatic compounds

Indene	Acenaphthene	Chrysene
Alkylindenes	Fluorene	Methylchrysenes
Naphthalene	Alkylfluorenes	Cholanthrene
Alkylanisole	Phenanthrene/anthracene	Benzofluoranthenes
Biphenyl	Alkylphenanthrenes	Benzopyrenes
Acenaphthylene	Fluoranthene	
Alkylnaphthalenes	Pyrene	

- Acidic compounds

Alkylphenols	Thionaphthols
Naphthol	Thiophenols
Alkylnaphthols	

- Basic compounds

Pyridine	Alkylacridines
Alkylpyridines	Indole
Quinoline	Alkylindoles
Alkylquinolines	Carbazole
Acridine	Alkylcarbazoles

Nitrogenous Compounds

In addition to the high nitrogen content of crude shale oil, other nitrogen-containing organic compounds are also found in retort water and spent shale (Figure 5-13). The nitrogen compounds in crude shale oil have been identified as pyridines, pyrrols, amides, nitriles, and other condensed-ring heterocyclics (Poulson, 1975). Retort water contains complex polar fractions

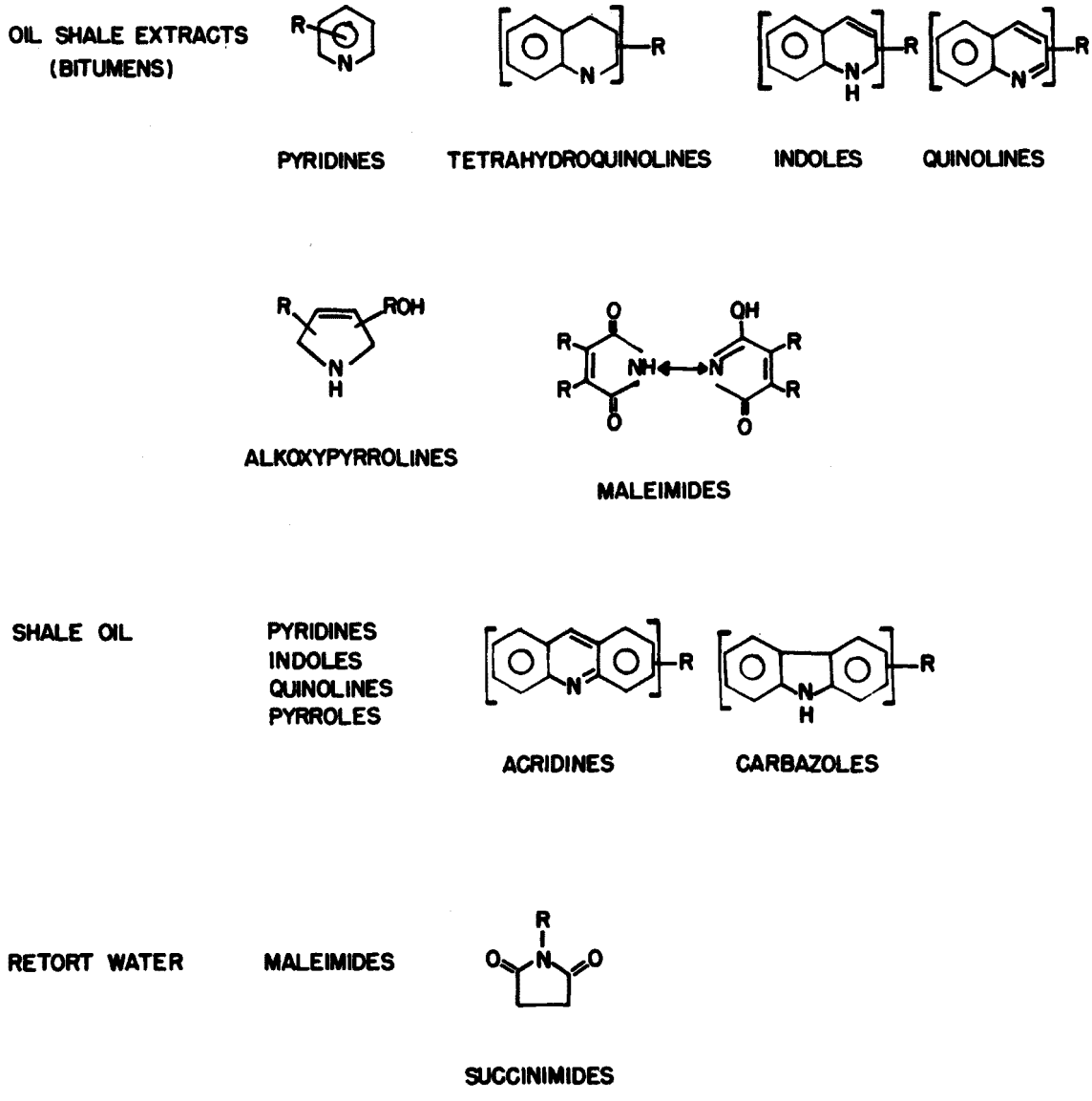


Figure 5-13. Nitrogenous organic compounds found in crude shale oil, retort water, and spent shale (Yen, 1976).

consisting of maleimides, succinimides, and alkoxypyrrolines (Wen et al., 1976). Nitrogen heterocyclics found in spent shale are acridine, dibenz(a,j)-acridine, phenanthridine, carbazole, etc. (Schmidt-Collerus et al., 1976).

Nitrogenous compounds play an important role in life processes and are part of the genetic coding material of nucleic acids. Many heterocyclic bases can disrupt the genetic coding by displacing normal bases and/or associating with the helix. At present, little is known about the type of nitrogenous compounds from oil shale and crude shale oil. Decora and Dineen (1961) used detergent as solid phase in gas chromatography to separate basic nitrogen compounds in shale oil. Dineen (1962) identified indoles, pyridines, quinolines, and tetrahydroquinolines in shale oil.

The uniquely high content of nitrogen in Green River oil shale is the result of the algal precursor of kerogen. Under high temperature pyrolitic conditions, the nitrogen functional groups are released from the kerogen structure together with other organic materials. After thermal processing, the nitrogenous compounds are distributed among shale oil, retort water, and spent shale as the oil soluble, water soluble, and insoluble high molecular weight fraction, respectively.

Yen (1976) has hypothesized that the nitrogen in oil shale contains amide bridges or heterocyclic components of the melanin type. It has been suggested that melanoidins could be the nitrogen-containing humic substance that is incorporated into kerogen under biostratinomy (Enders and Theis, 1938; Young et al., 1976; Nissenbaum et al., 1975; Manskaya and Drozdova, 1969; Ishiwatari, 1971).

Recently, Wen et al. (1976) positively identified a number of nitrogenous compounds in retort water by the use of GC-MS, particularly the succimide (Figure 5-14) and maleiamide (Figure 5-15). These polar compounds may be water soluble and thus mobile in the hydrosphere. Numerous similar water miscible nitrogenous compounds have also been associated with oil shale (Tables 5-8 and 5-9).

Sulfur Compounds

The content of sulfur is generally lower than of nitrogen in oil-shale-derived products (Figure 5-16). The fraction of sulfate sulfur and pyritic sulfur in oil shale is commonly small. The main body of sulfur in oil shale is combined in the organic matter. Organic sulfur is distributed among heterocyclic, aromatic,, and saturated hydrocarbons. The most abundant compounds have been identified as 2,2'-dithienyl, 2-phenylthiophenes, thionaphthenes, and thiophenes (Pailer and Gruenhaus, 1973). When thiophenes in shale oil undergo hydrogenation, normal alkanes or monomethyl alkanes are obtained as part of the shale oil product.

Desulfurization of organic sulfur compounds has been approached through chemical, physical, and biological methods (Davis and Yen, 1976). A large fraction of sulfur compounds react to form hydrogen sulfide and are removed simply during retorting processes. However, certain thiols and thiophenols

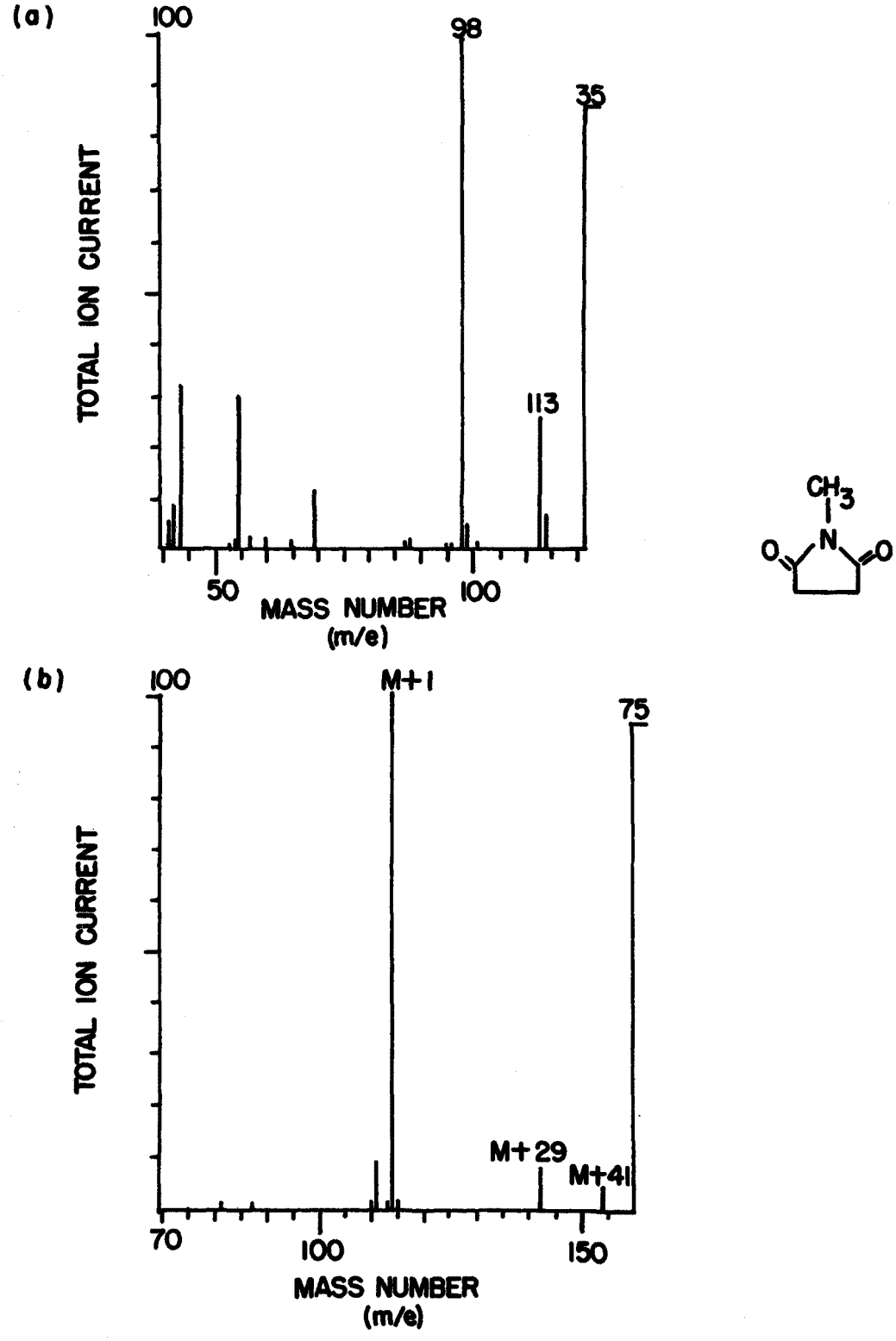


Figure 5-14. Mass spectra of succinimide in retort water: (a) electron impact and (b) chemical ionization (Wen et al., 1976).

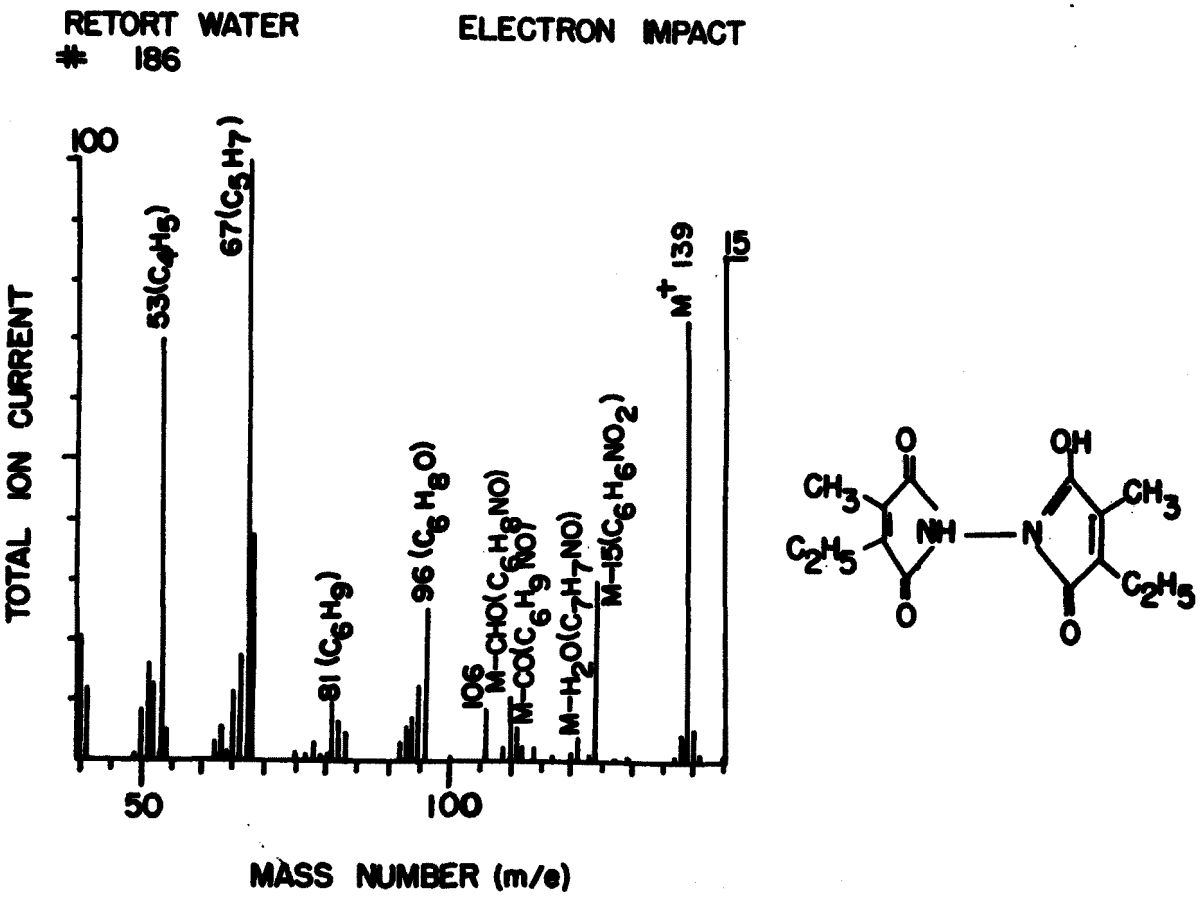


Figure 5-15. Organic nitrogen compound (maleimides) analysis from retort water (Wen et al., 1976).

TABLE 5-8. NITROGEN COMPOUND DISTRIBUTION IN OIL SHALE BITUMENS[a]

General types	Specific types
$C_nH_{2n-5}N$	alkylpyridines
$C_nH_{2n-7}N$	tetrahydroquinolines, dihydropyridines, cycloalkylpyridines
$C_nH_{2n-9}N$	indoles, pyridines, etc.
$C_nH_{2n-11}N$	quinolines, isoquinolines
$C_nH_{2n-13}N$	phenylpyridines
$C_nH_{2n-15}N$	carbazoles
$C_nH_{2n-17}N$	acridines
$C_nH_{2n-19}N$	cycloalkylacridines[b]
$C_nH_{2n-5}NO$	oxygenated pyridines
$C_nH_{2n-7}NO$	oxygenated tetrahydroquinolines
$C_nH_{2n-9}NO$	tetrahydroquinolines or oxygenated indoles
$C_nH_{2n-11}NO$	oxygenated quinolines

[a] Simoneit et al., 1971.
[b] Not found in Colony Mine.

TABLE 5-9. WATER-MISCIBLE POLAR CONSTITUENTS FROM GREEN RIVER OIL SHALE[a]

General types	Specific types
$C_nH_{2n}O$	substituted cyclohexanols, isoprenoid ketones
$C_nH_{2n-10}O$	tetralones, substituted indanones
$C_nH_{2n-2}O_2$	gamma lactones
$C_nH_{2n-7}N$	substituted tetrahydroquinolines
$C_nH_{2n-11}N$	quinolines
$C_nH_{2n-1}NO$	alkoxypyrrolines
$C_nH_{2n-5}NO_2$	maleimides
$C_nH_{2n-3}NO_2$	succinimides

[a] From Simoneit et al., 1971.

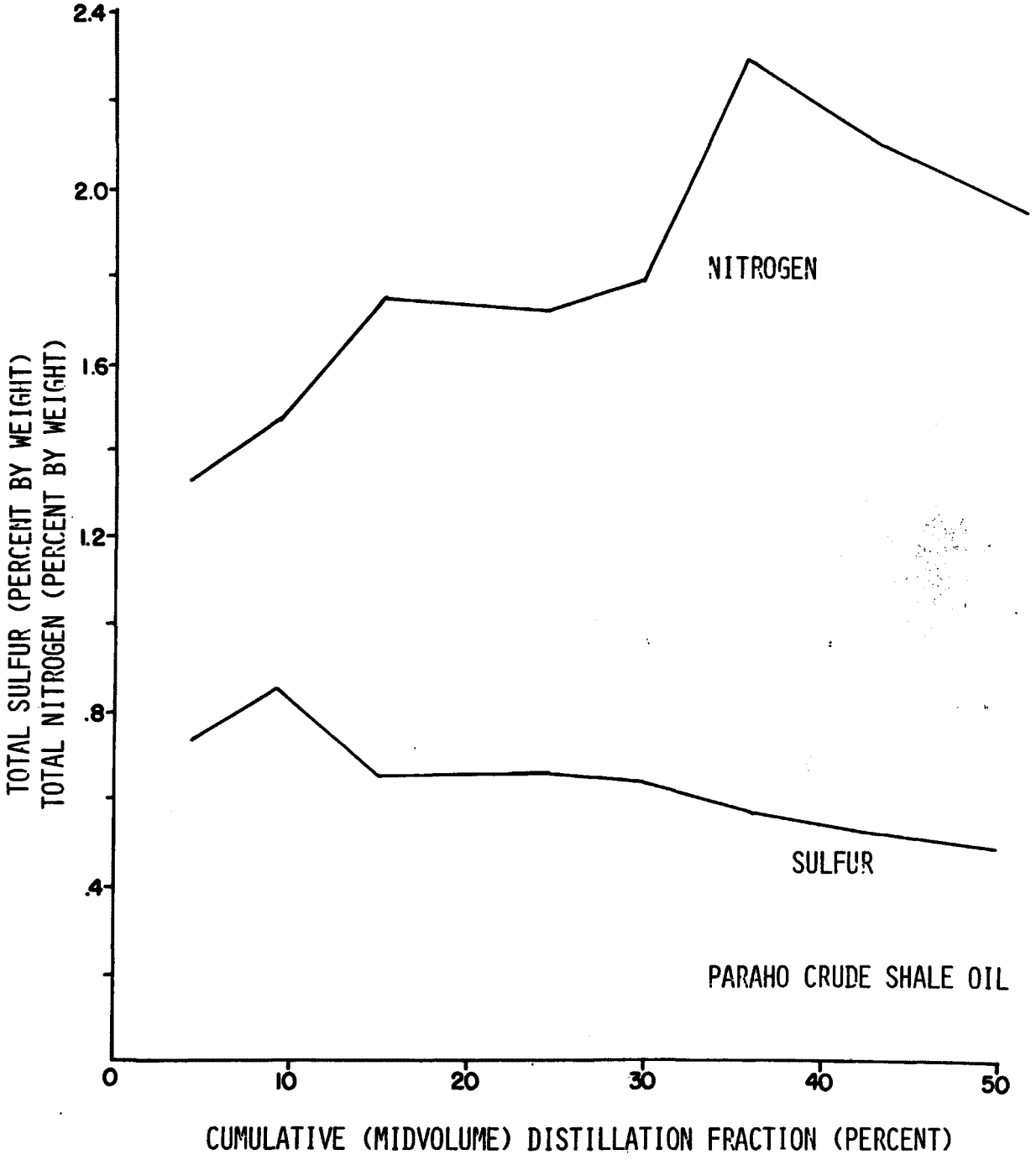


Figure 5-16. Total weight of nitrogen and sulfur in Paraho crude shale oil as a function of the cumulative midvolume distillation fraction.

resist heat treatment. Being polar, they can react with basic solutions to form ionizable salts.

Methylation-hydrogenation of unsubstituted thiophenes at 2-position by Raney nickel (Blicke and Sheets, 1949) can open thiophenic rings to yield corresponding alkanes that can be separated by catalytic cracking. Other methods, such as distillation (Kinney et al., 1952) have also been practiced to isolate the sulfur compounds occurring in oil shale. Generally, a combination of several of the above processes is applied for removal of sulfur compounds from the shale oil product stream.

Oxygen Compounds

Phenols are potential pollutants in all fossil-fuel-based refining operations. Petrochemical and other chemical wastewaters contain fairly large amounts of phenols. According to published work from the Soviet Union, phenols are the major organic components of oil shale retort water (Greenberg and Filts, 1975; Filts, 1977).

Different types of phenols—e.g., p-ethylphenol, isomeric cresols, as well as phenol—in retort water have been analyzed by gas chromatographic methods (Wen et al., to be published). Figure 5-17 shows some results of this work. Actually, the precision of gas chromatographic methods is greater than that of the traditional colorimetric method (Wen, 1976). Some comparable results are given in Table 5-10. Mass spectroscopy is another method for the identification of phenols (Wen et al., to be published) (Figure 5-18).

Higher homologous series of aromatic phenols, as well as sulfur-containing phenols, have also been detected in shale oil by GC/MS. Oxygen-containing heterocyclics such as furans have been identified as well. Many fatty acids (Wen and Yen, to be published) as well as esters (Figure 5-19) are found in retort water as well as other shale products.

Aromatic Hydrocarbons

A large number of volatile organics appear in by-product water from oil shale retorting. Various methods of analytical procedures usually result in different analytical data. For example, the varying analytical results reported by two laboratories working on the same retort water are shown in Tables 5-11 and 5-12.

Shale oil contains large number of aromatic hydrocarbons (Table 5-13). The degree of condensation of the aromatic system increases with the degree of severity of heat that has been exerted on the products during processing. For example, the carbonaceous spent shale or coke will experience association with highly condensed aromatic systems. The polynuclear aromatic systems also have been observed in oil shale (Figure 5-20). Biphenyl has been identified in retort water (Figure 5-21). Both azaares (AA) and polycondensed aromatic hydrocarbons (PAH) in oil-shale-related materials have been studied by Schmidt-Collerus et al. (1976). Their results are supported by thin-layer chromatography (TLC), fluorescence spectroscopy, and HPLC (Table 5-14).

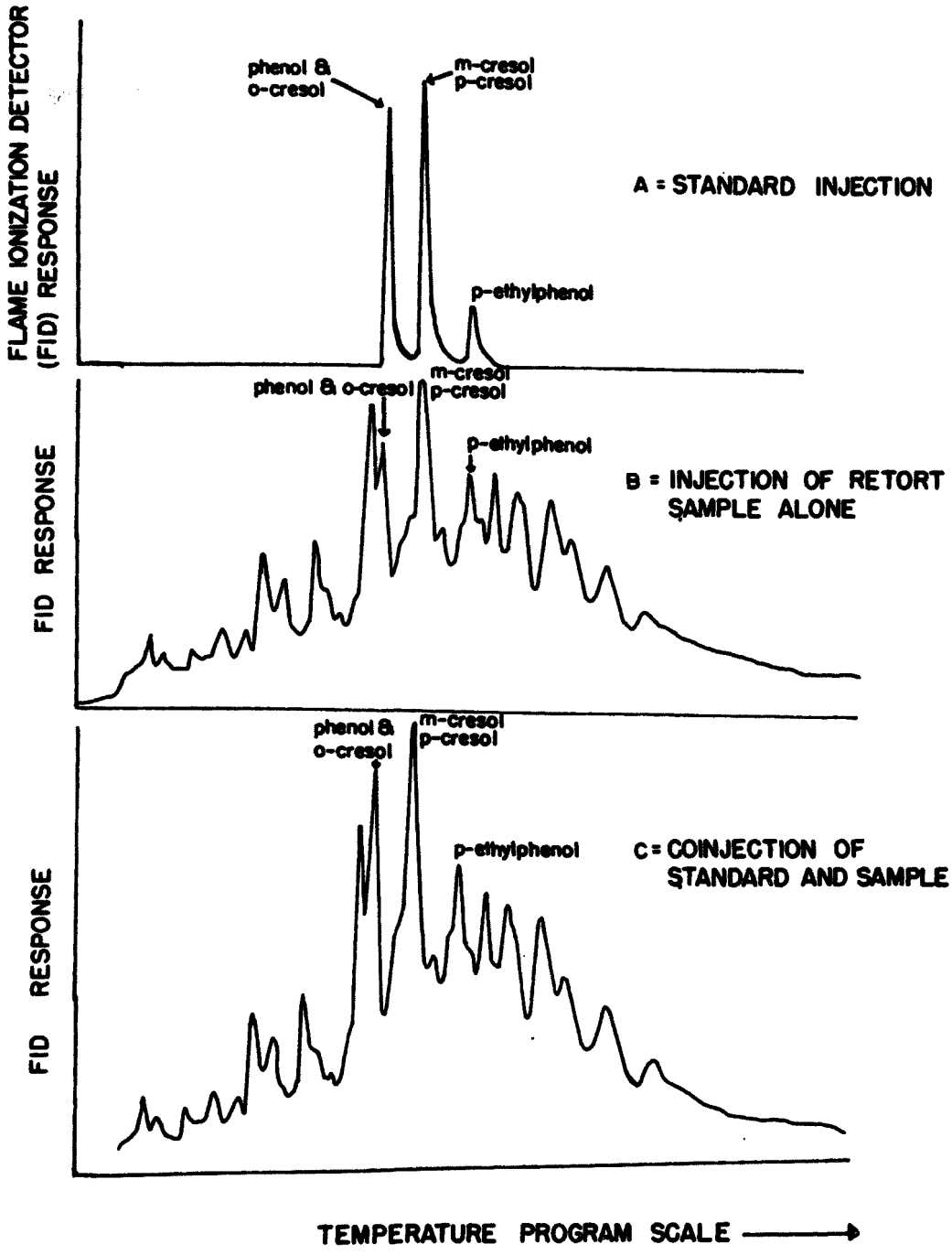


Figure 5-17. Analysis of phenols from retort water (Wen et al., to be published).

TABLE 5-10. PHENOLIC COMPOUNDS DETERMINATION IN RETORT WATER FROM LERC 10-TON RETORT[a]

	Phenolic compound (mg/l)		
	phenol and o-cresol	m-cresol and p-cresol	p-ethylphenol
Gas chromatograph:			
Retort Water I[b]			
1[c]	28.7	31.5	13.8
2	37.9	40.3	15.6
3	27.2	35.5	12.9
Retort Water II[b]			
1[d]	22.4	32.9	11.7
2	27.1	42.8	14.3
3	24.0	37.7	11.6
Colorimetric:[e]			
Retort Water I[f]			
1[c]		21.[g]	
2		37.6[h]	
3		169.[g]	
Retort Water II			
1[d]		37.6[h]	
2		2.2[g]	

[a] From Wen, 1976.

[b] Waters I and II are from two different runs of the 10-ton LERC retort.

[c] Samples 1, 2, and 3 listed here are repeated determinations from Retort Water I.

[d] Samples 1, 2, and 3 listed here are repeated determinations from Retort Water II.

[e] These values represent a composite of all phenolic compounds.

[f] Standard deviation for colorimetric method Retort Water I is 80.0.

[g] Data from Bio-Technics Laboratories, Inc., Los Angeles, California.

[h] Data from AGRI Science Laboratories, Inc., Los Angeles, California.

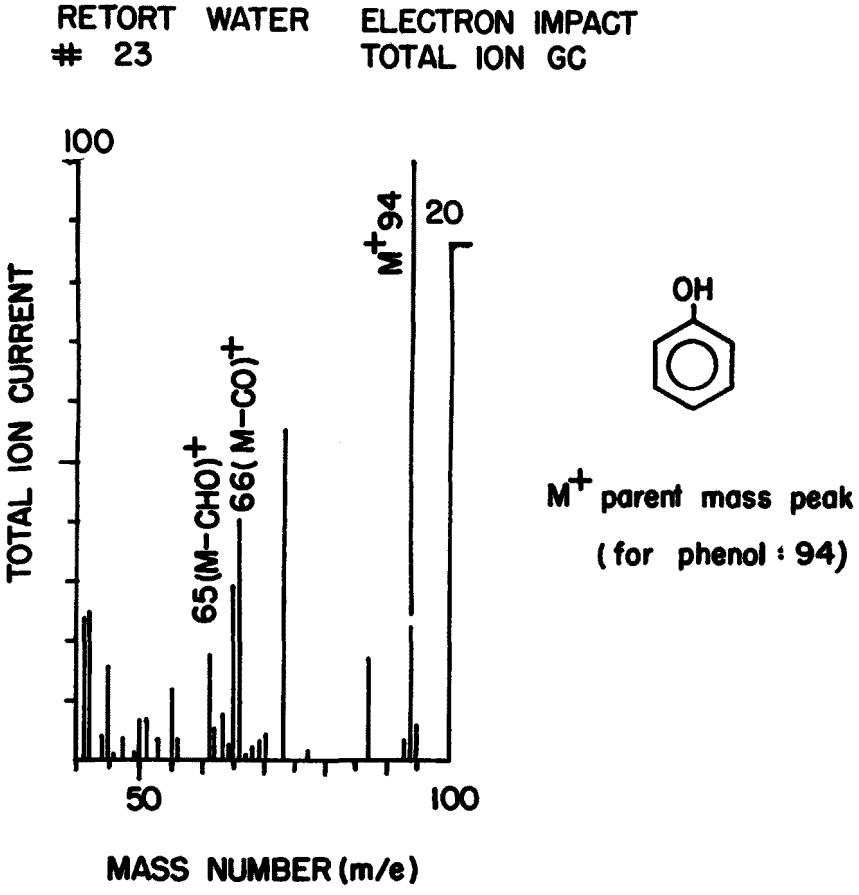


Figure 5-18. Mass spectrum of phenol in retort water (from Wen et al., to be published).

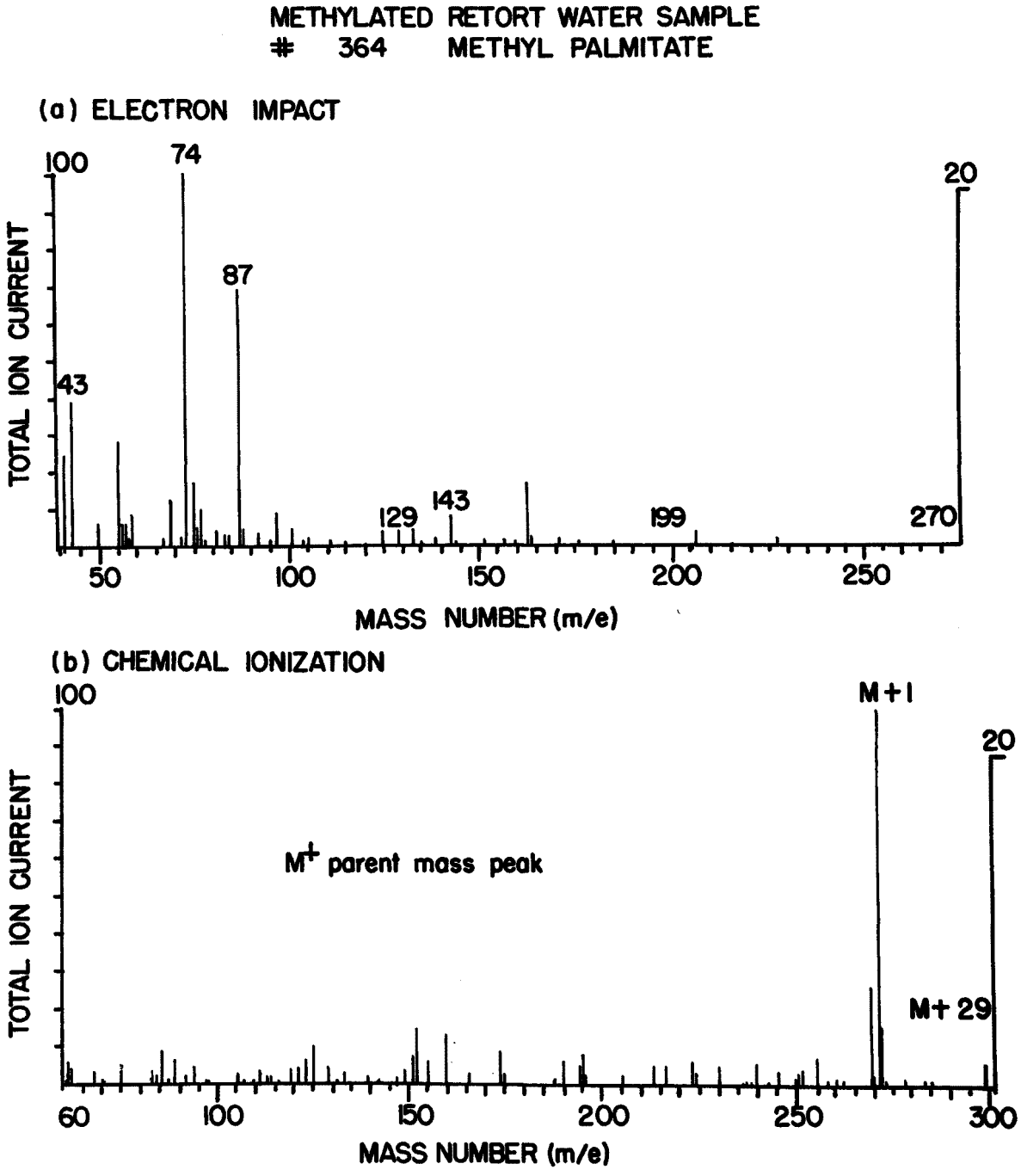


Figure 5-19. Mass spectra for methyl palmitate in retort water: (a) electron impact and (b) chemical ionization (Wen and Yen, to be published).

TABLE 5-11. VOLATILE ORGANICS IN RETORT WATERS FROM 150-TON RETORT (LERC)[a,b]

Chromatographic peak no.	Elution temperature (°C)	Compound	ppb
2	105	acetone	200±56
3	105	n-pentane	10±3
4	106	diethyl ether	13±9
6	107	t-butanol	130±91
7	108	nitromethane	16±7
8	109	methoxybutene-1 (tent.)	6±5
8A	110	cyanoethane (tent.)	53±21
9	111	3-methylpentane	13±2
10	115	n-hexane	53±5
12	123	methyl ethyl ketone (tent.)	6±1
13	128	methylcyclopentane	6.8±0.5
15	131	2-methylbutan-2-ol	17±3
16	133	benzene	14.5±7
17	134	thiophene	8±4
17A	138	cyclohexane	5±3
18	139	isobutylnitrile	9±1
20	148	n-heptane	10±2
21	153	n-methylpyrazole	7±2
22	162	2,3-dimethylbutan-2-ol or n-propyl t-butyl ether	trace
23	164	toluene	300±100
25	172	1-methylthiophene	9±7
26	173	pyridine	4±1
27	174	phenol	2±0.5[c]
28	175	ethylbenzene	11±2
29	176	p-xylene	28±6
29A	177	m-xylene	24±6
30	177	1,4-dimethylthiophene (tent.)	9±2
31	178	thiacyclohexane	22±6

[a] From Pellizzari, 1976b.
[b] These analyses and those listed in Table 5-12 were conducted on samples of the same retort waters.
[c] These levels are low relative to other reported results (e.g., see Table 5-10).

(continued)

TABLE 5-11 (continued)

Chromatographic peak no.	Elution temperature (°C)	Compound	ppb
32	179	o-xylene	7±1
33	181	methylthiacyclohexane isomer	trace
34	184	methylpyridine isomer (tent.)	9±2
35	190	n-propylbenzene	40±15
36	192	methylethylbenzene isomer	24±8
37	194	methylethylbenzene isomer	23±9
39	200	C_3-alkyl benzene	80±22
40	201	unknown	NQ
41	203	dimethylindene isomer (tent.)	2±2
43	209	C_3-alkyl benzene	4±1
44	212	o-methylphenol	10±5
45	215	2,2,6-trimethylcyclohexanone	9.5±1
46	220	C_4-alkyl benzene	3.2±5
47	225	acetophenone	2.7±0.4
48	229	C_4-alkyl benzene	4.6±0.6
49	230	unknown	NQ
50	230	p-methylphenol	4±1
51	233	C_4-alkyl benzene	8±1
52	236	o-ethyltoluene	17±3
53	237	4,5-dihydroxyheptane	68±21
54	240	m-ethylphenol	12±3
55	240	C_4-alkyl benzene	trace
56	240	unknown (aromatic)	NQ
57	240	naphthalene	75±32
58	240	dimethylbenzofuran	3.6±0.3
59	240	methylbenzocyclopentenone	4.2±0.3
60	240	unknown	NQ
61	240	β-methylnaphthalene	61±10
62	240	α-methylnaphthalene	52±17

TABLE 5-12. ORGANIC COMPOUNDS DETERMINED IN BY-PRODUCT WATERS FROM OIL SHALE RETORTING (LERC)[a,b]

Peak	Compound	Concentration (ppm)
1	acetic acid	600
2	propanoic acid	210
3	n-butanoic acid	130
4	acetamide	230
5	n-pentanoic acid	200
6	propionamide	50
7	n-hexanoic acid	250
8	butyramide	10
9	phenol	10
10	n-heptanoic acid	260
11	o-cresol	30
12	m- and p-cresols	20
13	n-octanoic acid	230
14	2,6-dimethylphenol	-
15	o-ethylphenol	-
16	2,5-dimethylphenol	-
17	3,5-dimethylphenol	-
18	2,3-dimethylphenol	-
19	n-nonanoic acid	100
20	3,4-dimethylphenol	-
21	n-decanoic acid	50
22	α-naphthol	-
23	β-naphthol	-

[a] From Ho et al., 1976.

[b] Pellizzari (1976b) and Ho et al. (1976) used the same water with different results (see Table 5-11).

TABLE 5-13. COMPOSITION OF AROMATIC HYDROCARBONS IN TOSCO SHALE OIL[a]

Compound	Percent present in crude shale oil
benzene	0.01
toluene	0.06
ethylbenzene	0.04
p-xylene	0.03
m-xylene	0.14
o-xylene	0.05
isopropylbenzene	0.01
m-propylbenzene	0.01
1-methyl-4-ethylbenzene	0.15
1-methyl-z-ethylbenzene	0.05
1,3,5-trimethylbenzene	0.05
1,2,3-trimethylbenzene	0.05
1-methyl-2-isopropylbenzene	0.38
1-methyl-3-isopropylbenzene	0.38
1-methyl-4-isopropylbenzene	0.38
tert.-butylbenzene	0.14
sec.-butylbenzene	0.14
iso-butylbenzene	0.14
1.3-diethylbenzene	0.04
1.4-diethylbenzene	0.16
other C_{10}-alkyl benzenes	0.12
C_{11}-alkylbenzenes	0.40
naphthalene	0.002

[a]From Denver Research Institute (1976) and Schmidt-Collerus et al. (1976).

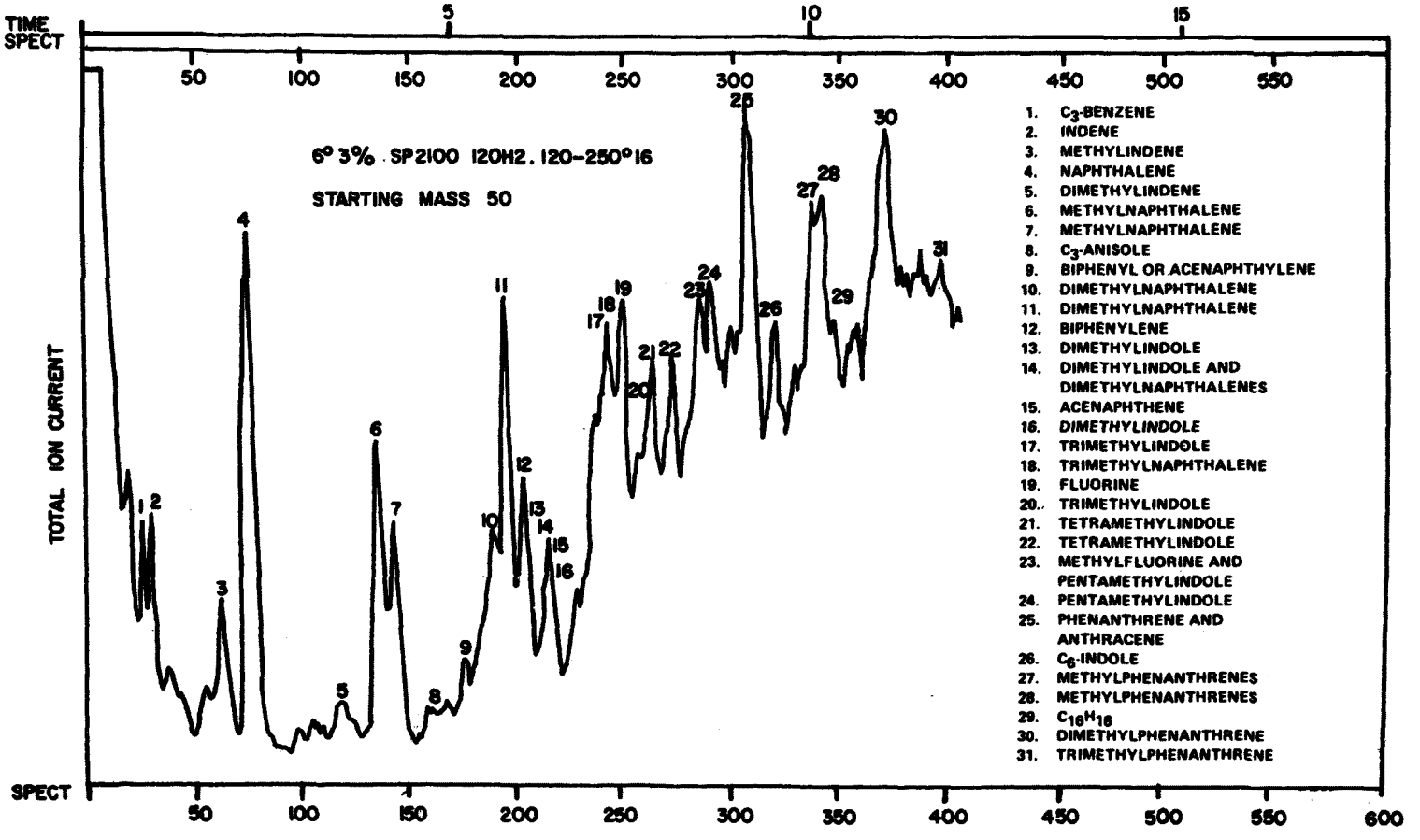


Figure 5-20. Typical gas-liquid chromatogram of oil shale pna fraction (Schmidt-Collerus et al., 1976).

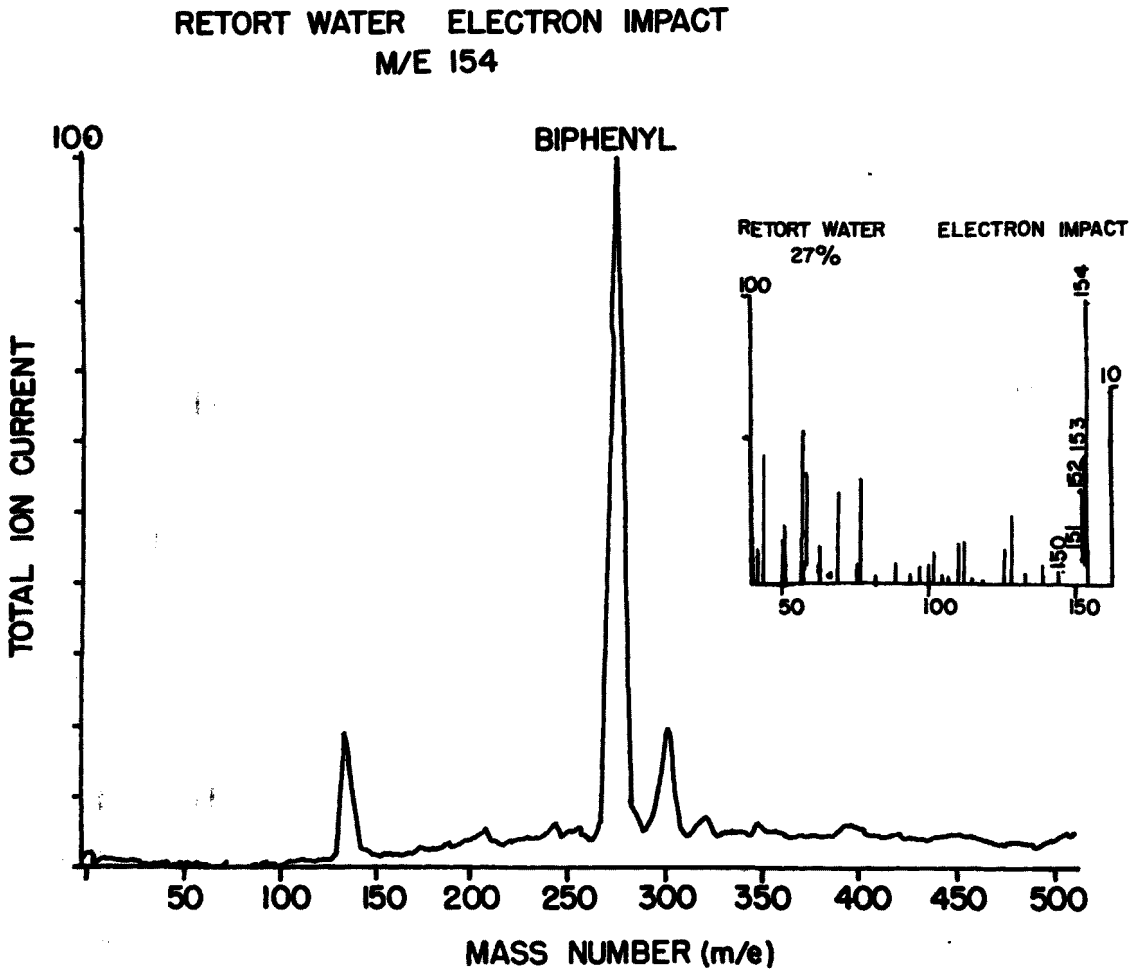


Figure 5-21. Mass spectrum of biphenyl from retort water (Schmidt-Collerus et al., 1976).

TABLE 5-14. POLYCONDENSED AROMATIC HYDROCARBONS IDENTIFIED IN BENZENE EXTRACTS OF CARBONACEOUS SPENT SHALE[a,b]

Compound	TLC, R_B, color	Fluorescence spectrum	HPLC retention time	Remarks
phenanthcene	x	-	-	
benz(a)anthracene	x	x	x	
dibenz(a,h)anthracene	x	x	-	
7,12-dimethylbenz(a)anthracene	x	x	-	Fluorescence spectrum indicates a possible mixture with another compound; separation of these by HPLC in progress
fluoranthene	x	x	-	
3-methylcholanthrene	x	x	-	Further confirmation by HPLC in progress
pyrene	x	-	-	
benzo(a)pyrene	x	x	x	
dibenz(c,d,j,k)pyrene	x	x	x	Separated by HPLC from BaP
perylene	x	x	x	
benzo(g,h,i)perylene	x	-	-	Fluorometric identification in progress

[a] From Schmidt-Collerus et al. (1976).

[b] Spent shale from TOSCO process.

TECHNIQUES FOR POLLUTANT CHARACTERIZATION, MEASUREMENT, AND MONITORING

The current and emerging problems in the development of new sources of energy, such as oil shale, require new approaches to the abatement and control of pollution. The following paragraphs provide a discussion of aqueous effluents from oil shale operations. Potential air pollutants are discussed in Section 7.

The compositions of liquid effluents from oil shale processing are rather complicated. The effluents include process water from various types of above-ground and in situ retorting processes, as well as the leachate and seepage water from the retorted shale and the underground residues from in situ retorting. They have a high pH value and salt content and contain a large fraction of polar organic components. Characterization of these organic contaminants and techniques for measuring and monitoring them are discussed in the following subsections.

Characterization

When dealing with organic compound identification or characterization, there is always the question of how far or how much to analyze before stopping. An analysis may be as simple as total organic carbon (TOC), or as sophisticated as single compound identification by GC/MS or differential scanning infrared spectrophotometry with computerized pattern recognition. For a newly developed process such as shale oil production, many of the potential environmental impacts from full-scale commercial production are still unknown. In order to operate a monitoring program, more detailed analyses are needed to identify certain important organic components before nonspecific parameters, such as TOC, BOD, and COD, can be used for monitoring purposes.

The most common type of organic pollutant analysis is the determination of some preselected compounds that have previously (often accidentally) been recognized as harmful, e.g., pesticides and carcinogens. But many other compounds have been neglected simply because their presence and biological activity are not known. Also, the knowledge of organic substances is biased by using limited available methods. There is no one method or technique that can completely address the problem of organic analysis. Each technique has its own limitations and advantages.

Several analytical techniques are commonly used in wastewater organic analysis. They are total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), gas chromatography (GC), thin layer chromatography (TLC), liquid chromatography (LC), and GC/mass spectrometry (GC/MS).

Total Organic Carbon Analyzer—

A TOC analysis measures the difference between the total carbon (TC) and total inorganic carbon (TIC). The quick response and easy operation of TOC analyzers provide a significant advantage over the BOD and COD tests. However, TOC analysis may be complicated by the very high concentrations of carbonate carbon. In addition to monitoring the effluents from waste treatment plants, automatic carbon analyzers can be used to monitor other industrial processes

(Hill, 1968). Because of its nonspecificity, TOC analysis offers a general tool for monitoring established processes such as municipal and industrial effluents. More specific analytical instruments may be applied when changes are detected in TOC levels or when information on specific pollutants is required.

Gas Chromatography and GC/MS—

Gas chromatography is currently being used as a universal instrument for quantitative analysis of pesticides and most smaller organic compounds. The technique is suitable for compounds with a moderate boiling point and high thermal stability. This, of course, limits the range of its application. For diluted liquid effluents, concentration procedures are required before the GC analysis can be employed.

Adsorption seems to be the most promising sampling technique compared to others available (e.g., distillation, freeze-drying, liquid-solid adsorption, headspace analysis, gas-phase stripping, batchwise and continuous liquid-liquid extraction, etc. [Mieure and Dietrich, 1973; Grob, 1973; Bentreich et al., 1975; Bowty et al., 1975; Leoni et al., 1975; Osterroht, 1974]). Activated carbon is preferred as an adsorbent for aqueous solutions and is widely used. The advantage of activated carbon adsorption is the high degree of enrichment from a large volume of water. Its disadvantage, however, is that a completion elution of the adsorbates (chemically modified or activated carbon) is not always possible. A GC column packing material—Porapak Q—can also be used as an adsorbent instead of activated carbon.

The large number of contaminants in the water sample creates problems in the detection of ultratrace concentrations of pollutants and the positive identification of structurally similar compounds. The application of GC/MS can solve both the sensitivity and identification problems (Hites and Biemann, 1972; Eichelberger et al., 1974). These two techniques have been applied to the organic analysis of process water from shale oil production (Wen et al., 1976).

Liquid Chromatography—

High-pressure liquid chromatography may become a major separation method for polar, high-boiling-point, and thermally unstable compounds. This would be a great advantage for the analysis of wastewater from shale oil production. Three modes of operation of HPLC can be fully utilized. First, the organics are concentrated using a C_{18} reverse-phase liquid partitioning column. Then the concentrate is separated using a size exclusion column for molecular weight distribution. The low molecular weight compounds are trapped for GC analysis, and the remaining compounds go through further separation by liquid-solid adsorption column (silica gel or alumina), or liquid-liquid partitioning column (C_{18} or NH_2). The eluted peaks can be trapped for mass spectrometric (MS) analysis, or the liquid chromatograph can be interfaced directly to the MS equipment for positive identification.

Measurement

In recent studies (Kwan et al., 1977), retort water or process water was first separated into four fractions (basic, acidic, neutral, and residual) by liquid-liquid extraction with pH adjustment (Figure 5-22). COD distributions of these fractions are shown in Table 5-15. The gel permeation chromatography (GPC) separation is shown in Figure 5-23. Low molecular weight compounds have been found in both the basic and acid fractions. Figures 5-24 and 5-25 correspond to set 1 and set 2 in Table 5-15. The similarity between the neutral fraction (in Figure 5-24) and the basic fraction (in Figure 5-25) suggests that the extraction order may affect the COD distribution. The change of pH during the extraction process might change the original composition of retort water. This is why a new extraction procedure is now being used that increases the polarities of the extraction solvents from benzene, ether, chloroform, and methylene chloride. Liquid-liquid extraction may have some advantage over the use of macroreticular resins (Leenheer and Huffman, 1976) in that no solid matrix is employed in the former approach and hence irreversible adsorption is not a problem. However, costs and ease of analysis are other considerations in selection of analytical methods for monitoring purposes.

The micro-Porasil (silica gel) column separations with solvent programming are shown in Figures 5-26 to 5-29. Individual compounds that have not been identified in these spectra can be identified easily by the LC/MS technique.

Monitoring

For a monitoring technology, the analysis should be able to ascertain whether the process is working according to some defined expectation. Although this monitoring concept is simple, it may be rather sophisticated in terms of analytical requirements. However, one of the main concerns in monitoring is quick response and easy operation. Nonspecific analytical techniques, such as COD, BOD, and TOC, are useful to monitor well-established processes like sanitary treatment processes. But it would be rather shortsighted to use only the techniques for newly developed processes such as shale oil production because the appreciable uncertainties about the environmental impact of these developments. More detailed information is needed for successful monitoring investigations. Since individual compound identification can be very time-consuming and expensive, it may be more practical to separate and analyze complex organic mixtures by chemical or functional classes.

Figure 5-30 shows a functional group separation chromatograph by HPLC (Kwan et al., 1977). Three groups are identified: hydrocarbons (saturated and aromatic), organic acids, and polar compounds (nitrogenous, etc.). Their elution volumes are 4 milliliters, 9-12 milliliters, and 16-20 milliliters (9.1, 20.4-27.2, and 36.3-45.4, $x10^{-4}$ gallons) respectively. An injection volume of 20 microliters was used for this analysis. The retort water sample only goes through 0.2 micron membrane filter treatment. This technique shows high potential for satisfying the requirements of monitoring technique for liquid effluents from shale oil production. The utilization of this technique is discussed further in Section 7 for monitoring the biological treatment of retort water.

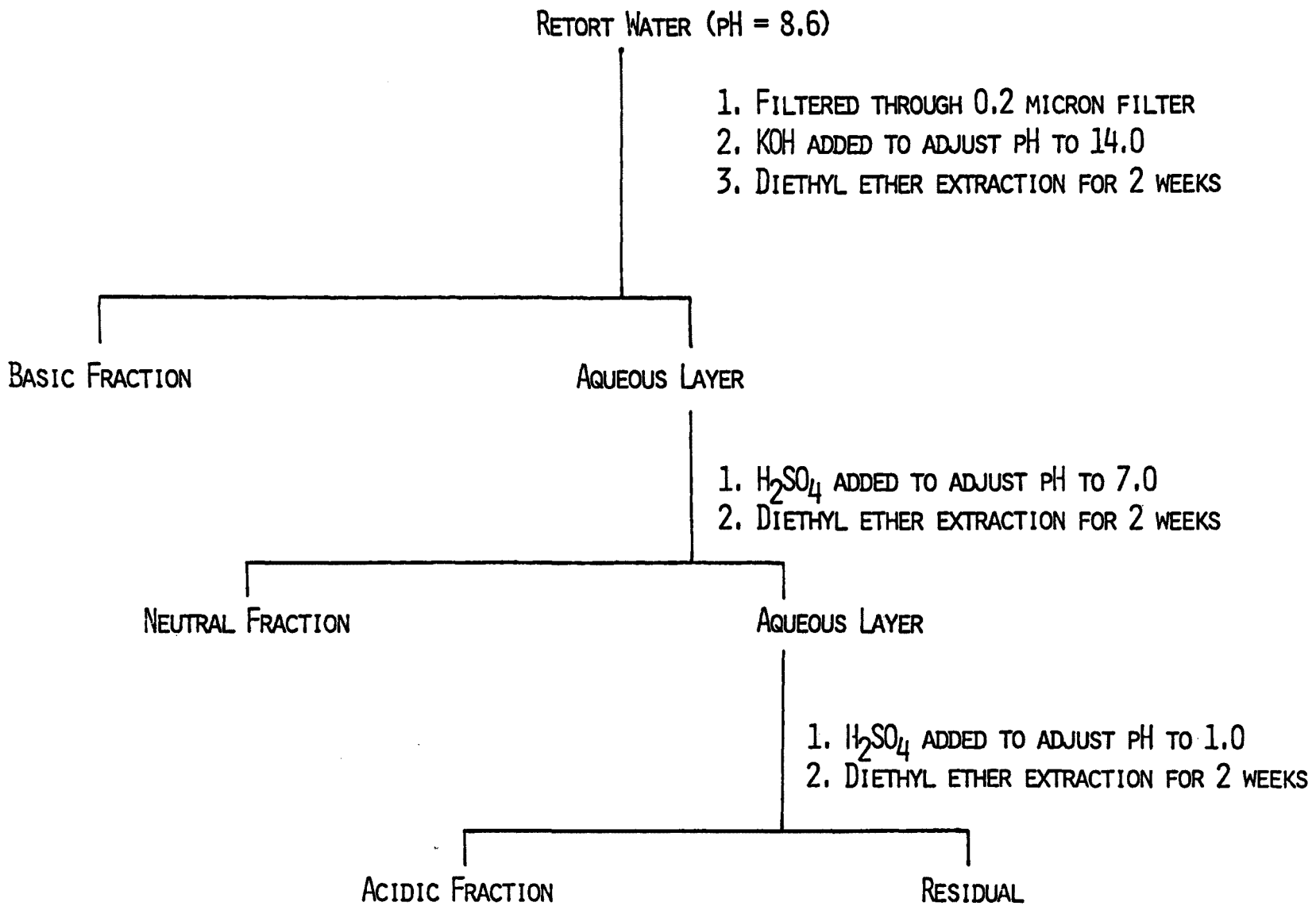


Figure 5-22. Liquid-liquid extraction scheme (Kwan et al., 1977).

TABLE 5-15. COD DISTRIBUTION AMONG THE FOUR FRACTIONS (Kwan et al., 1977)

Fraction	Extraction order	COD	Percent	Extraction order	COD	Percent
Basic	2	290	3	1	2,332	21
Neutral	1	3,970	36	2	1,572	14
Acidic	3	2,463	22	3	1,980	18
Residual		2,460	22		4,558	42
Total recovered		9,183[a]	83[a]		10,442	95[a]

[a] Based on 11,000 mg/l COD for original retort water.

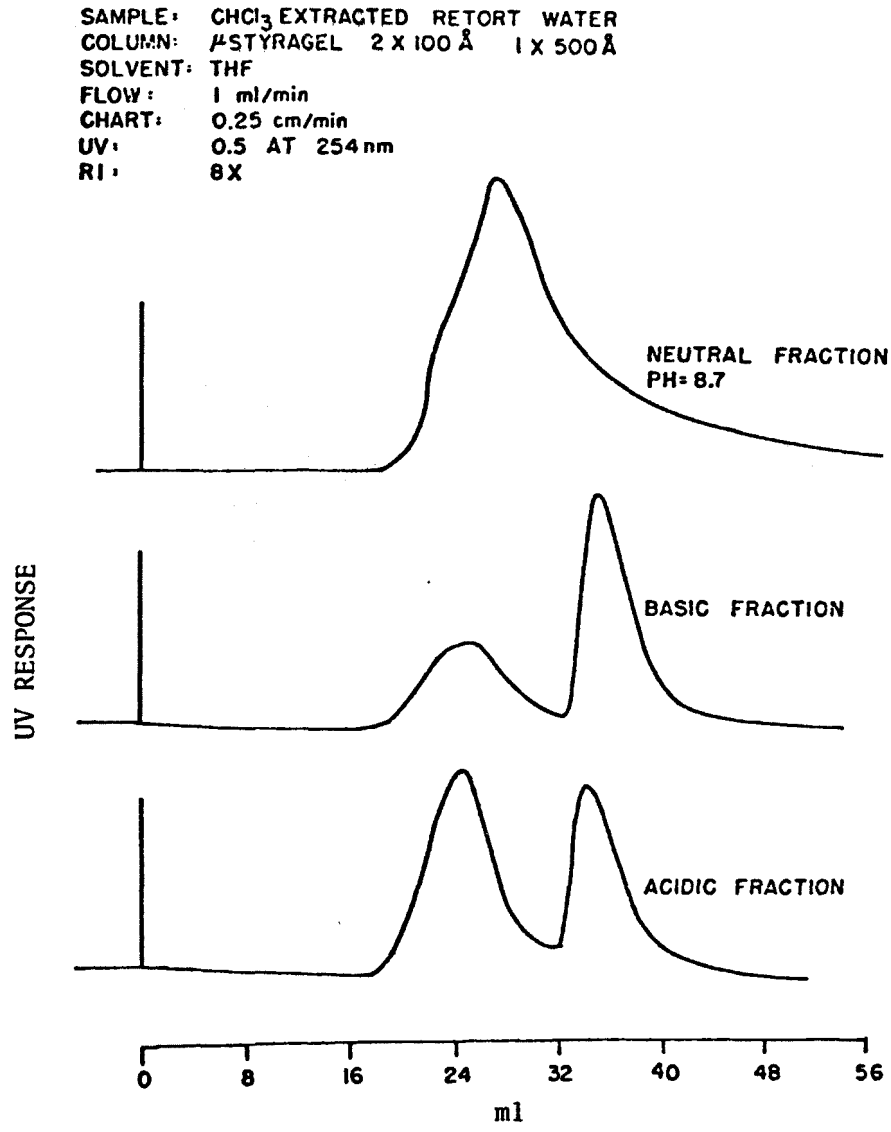


Figure 5-23. Gel permeation chromatography separation (Kwan and Yen, unpublished data).

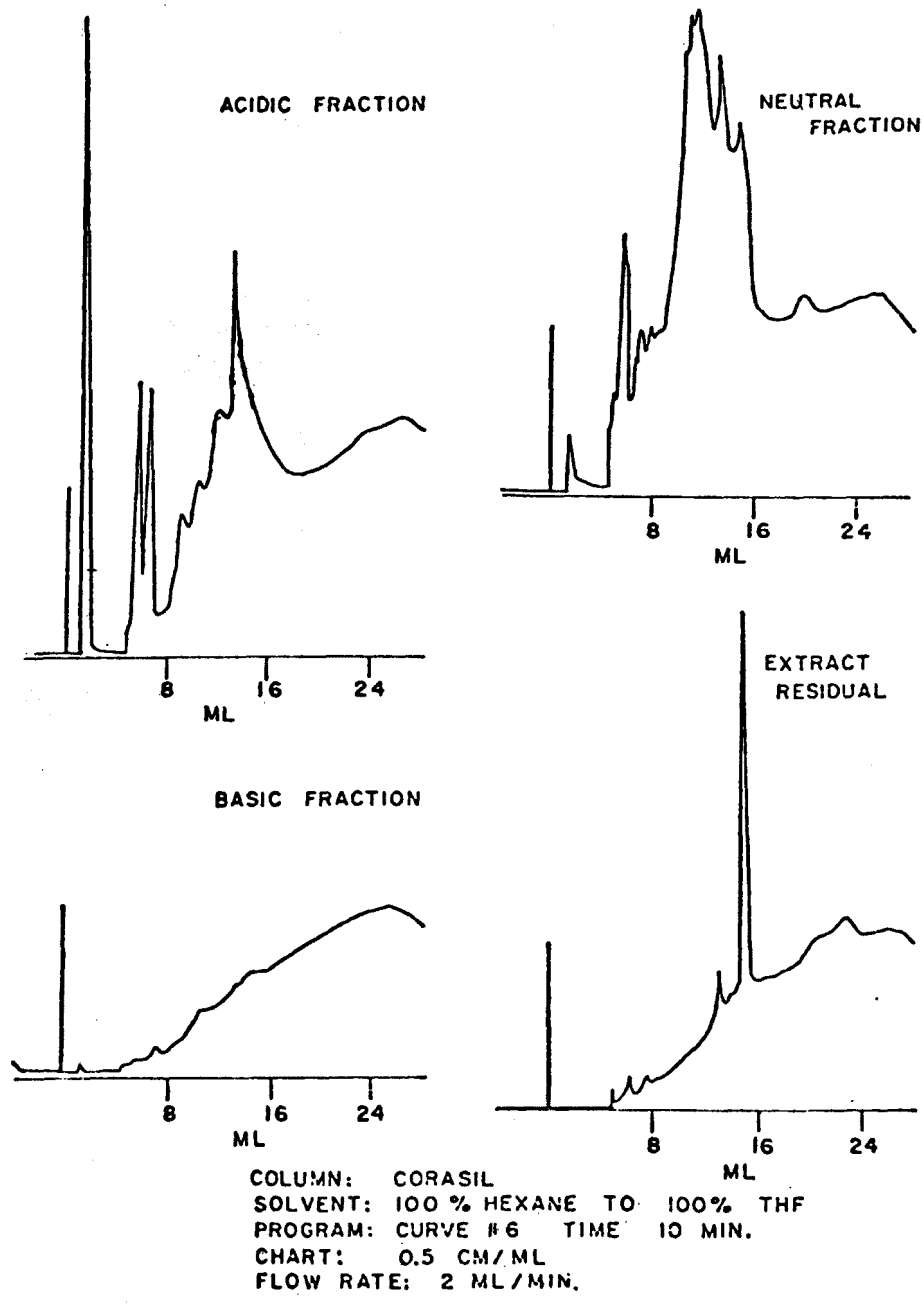


Figure 5-24. Chromatographic separation of set 1 extractions shown in Table 5-15 (ordinates are UV response).

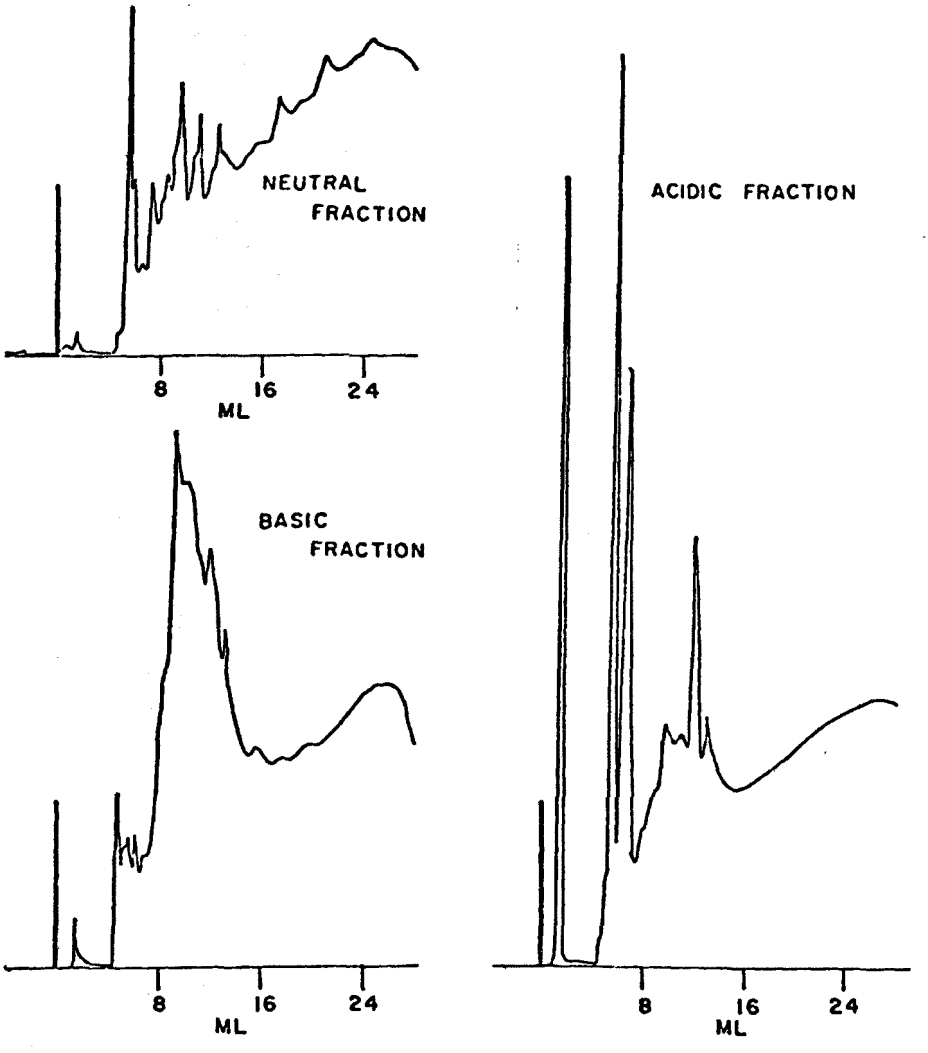
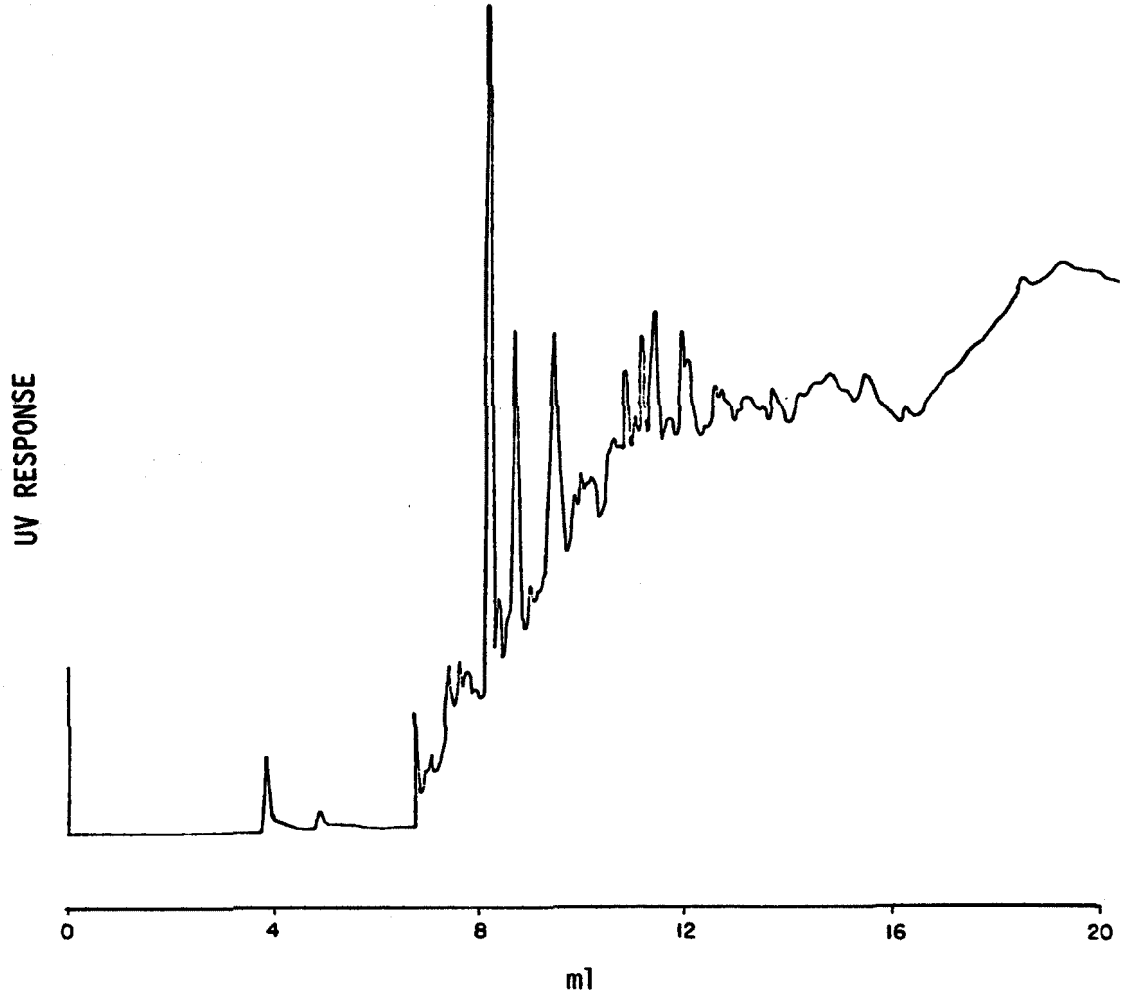


Figure 5-25. Chromatographic separation of set 2 extractions shown in Table 5-15 (ordinates are UV response).



COLUMN: μPORASIL
SOLVENT: 100% HEXANE TO 100% THF
PROGRAM: CURVE # 6 TIME: 20 min
FLOW: 0.5 ml/min
CHART: 0.5 cm/min
U.V.: 0.5 AT 254 nm

Figure 5-26. Sample of retort water (pH 8.8), benzene extracted (Kwan and Yen, unpublished data).

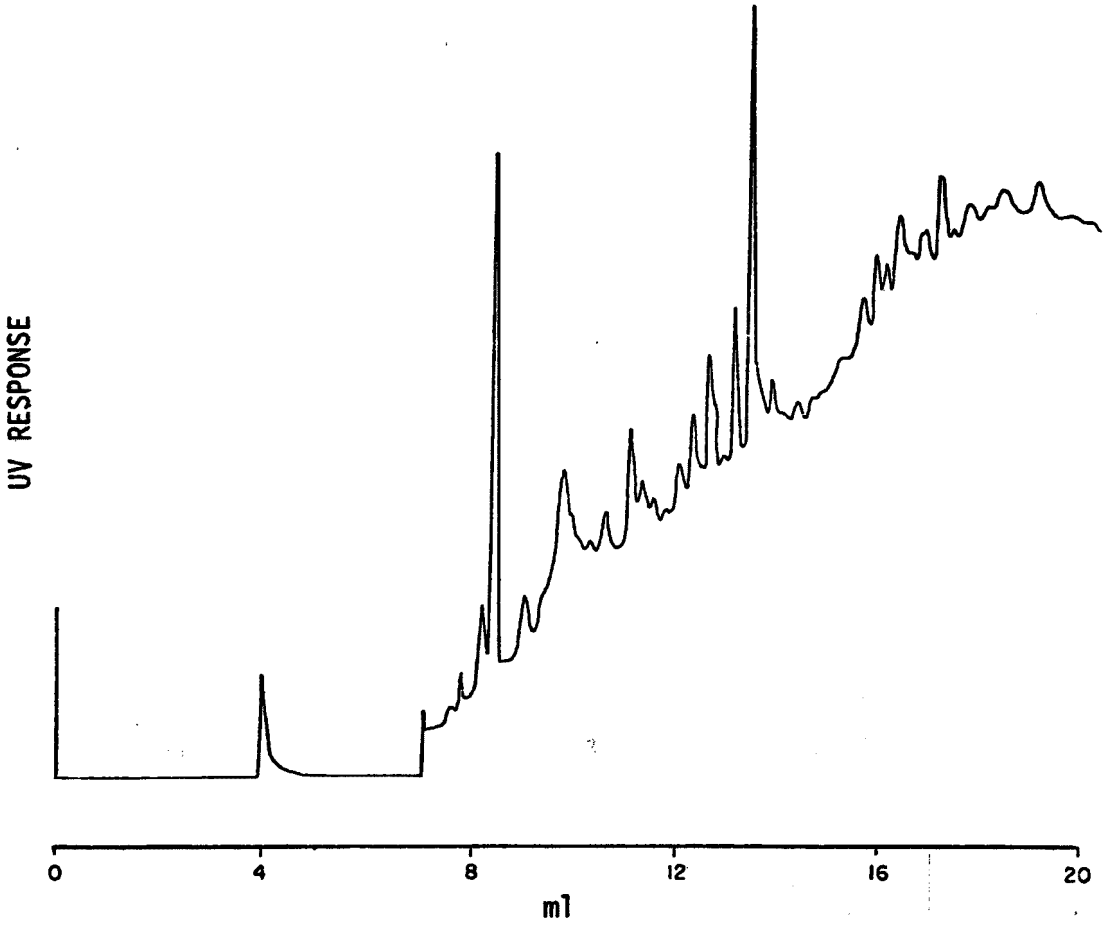


Figure 5-27. Sample of retort water (pH 8.8), ether extracted (Kwan and Yen, unpublished data). Analysis conditions are shown in Figure 5-26.

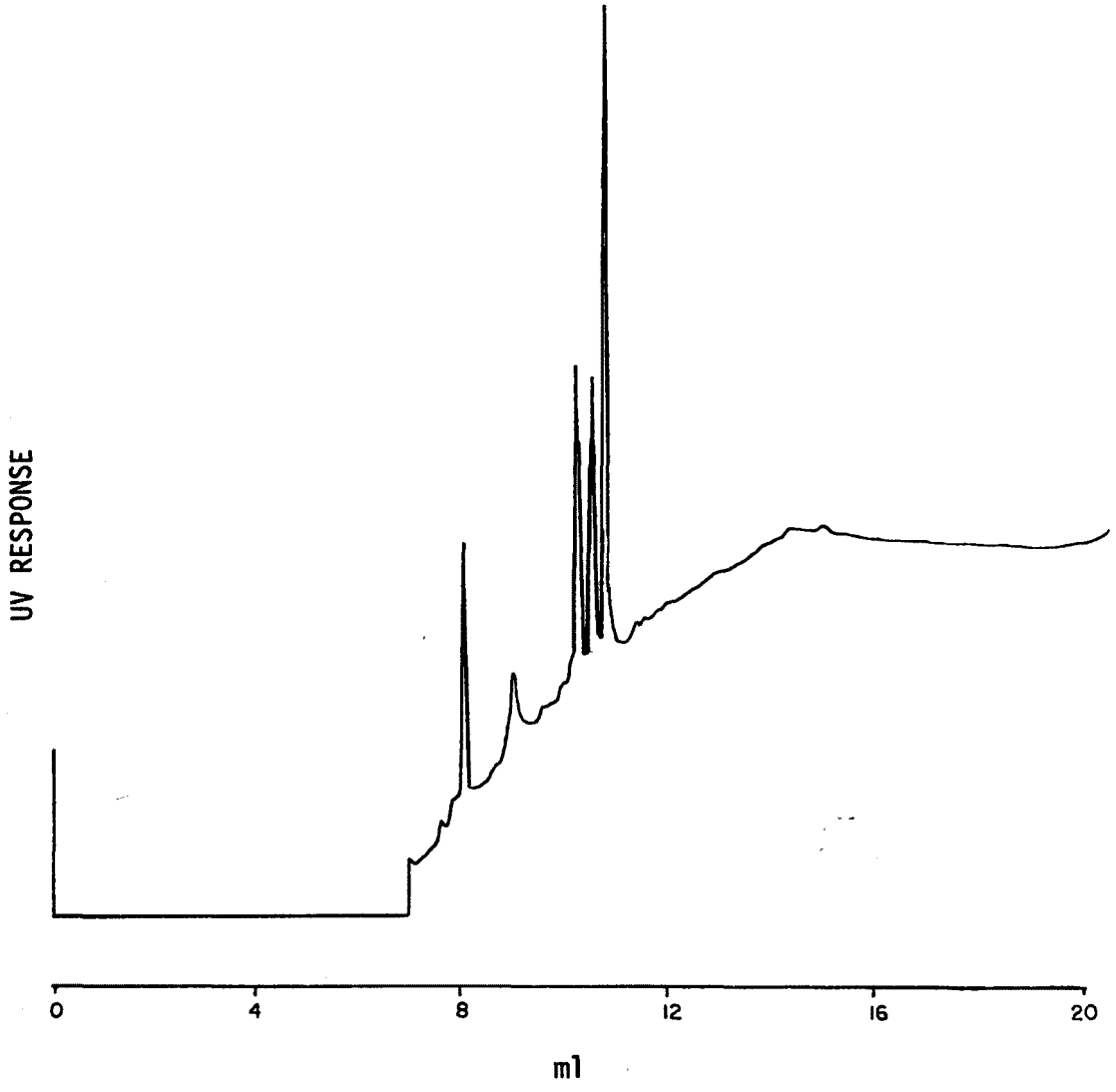


Figure 5-28. Sample of retort water (pH 8.8), chloroform extracted (Kwan and Yen, unpublished data). Analysis conditions are shown in Figure 5-26).

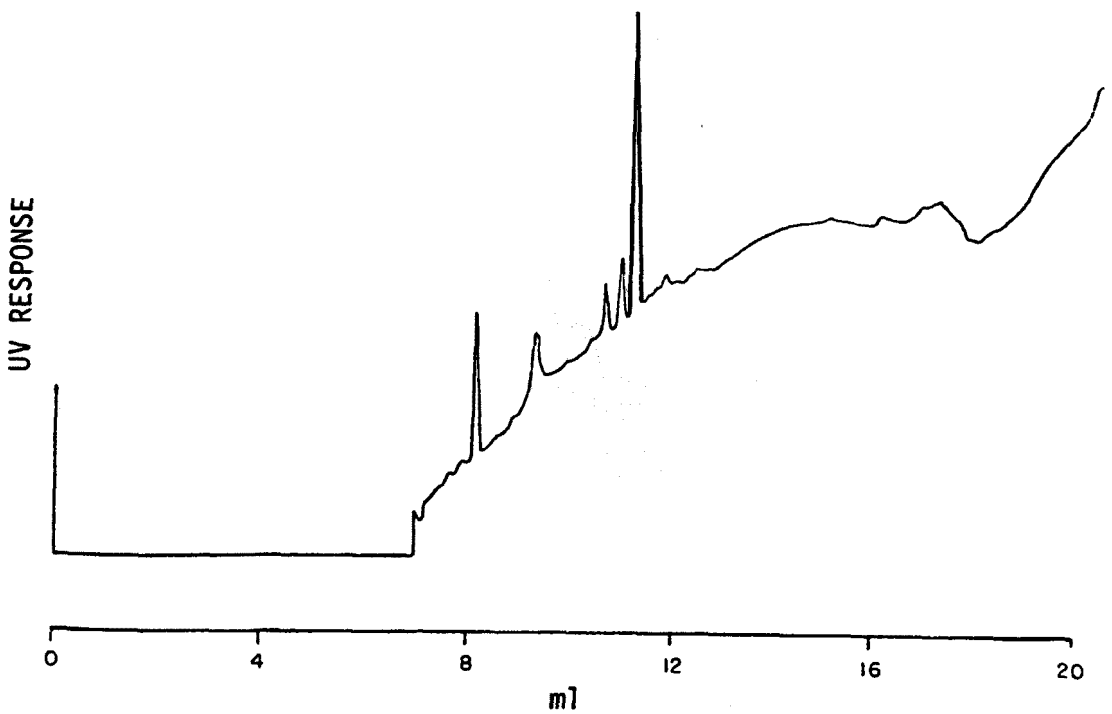


Figure 5-29. Sample of retort water (pH 8.8), methylene chloride extracted (Kwan and Yen, unpublished data). Analysis conditions are shown in Figure 5-26.

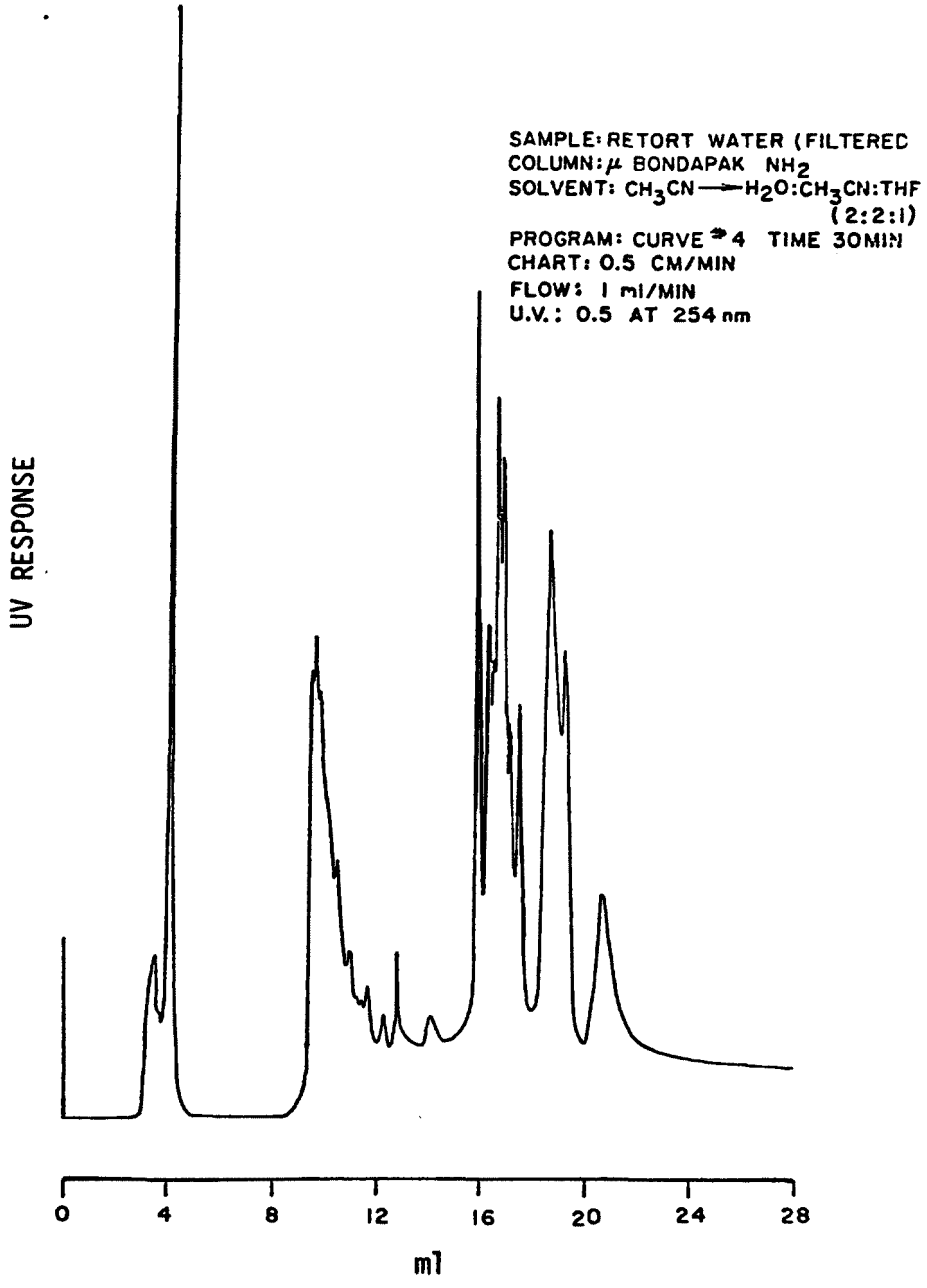


Figure 5-30. HPLC functional group separation spectrum for hydrocarbons, organic acids, and polar compounds.

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SECTION 6

INORGANIC CONTAMINANTS

Oil shale operations involve mining and processing of huge quantities of material. In general, a daily production of 16,000 m^3 (100,000 bbl) of shale oil by underground mining with surface retorting will utilize about 45 million tonnes (50 million tons) of raw oil shale a year. The annual water requirement will total 19.2 million m^3 (15,600 acre-feet) with a permanent land requirement of 242 hectares (600 acres). Each year, 61 hectares (150 acres) of land would be disturbed by the disposal of spent shale (U.S. Energy Research and Development Administration, 1976a). In addition to these solid wastes, tons of sulfur dioxide (SO_2), particulates, oxides of nitrogen (NO_x), and hydrocarbons (HC) would be generated as potential atmospheric pollutants (Table 6-1). Potential impacts of the developing oil shale industry include effects on soils, water resources (both surface and subsurface), and air quality. Oil Shale development may pose serious pollution impacts on the environment; some of them are significant locally and others affect wider regions. Oil shales are composed of tightly-bound organics (13.8 percent) and inorganics (86.2 percent) (Table 6-2). In this section, potential inorganic contaminants are discussed.

TABLE 6-1. EMISSION OF AIR POLLUTANTS FROM TOSCO II OIL SHALE RETORTING AND UPGRADING (PER 100,000 BBL OF PRODUCT)[a,b]

Emission constituent	Amount in tonnes (tons)	
SO_2	36.3	(40)
Particulates	9.1	(10)
NO_x	65.3	(72)
Hydrocarbons	6.9	(7.6)

[a]From U.S. Energy Research and Development Administration (1976a).

[b]Actual emissions are expected to vary widely depending on retorting and emission control technology.

TABLE 6-2. AVERAGE MINERAL COMPOSITION OF GREEN RIVER OIL SHALE[a]

Mineral matter	Weight percent
Dolomite and calcite, $CaMg(CO_3)2$, $CaCO_3$	43.1
Feldspars, $KAlSi_3O_8$	16.4
Clays, $KAl_4Si_7AlO_{20}(OH)_4$	12.9
Quartz, SiO_2	8.6
Analcite, $NaALSiO_6H_2O$	4.3
Pyrite, FeS_2	0.86
Approximate total inorganic matter	86.2

[a]From Hendrickson (1975).

Mining, retorting, upgrading processes, and vehicular transportation all produce possible inorganic contaminants. The most direct and effective manner of addressing the environmental impacts is through both identification and quantification of the emissions, effluents, and solid wastes associated with each process. Sources of pollutants are discussed in the following subsections.

WATER POLLUTION

Contamination of both surface and underground waters is a potential hazard associated with surface mining. In general, physical disturbance as a result of mining may cause deeper saline groundwater to contaminate upper, good quality waters. Groundwater percolating into the mined area from a highly saline zone may necessitate dewatering of the mine, producing large quantities of saline wastewater for disposal. Leaching from raw shale storage piles, as well as overburden, may also contaminate surface water and groundwater. Explosions and overburden handling will result in sediments and mineral matter that are easily picked up in surface runoff.

Underground and In Situ Mining

Much of the groundwater in the oil shale region is saline as a result of the leaching of soluble salts present in various geologic strata. Groundwater in the mining zone interferes with both mining and in situ processing, and, thus, dewatering may be required in some areas. Relatively good quality groundwater lying above the shale layer can be contaminated by the saline groundwater during mining operations if connection with saline strata occurs. Subsidence caused by mining operations could change local surface water drainage patterns and degrade water quality.

Groundwater or surface water contamination might be caused by materials

used in well drilling, including drilling fluids containing crude or refined oil, organic acids, alkali, and asphalt, and muds with high salt content (20 percent sodium chloride and high pH of 12), corrosion inhibitors, and other compounds added to well systems (Weaver, 1974). Improperly cased wells or well blowouts would result in interformational leakage of native brines (high in carbonates, sulfates, calcium, and magnesium), contaminated retort water, retort gas, and shale oil.

Process Waters

Retort Water—

During surface retorting, water is produced as well as oil and gas. Up to 38 liters (10 gallons) of retort water per ton of shale may be produced, with an average range from 7.6 to 18.9 liters (2 to 5 gallons) per ton (Cook, 1971). Retort waters contain large amounts of dissolved minerals. The inorganic components are mostly ammonium, sodium, magnesium, calcium, bicarbonate, carbonate, sulfate, and chloride ions. The concentration of inorganics depends on the characteristics of the oil shale and the retorting process. Major components in different process retort waters are shown in Table 6-3 (Hendrickson, 1975). Some trace metals identified in retort water are shown in Figure 6-1 (Wen, 1976).

TABLE 6-3. COMPONENTS IN DIFFERENT OIL SHALE PROCESS RETORT WATERS[a]

	(Concentrations in gm/l)		
Components[b]	Water 1[c]	Water 2[d]	Water 3[e]
Ammonia (NH_3)	12.4	4.8	2.4
Carbonate (CO_3)	14.4	19.2	20.8
Chloride	5.4	13.3	1.8
Sodium	1.0	3.1	0.5
Sulfate (SO_4)	3.1	4.5	1.2
Sulfur, nonsulfate	1.9	0.3	1.0

[a]From Hendrickson (1975).

[b]The major components are similar in retort waters from different retort processes.

[c]Water 1 is from gas combustion retorting.

[d]Water 2 is from in situ retorting.

[e]Water 3 is from 150-ton batch retorting.

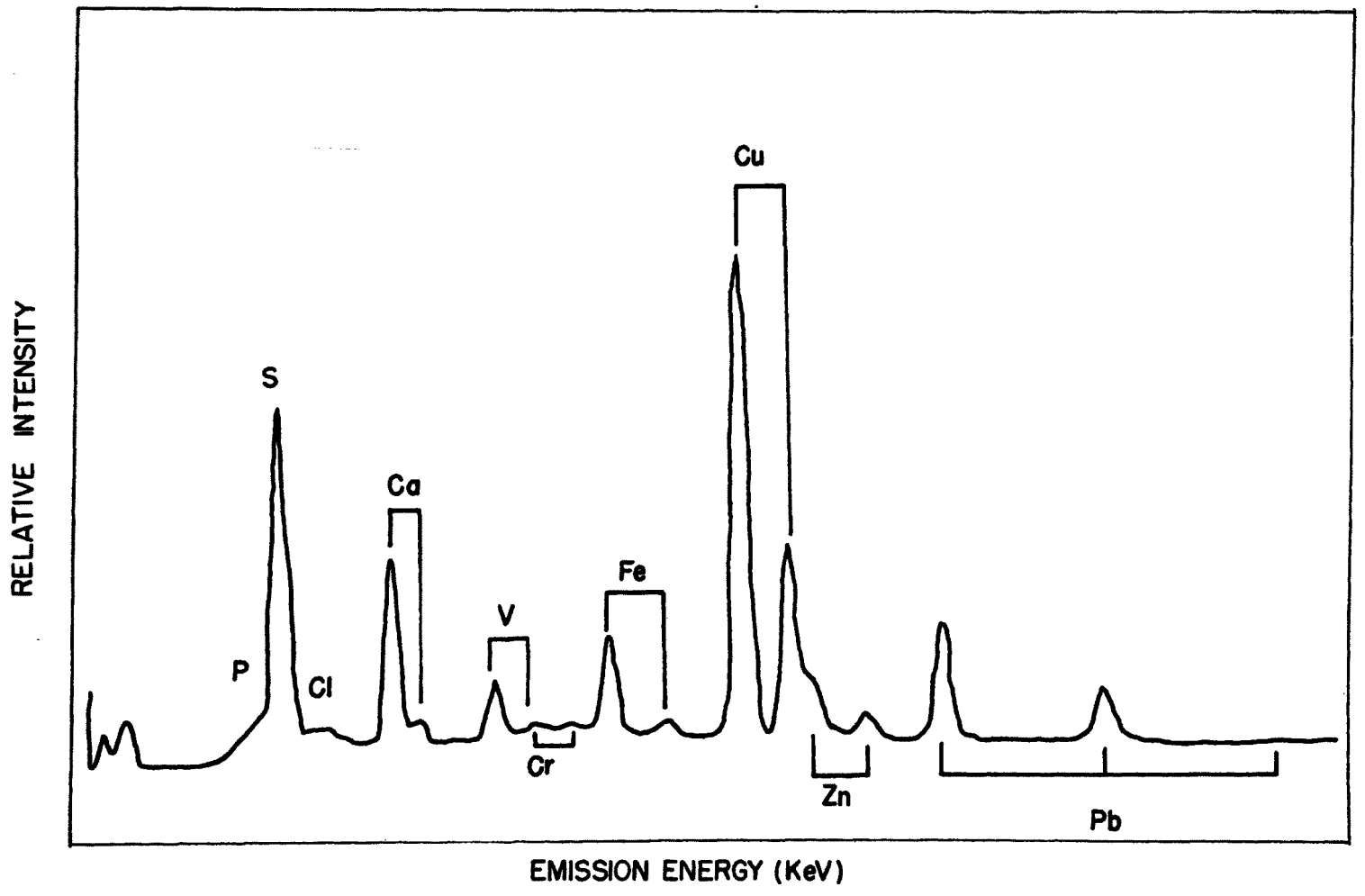

Figure 6-1. Deposited metals on cathode from electrolytical treatment of oil shale retort water and determined by X-ray fluorescence method (Wen, 1976).

In situ processing demonstrations have reportedly had greater rates of retort water production than surface retorting processes. In situ retorting produces approximately one unit volume of retort water per unit volume of oil produced (McCarthy and Cha, 1975). This wastewater stream is expected to contain the same types of inorganic contaminants as aboveground retorting. Anticipated inorganic contents of in situ retort water are shown in Tables 6-4 and 6-5 (Jackson et al., 1975). Similar levels of potential pollutants may be expected from both in situ and ex situ retorting.

TABLE 6-4. WATER EXTRACTED FROM EXPERIMENTAL IN SITU RETORT TEST AREA NEAR ROCK SPRINGS (ppm)[a]

Constituent	Site 9 production wells[b]	Site 9 observation wells[c]
Calcium	13.8	5.9
Magnesium	26.0	11.1
Sodium	5,947.8	5,286.6
Potassium	14.8	12.3
Carbonate (CO_3)	1,621.1	3,499.0
Bicarbonate (HCO_3)	7,791.1	3,219.2
Sulfate (SO_4)	1,327.8	550.4
Chloride	2,156.7	2,024.0
Nitrate (NO_3)	2.3	1.4
Fluoride	33.0	16.0
Dissolved solids	15,578.9	13,303.0
Boron	45.3	46.0
Silica (SiO_2)	16.8	12.4
pH	8.7	9.6

[a]From Jackson et al. (1975).

[b]Average of analyses from 9 wells.

[c]Average of analysis from 10 wells.

TABLE 6-5. TRACE ELEMENTS IN WATER EXTRACTED FROM EXPERIMENTAL IN SITU RETORT TEST AREA (ppm)[a]

Element	Site 9 production wells[b]	Site 9 observation wells[c]
Uranium	1.082	0.064
Lead	0.0356	0.1924
Mercury	0.00152	0.00086
Cadmium	0.0035	0.00175
Molybdenum	4.1	1.0411
Strontium	0.56	0.3544
Bromine	0.48	5.7598
Selenium	0.007	0.00475
Arsenic	0.1487	0.0189
Zinc	0.774	0.0904
Copper	0.087	0.0417
Nickel	0.329	0.11125
Cobalt	0.0146	0.0155
Manganese	0.0503	0.1562
Chromium	0.0149	0.0075
Vanadium	0.0779	0.05175
Aluminum	4.779	2.1228
Fluorine	33.25	31.99
Boron	30.17	41.03

[a]From Jackson et al. (1975).

[b]Average of analyses from 9 wells.

[c]Average of analyses from 10 wells.

Recycle-Gas Condensate—

Recycle-gas condensate water contains inorganic contaminants similar to those contained in retort water (Table 6-6). Trace metals (lead, mercury, molybdenum, selenium, arsenic, zinc, manganese, chromium, and vanadium) are also present in both retort water and condensate water. Trace metal contaminants are discussed in more detail in Section 7.

TABLE 6-6. INORGANIC COMPONENTS OF RECYCLE-GAS CONDENSATE (ppm)[a]

Components[b]	Direct heating mode	Indirect heating mode
Ammonia (NH_3)	14,060	16,800
Ammonium (NH_4+)	5,652	13,540
Bicarbonates (HCO_3)	31,265	6,280
Calcium	60.7	39.2
Fluoride	0.35	0.10
Magnesium	<0.1	<0.1
Nitrate (NO_3)	118	1.0
Potassium	0.08	0.18
Sodium	0.2	0.29
Sulfate (SO_4)	113.6	1.65
Sulfide (S)	0.1	390
Total solids	22,000	429
Suspended solids	200	-
pH	9.8	9.5
Total alkalinity	68,550	12,900

[a]From Cotter et al. (1977).

[b]These data are for Paraho process. Data for the TOSCO II process (an indirect heating process) would be similar to the indirect mode of the Paraho process (see Section 3).

Retort and condensate waters also contain high concentrations of ammonia and some hydrogen sulfide, both volatile and toxic substances. Other sulfur forms such as thiosulfite and sulfate are also present. Ammonia stripping and sulfur recovery systems will be designed to handle these wastes (Section 3).

Other Wastewater—

Several other kinds of liquid wastes are associated with shale oil recovery and processing. These include cooling-tower blowdown, boiler water blowdowns (with high salt and trace metal levels); mine dewatering wastes (saline water containing mining contaminants); and sour water from refining operations (oily cooling waters and waters with appreciable ammonia and hydrogen sulfide content). Data on these waste streams are limited.

Processed Shale

Spent shale is moisturized with process water (an amalgam of mine, retort, condensate, sour, and cooling waters) and transported to the disposal site. Runoff and leachate from the spent shale disposal pile, resulting from rain or melting snow, is expected to be highly saline and alkaline because of the characteristics of spent shale and process waters.

In in situ operations, spent shale and retort waters are mixed together in the retorting zone. The mechanism of their interaction is not clear. Retort water may leach out inorganics from retort shale. Conversely, spent shale may absorb inorganics from retort water. In addition, soluble retorting products may be leached by infiltrating groundwaters. Thus, inorganic contaminants produced during retorting (salts, alkaline materials, and trace metals) may be mobilized. The contact time between spent shale and retort waters may be shorter in surface retorting than in situ processes because of the longer in situ cooling (and condensation) period. Thus, in surface retorts, their interaction would be lessened.

AIR POLLUTION

Mining

Emissions of particulate matter and gases result from blasting to loosen overburden and shale. The use of ammonium nitrate-fuel oil (ANFO) mixture in explosives produces carbon monoxide, nitrogen oxides, ammonia, and particulates. The use of fuel oils in mining equipment produces carbon monoxide, sulfur dioxide, and nitrogen oxides, as well as particulate matter. Preparation of oil shale for retorting, including crushing and screening, also generates particulate matter (Figure 6-2; Kirkpatrick, 1974).

Underground and in situ mining reduces the dust and particulate problems associated with surface mining. However, gaseous emissions still occur as with surface mining. Carbon monoxide, sulfur dioxide, nitrous oxides, and particulates are created by using fuel oils in mining and transport equipment. The major source of dust is wind erosion of access roads and graded mine sites. Fracture interconnection with open surface joints and underlying in situ retorts may result in gaseous emissions. For underground mining safety, gases produced during blasting will be removed through ventilation systems to the atmosphere. Thus, nitrogen oxides, carbon monoxide, ammonia, and other gases may be released.

Process Gases

The internal combustion, or directly heated process, yields gases that are diluted with nitrogen and oxygen from air injection. The gas produced from the internal combustion process has low heating value, but it may be utilized as fuel gas for the generation of power and process steam. The gas from an indirectly heated retorting process, such as TOSCO II or Paraho IH mode, is composed only of undiluted constituents from the oil shale itself and is less limited for further utilization (i.e., it has a higher heat content) (U.S. Energy Research and Development Administration, 1976b). The properties of the

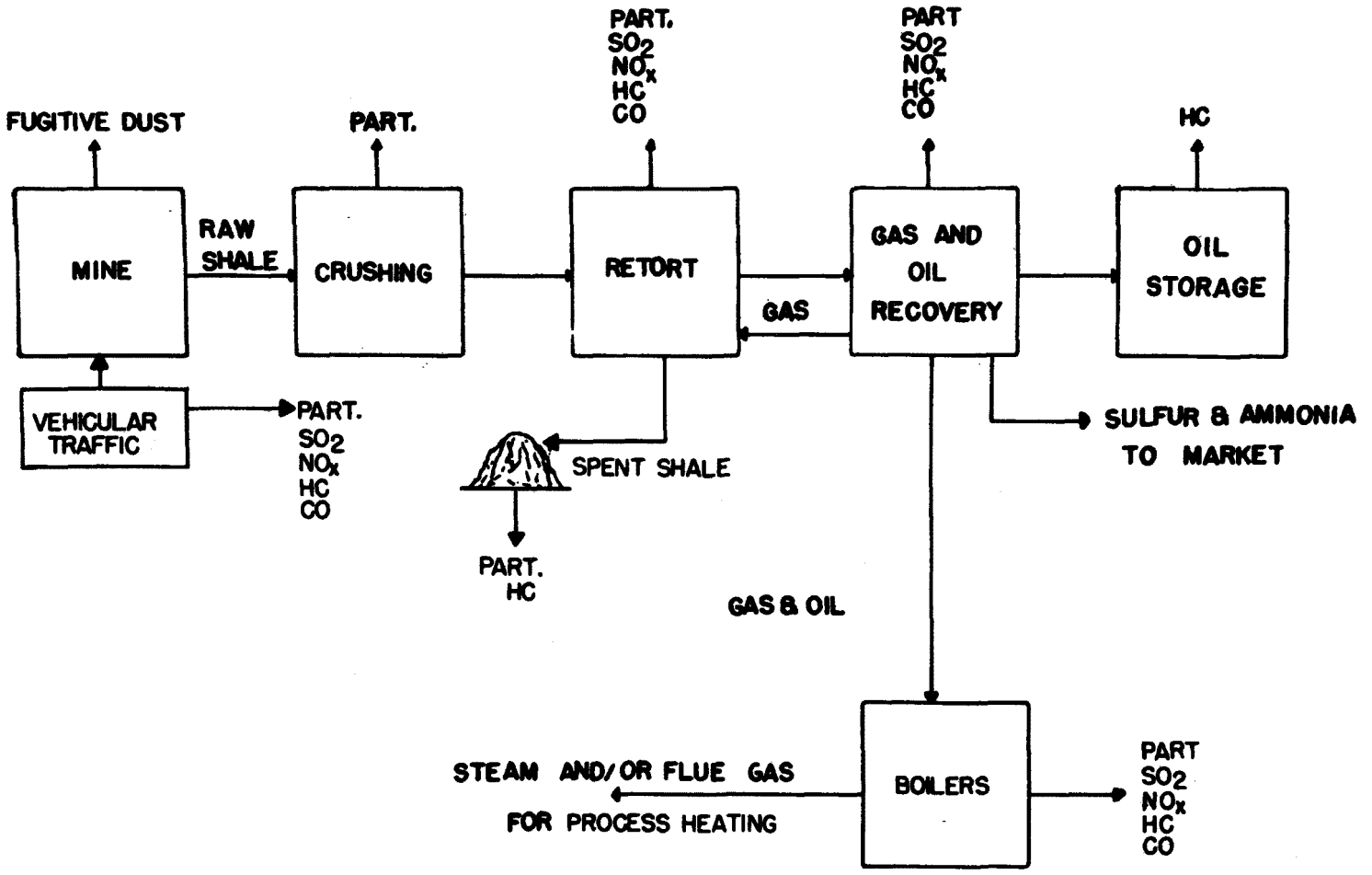

Figure 6-2. Emissions from oil shale operations (from Kirkpatrick, 1974).

retorting gases from the Paraho operation and the TOSCO operation are shown in Tables 6-7 (Jones, 1974) and 6-8 (U.S. Department of the Interior, 1973).

TABLE 6-7. PARAHO RETORTING GAS PROPERTIES (PERCENTAGE, VOLUME, DRY BASIS)[a]

Constituent	Direct heating mode	Indirect heating mode
H_2	2.5	24.8
N_2	65.7	0.7
O_2	0.	0.
CO	2.5	2.6
CH_4[b]	2.2	28.7
CO_2	24.2	15.1
H_2S	2,660 ppm	3.5
NH_3	2,490 ppm	1.2

[a]From Jones (1974).

[b]Other hydrocarbons less than 1 percent (C_2H_4 [0.7 percent], C_2H_6 [0.6 percent], C_3 [0.7 percent], C_4 [0.4 percent]).

TABLE 6-8. PROPERTIES OF UNTREATED RETORT GASES FROM DIFFERENT RETORTING PROCESSES[a]

Composition, Vo. Pet.	Paraho (Internal Combustion)	TOSCO (Indirectly heated)
N	60.1	-
CO_2	4.7	4.0
CO	29.7	23.6
H_2S	0.1	4.7
HC	3.2	42.9
Gross heating value:		
KJ/m^3	3,071	28,675
Btu/scf	83	775
Yield:		
scf/bbl oil	20,560	923
m^3/8,000 m^3 (50,000 bbl) oil	29.1×10^6	1.3×10^6

[a]From U.S. Department of the Interior (1973).

Carbon monoxide, nitrogen oxides, sulfur dioxide, and particulates are the dominant emissions from the generation and use of recycle gas. The major source of carbon monoxide, nitrogen oxides, and sulfur dioxide is fuel combustion in process heaters.

Nitrogen oxides (NO_x) are formed in almost every step of the oil shale process. Retorting is the major source, since nitrogen is chemically bound with organic components of the kerogen matrix. This organic bounded nitrogen is released as nitrogen oxides and ammonia during the retorting process. Combustion of product gas and shale oil also generates nitrogen oxides. Gas concentrations from the TOSCO process are shown in Table 6-9 (U.S. House of Representatives Hearings, 1974). TOSCO II and other indirect heating processes produce much lower emissions of sulfur dioxide and nitrous oxides than does the Paraho direct heating mode. This is because air is not used in the indirect heated processes. However, the indirect heated processes produce higher carbon monoxide emissions as a result of incomplete combustion. Particulate emissions are comparable for both (Paraho) indirect and direct heating processes. Emission sources are identified in Table 6-10 (TRW and Denver Research Institute, 1976).

TABLE 6-9. MAXIMUM EMISSION RATE IN kg/hr (lb/hr), TOSCO PROCESS[a]

Source	SO_2[b]	NO_x[c]	Particulates	CO
Raw shale crushing and handling	low	low	91 (200)	low
Retorting	363 (800)	2268 (5000)	273 (600)	18 (40)
Gas and oil recovery	91 (200)	363 (800)	7 (15)	6 (14)
Boilers and superheater	50 (110)	317 (700)	7 (15)	2 (5)
Total	504 (1110)	2948 (6500)	378 (830)	26 (59)

[a]From U.S. House of Representatives Hearings (1974).

[b]Values given are maximum rates; reported average rate is approximately 130 kg/hr (286 lb/hr).

[c]Values given are maximum rates; reported average rate is approximately 700 kg/hr (1,540 lb/hr).

TABLE 6-10. SOURCES AND NATURE OF ATMOSPHERIC EMISSIONS FROM OIL SHALE EXTRACTION AND PROCESSING[a]

Process and activity	Potential criteria pollutants	Potential noncriteria pollutants
Blasting and explosion	PM, CO, NO_x, HC	Hg, Pb salts, silica
Mine equipment (fuel use)	PM, CO, NO_x, SO_2, HC	silica
Preparation of retort feed	PM	silica
Retorting	PM, CO, NO_x, SO_2, HC	trace element and trace organics
Spent shale discharge	PM, HC	H_2S, NH_3, volatile compounds
Refining	PM, CO, NO_x, SO_2, HC	
Tail gas cleaning sulfur recovery	SO_2	CS_2, COS
Solid waste disposal	PM, CO, NO_x, SO_2, HC	trace organics trace metals (Ni, Co, Fe, Mo)

[a]From TRW and Denver Research Institute (1976).

Processed Shale

Fugitive dust emissions from spent shale piles may create air quality problems. Particulate emissions from fugitive [illegible] and spent shale handling and disposal contain certain toxic trace metals. Spent shale may release gases, ammonia, hydrogen sulfide, and other volatile compounds during moisturizing and subsequent cooling. Carbon monoxide, nitrogen oxides, and sulfur dioxide are generated during spent shale handling processes. Underground disposal would result in less air pollution than surface disposal.

SOLID WASTE

Mining

As discussed in Section 2, solids handling (overburden, raw shale, and processed shale) requirements vary widely with the mining approach used.

Strip mining and open-pit methods have the largest materials handling need. The requirement for moving large volumes of oil shale and overburden is reduced in underground and in situ mining. Only oil shale strata are affected with about 75 percent removal for room-and-pillar mining and perhaps 20 percent for modified in situ. True in situ, of course, requires no mining.

Processed Shale

Spent shale is the major solid waste from mining and retorting processes. Each type of retorting process produces a specific spent-shale product. The characteristics of the retort feed also affect the properties of spent shale. For example, the feed shale contains soluble sodium minerals. Several soluble compounds may be found in the spent shale because sodium compounds may contribute to the fusion of spent-shale particles by lowering the softening, or melting, temperatures of certain inorganic mineral constituents (Hendrickson, 1975).

The disposal of spent shale is potentially the most serious source of environmental impact of a surface retort oil shale facility. Spent shale is approximately 85 percent of the original resource mass. During retorting, the volume of shale expands by 10 to 30 percent. The high content of water-soluble minerals in spent shale creates a great potential for environmental contamination from leaching. Trace metals from processed shale also contribute to the hazard potential of shale oil recovery.

Spent shale from retorting is highly saline and alkaline. The chemical properties of spent shale are shown in Tables 6-11 and 6-12 (Hendrickson, 1975). Alkaline minerals present in the inorganic portion of oil shale are transformed during retorting into expanded alkaline-oxides, accounting for some of the increase in volume of spent shale over that of the raw shale material. The rest is a function of crushing.

There are two options for spent-shale disposal—namely, surface and underground. Since the volume of processed shale exceeds that of the original shale, some surface disposal is required even where the underground disposal option is utilized.

HEALTH AND ENVIRONMENTAL PROBLEMS

Oil shale operations will create some potential for direct and indirect adverse effects on human health. The major categories of inorganic pollutants and their hazardous effects are discussed in the following subsections.

Emission Gases and Particulates

Regulations addressing the Clean Air Act provide primary and secondary standards for air quality. Primary standards are intended to protect the public health. These standards are set at levels below which no deteriorative health effects are expected to be observed. Secondary standards are intended to protect the public welfare from any known or anticipated effects of a pollutant. Secondary standards deal with nonhealth-related impacts.

TABLE 6-11. CONSTITUENTS OF SPENT SHALE[a,b]

Constituents	Average values (average percent)
SiO_2	43.8
Fe_2O_3	4.6
Al_2O_3	12.1
CaO	22.1
MgO	9.3
SO_3	2.2
Na_2O	3.4
K_2O	2.4

[a]From Hendrickson (1975).

[b]Data are from Fischer assay spent shales obtained from Colorado Green River Formation oil shale.

TABLE 6-12. LEACHABLE INORGANIC IONS FROM SPENT SHALE (kg/tonne) OF DIFFERENT RETORTING PROCESSES[a]

Ion	TOSCO II	USBM	Union A
K^+	0.32	0.72	6.25
Na^+	1.65	2.25	21.0
Ca^{++}	1.15	0.42	3.27
Mg^{++}	0.27	0.04	0.91
HCO_3^-	0.20	0.38	0.28
CL^-	0.08	0.13	0.33
SO_4=	7.3	6.0	62.3
Total:			
- kg/tonne	10.7	9.94	94.34
- lb/ton	22.0	19.9	189.2

[a]From Ward et al. (1971).

In addressing the Clean Air Act, the U.S. Environmental Protection Agency has promulgated regulations for prevention of significant deterioration (PSD) of air quality in areas already cleaner than Federal secondary standards require. PSD permits are a method of government assurance that given projects will not result in detrimental effects on ambient air quality.

Sulfur dioxide, nitrogen oxides, carbon monoxide, and particulates are discussed in the following paragraphs. Projected levels listed are from development plans by Colony Development Operation and the White River Shale Project. A Gaussian air-dispersion model developed by Battelle Pacific Northwest Laboratories (1975) was used for the Colony projections. Developers of Tracts U-a and U-b (White River Shale Project, 1976) utilized EPA's PTMTP model for short-term (less than 24 hours) predictions and EPA's terrain model for long-term predictions.

Sulfur Dioxide

Sulfur dioxide (SO_2) is a pungent respiratory irritant. Below about 25 ppm, it affects only the upper respiratory system. It becomes an irritant of the lower respiratory system when SO_2 is absorbed onto the surface of aerosols and can thereby be carried deep into the lungs. In the atmosphere, sulfur dioxide can react with water vapor and be oxidized to form sulfuric acid mists. Thus, sulfur dioxide may cause health problems including eye irritation, acute and chronic respiratory stress, and possibly pulmonary disease. Sulfur dioxide also causes plant leaf damage and corrosive damage to materials such as metals. The predicted highest annual mean concentration for the Colony oil shale operation is 3.5 $\mu gm/m^3$, which is about 4.3 percent of the primary Federal standard (Colony Development Operation, 1975). The maximum average expected for Tracts U-a and U-b is 2.66 $\mu gm/m^3$ (White River Shale Project, 1976).

Nitrogen Oxides—

Two important oxides of nitrogen found in air pollution are nitric oxide (NO) and nitrogen dioxide (NO_2). The term nitrogen oxides (NO_X) represents a composite atmospheric concentration of nitrogen oxides and nitrogen dioxide. Nitrogen oxides are poisonous and acutely irritating gases. They are also associated with chronic pulmonary disease. Nitrogen dioxide can result in restrictions in respiratory passages and pulmonary edema (Ross, 1972). Nitrous oxides can react with organic compounds to form secondary nitrous oxide pollutants including ozone (O_3) and aerosol. The combination of these primary and secondary pollutants is known as photochemical smog. Plant damage, material damage, coloration of the atmosphere, eye irritation, and toxic effects are all possible effects of ozone and nitrous oxides (Williamson, 1973). The primary and secondary Federal standards for nitrous oxides are 100 $\mu gm/m^3$ (0.05 ppm). The predicted maximum annual mean concentration is 15.85 $\mu gm/m^3$, or 15 percent of the Federal standards (Colony Development Operation, 1975). The maximum mean expected for the U-a and U-b project is 14.1 $\mu gm/m^3$ (White River Shale Project, 1976).

Carbon Monoxide—

Carbon monoxide (CO) is a toxic gas formed from incomplete combustion. In the lungs it can combine with the hemoglobin in the bloodstream to form carboxyhemoglobin (COH_b). As a result, the ability of the hemoglobin to carry oxygen to body tissues is reduced. Thus, the most critical pathological effect of carbon monoxide is the elimination of the red blood cell function. Federal primary and secondary standards for CO are 40 mg/m^3 (35 ppm) for 1 hour and 10 mg/m^3 (9 ppm) for 8 hours, respectively. The estimated annual mean concentration ranges from 0.1 to 0.8 μgm/m^3 (Colony Development Operation, 1975).

Particulates—

Particulates are composed of such constituents as ions, molecular clusters (e.g., unburned hydrocarbon), dust, soot, and raindrops. The particle size and chemical composition affect optical and toxicological properties considerably. Three size ranges are used for the classification and discussion of particulates: smaller than 0.1 micron, 0.1 to 1.0 micron, and larger than 1.0 micron.

Particules of the size of 0.5 micron are retained by the nose while those smaller than 0.5 micron are easily transported to the pharynx or the lungs. Various respiratory and pulmonary problems may be caused by these particulates. Smaller particles are likely to be deposited in the lungs and pose the greatest hazard to human health. Soot is an example of the small particulates that can be retained in the lungs. Aqueous droplets may dissolve gaseous constituents and form acids, resulting in so-called "acid rain."

The Federal primary standard for particulate matter is 75 gm/m^3 (as an annual mean). The secondary standard is 60 gm/m^3. The estimated annual mean concentration for particulates ranges from 1 to 10 μgm/m^3 (Colony Development Operation, 1975), while for U-a and U-b operations it is 39.3 μgm/m^3 (White River Shale Project, 1976).

Trace Metals

Another major source of inorganic pollution resulting in health and environmental problems is trace metals. The Green River oil shale contains many trace elements. The major portion of most trace metals remains with the spent shale although portions of some are found in process water, shale oil, and retort gases. Metals, including nickel, cobalt, molybdenum, zinc, and chromium, are used as catalysts in upgrading processes. Spent shale, wastewater, and particulate emissions contain components of spent shale catalysts.

Arsenic—

Arsenic (As) poisoning is commonly the result of the cumulative effect on the general system. It causes dermatitis and bronchitis. It is carcinogenic to mouth, esophagus, larynx, and bladder tissues. It inhibits ATP synthesis as well as thiodependent enzymes (i.e., enzymes that utilize or convert sulfur compounds). The median lethal dose (LD_{50}) from rat experiments is 0.07 gmAs/kg

(Dulka and Risby, 1976). Most arsenic associated with oil shale processing is found in spent shale, retort water, and raw shale oil.

Lead—

Lead (Pb) is toxic and can accumulate in bones and soft tissues. It causes reduction of brain functioning, interferes with the formation of amino acids and enzymes, and can cause damage to the kidneys. The LD_{50} for rats consuming lead is 0.15 gm/kg (Dulka and Risby, 1976). Spent shale is the major source of this contaminant.

Vanadium—

Vanadium (V) poisoning in man results from impairment to tissue metabolism. It inhibits activities of enzymes and adversely affects tissue oxidation. Vanadium also inhibits many other metabolic processes in the human body. The toxicity, LD_{50} (rabbits), is 0.2 gm/kg (Dulka and Risby, 1976). Most vanadium associated with oil shale processing is found in spent shale and shale oil.

Selenium—

Selenium (Se) can cause irritation of nose, throat, and respiratory tract tissues. It may also cause liver cancer, pneumonia, degeneration of liver and kidney tissue, and general gastrointestinal disturbance. The LD_{50} for selenium (on rats) is 0.003 gm/kg (Dulka and Risby, 1976). The selenium of oil shale and waste products is relatively low in comparison to other trace elements.

Zinc—

In comparison with other trace metals such as arsenic, lead, and vanadium, zinc (Zn) is relatively nontoxic. Zinc is noncumulative since the proportion absorbed is inversely related to the amount ingested (Prasad and Oberleas, 1976). However, large quantities of zinc will cause malaise, dizziness, vomiting, dehydration, and loss of muscular coordination. The toxicity of zinc (LD_{50} for rabbits) is 2 gm/kg (Dulka and Risby, 1976). Most zinc is found in the processed shale and coke, which contain spent catalytic materials.

Chromium—

Chromium (Cr) in the hexavalent state is much more toxic than trivalent chromium. It is considered to be a potential carcinogen (Van Hook and Schultz, 1976). Cancer of the respiratory tract can be caused by chromium. It causes perforation of nasal septum, congestion, hyperemia, bronchitis, and dermatitis. The toxicity of chromium (LD_{50} for rats) is 0.18 gm/kg (Dulka and Risby, 1976). Processed shale and coke contain most of the chromium associated with oil shale processing.

Nickel—

Nickel (Ni) can cause respiratory disorders and cancer of the respiratory system. It acts to reduce the activity of cytochrome oxidase, isocitrate dehydrogenase of the liver, and maleic dehydrogenase of the kidneys. The

toxicity (LD_{50} for dogs) is 0.8 gm/kg. Most of the nickel is to be found in the spent shale.

Beryllium—

Beryllium (Be) is toxic and causes chemical pneumonitis. Beryllium also acts as a potential carcinogen in lungs and bones. It will do damage to skin and mucous membrances and inhibit metabolic activities. The toxicity (LD_{50} for mice) is 0.5 mg/kg (Dulka and Risby, 1976). Spent shale contains most of the beryllium associated with oil shale processing.

Mercury—

Mercury (Hg) is highly toxic as Hg^{++}, which is formed in tissues from oxidation of Hg^{+} salts. Mercury can accumulate in brain, lung, heart, kidney, liver, and muscle tissues. Complexation with HS^{-} groups may occur. It can inhibit some amino reactions and damage the central nervous system. The toxicity (LD_{50} for mice) is 0.027 gm/kg (Dulka and Risby, 1976). Most of the mercury in oil shale probably either will remain in the processed shale or will be in the gas streams of retorting.

Other Trace Elements—

Some other toxic trace elements including cobalt, molybdenum, manganese, and strontium are also found in processed shale in appreciable quantities. Toxic metals found in trace amounts in spent shale and retort water are shown in Table 6-13 (University of Southern California, 1976-77). Metals are the most insidious pollutants because of their nonbiodegradable and bioaccumulative properties. Only a few metals are nontoxic at any level. In general, spent shale contains most of the trace metals. Trace metals in raw shale are relatively insoluble. Thus, disposal methods and control technology should be oriented toward prevention of leaching problems.

CHARACTERIZATION, MEASUREMENT, AND MONITORING

Heavy Metals

The potential environmental effects of toxic metals in oil shale conversion processes are an important consideration. Highly toxic metals, such as arsenic, lead, mercury, cadmium, selenium, and others, are potentially capable of entering the air, water, or soil and posing environmental and human hazards.

The fate of the heavy metals in oil shale processing has not been thoroughly studied. Some volatile elements (e.g., arsenic, mercury, and lead) are introduced into the air and process water during retorting and upgrading, while the nonvolatile elements are primarily found in the spent shale. The leaching problem caused by spent shale may also contribute to contamination by trace metals. Toxic heavy metal levels observed in the Green River oil shale are shown in Table 6-14 (Colony Development Operation, 1974). Trace metals are also present in crude shale oil products. Twenty-nine trace elements have been identified in raw shale oil (Colony Development Operation,

TABLE 6-13. SEMIQUANTITATIVE X-RAY EMISSION ANALYSIS OF METALS IN RETORT WATER FROM EXPERIMENTS USING A UTAH OIL SHALE[a]

Metals	Concentration (ppm)[b]
Ti, Ag, Ba	0.06 - 0.6
Ni, B, Co, Mn, Fe	0.6 - 6
Si, Mo	6 - 60
Al, U[c], Ca, Cu	60 - 600

[a]Data from University of Southern California (1976-77).

[b]Retort water was obtained from a simulated in situ retorting operation, ERDA Laramie Energy Research Center.

[c]The uranium (U) content of this sample may be unusually high.

TABLE 6-14. TOXIC HEAVY METALS CONTENT IN OIL SHALE[a]

Element	Concentration (wt, ppm)
Arsenic	7.2
Beryllium	35.
Cadmium	0.14
Fluorine	1,700.
Lead	10.
Selenium	0.08
Mercury	<0.1

[a]From Colony Development Operation (1974).

1974). A large fraction of the heavy metals remains in the spent shale (Table 6-15). Upgrading processes also introduce trace metals into wastewater streams (Table 6-13).

TABLE 6-15. HEAVY METALS CONTENT IN RAW SHALE AND RETORTED SHALE (VALUES IN ppm)[a]

Element	Raw shale[b]	Retorted shale[c]
Arsenic	50	35
Boron	30	48
Barium	300	180
Cobalt	-	19
Chromium	70	230
Copper	80	57
Lead	900	23
Manganese	800	800
Mercury	-	0.06
Molybdenum	10	14
Selenium	10	0.5
Strontium	800	970
Titanium	600	1,000
Uranium	-	5
Vanadium	600	180
Zinc	1,000	22

[a]These data are provided as a general characterization of trace metal levels. Actual levels are expected to be site specific and to vary with process conditions. In addition, density changes during retorting of the oil shale must be considered to assess the mass balance of trace metals.

[b]From Hendrickson (1975).

[c]From Cotter et al. (1977).

Heavy metals can be measured and monitored by using the following methods:

- Standard wet chemical or atomic absorption procedures (American Public Health Association, 1974; U.S. Environmental Protection Agency, 1974)

- Spark source mass spectrometry (SSMS)
- X-ray emission and X-ray fluorescence methods.

Cations

Major cationic species may be examined using the following methods:

- Calcium – Permanganate and EDTA, titrimetric, and gravimetric standard methods
- Magnesium – Gravimetric, photometric, and atomic absorption spectrophotometric standard methods
- Sodium – AA and flame photometric standard methods
- Potassium – AA and flame photometric standard methods
- Ammonium – Computed value based on NH_3-N determination, equilibrium constant and pH and specific ion electrode standard methods
- Aluminum – AA standard method
- Silica – Gravimetric standard method
- Boron – Potentiometric standard method
- Iron – AA and specific ion electrode standard methods.

Anions

Major anionic species may be examined using the following methods:

- Carbonates – Computed value based on total inorganic carbon (TIC)
- Bicarbonates – Computed value based on total inorganic carbon (TIC)
- Sulfates – Gravimetric standard method
- Sulfide – Photometric standard method and titrimetric (iodine) method
- Chloride – Potentiometric standard method and specific ion electrode method
- Fluoride – EPA manual-automated complexone method and specific ion electrode method
- Nitrate – EPA manual-brucine sulfate method, spectrophotometric standard method, and specific ion electrode method

- Nitrite — Diazotization and photometric standard methods.

Gases

Gaseous emissions may be monitored using the following methods. Gaseous samples can be captured in impinger solutions and analyzed by standard methods from American Society for Testing and Materials (ASTM 1974 and 1977) or USEPA (1977).

Parameters	Characterization	Measurement
SO_2	Major sources are from retorting, plant fuel use, and tail gas cleaning.	Barium perchlorate titration, conductivity and electrolysis, or EPA Pararosaniline method.
NO_x	Mostly produced from retorting and upgrading processes.	Total NO_x is measured as NO_2 using Kjeldahl distillation, titration, chlorimetric, or EPA gas phase chemiluminescence method.
NH_3	High concentrations are found in retort water, condensate, recycle gas, and sour water.	Kjeldahl distillation, titration, or direct Nesslerization.
H_2S	High concentrations are found in recycle gas, condensate, and sour water.	Colorimetric method.
CO	Largely from mining and transport mobile equipment.	Nondispersive infrared spectrometry method (EPA).
Particulates	Mining, crushing, shale handling, and disposal are the major sources. Fuel combustion also generates large amounts of particulates.	Mass concentration and light-scattering method, filter method, or EPA high-volume method.

SECTION 6 REFERENCES

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SECTION 7

ENVIRONMENTAL CONTROLS IN OIL SHALE DEVELOPMENT

INTRODUCTION

The water requirements and its availability for synfuel production may be major constraints on this emerging industry. In oil shale development, one of the primary concerns is the disposal of spent shale in an economic and environmentally acceptable way. This requires large volumes of water for cooling, dust control, and compaction. Since the water supply in the Western United States has become a very important natural resource issue, especially in terms of agricultural irrigation, it is essential to minimize environmental impairment and to emphasize water reclamation and reuse from oil shale retorting processes.

The Colorado River supplies water for irrigation, energy production, municipal and industrial use, mining, recreation, and livestock watering. In all these activities, the river serves as both a source of water and as a carrier for manmade as well as natural residues. Salinity is the most serious water quality problem in the Colorado River Basin. The heavy salt burden is due to a variety of natural and manmade causes. Depletion of streamflow caused by natural evapotranspiration and consumption of water for municipal, industrial, and agricultural uses reduces the volume of water available for dilution of this salt burden. As a result, salinity concentrations in the lower river system exceed desirable levels and are approaching critical levels for some water uses. Future water resource development and economic development may be expected to increase streamflow depletions and consequently to result in higher salinity concentrations.

It is estimated that when the Colorado River was in its natural state, salinity concentrations at the site of Hoover Dam averaged about 330 ppm (U.S. Environmental Protection Agency, 1972). By 1960 the average concentration had more than doubled (697 ppm) and it may triple by 2010 if further development and utilization of water resources are undertaken.

WATER AVAILABILITY

The production of synthetic liquid fuel from oil shale requires extensive water use. The problem in this semiarid western region is getting enough water to meet this demand while also considering other use priorities and future water allocations. This is both a legal and economic problem.

For example, an adequate amount of water for development of Tracts U-a and U-b is available from existing impoundment facilities on the Green River.

However, it would be costly to deliver the water to the facilities to be built in the White River Basin (Schramm, 1975). Reservoirs on the White River may be a less expensive source of water supply. Groundwater may also play a role but this is as yet undefined.

The factor that may limit the ultimate growth of the shale oil industry is water supply. Based on existing and authorized storage facilities, the amount of surface water potentially available for the oil shale operation in the western oil shale area has been estimated at 541 million m^3 per year (451,000 acre-feet per year) (Schramm, 1975). The distribution among the three states is: Colorado, 108 million m^3 per year (90,000 acre-feet per year); Utah, 154 million m^3 per year (128,000 acre-feet per year); and Wyoming, 280 million m^3 per year (233,000 acre-feet per year). It is not likely that all of this water will be available for the oil shale operation since there are competing demands such as agricultural, municipal, and other industrial uses. The role of groundwater in future development is unclear at this time.

Approximately 1.53-2.29 million m^3 (2-3 million bbl) per day is the upper limit of the shale oil production capacity, assuming full use by the oil shale industry of the 555 million m^3 (451,000 acre-feet) per year of surface water potentially available. Constraints on the industry might be reduced by reducing the water consumption per cubic meter of oil produced and using groundwater resources where possible.

Several possible means of increasing water supply are being studied. A plan is being developed by the Colorado River Basin Project Act to increase the flow below Lee Ferry by 3.1 billion m^3 per year (2.5 million acre-feet per year) using weather modification techniques to increase precipitation. Another possibility being considered is the utilization of the superheated water in the geothermal reservoirs of the Imperial Valley. The geothermal energy can be used both in power generation and in water desalination. Another alternative is to build a nuclear seawater desalting plant and transport the water to the lower Colorado River Basin.

The water availability will also be affected by the population growth. One estimate of population growth from the construction and operation of a 16,000 m^3 per day (100,000 bbl per day) oil shale industry would add an estimated 1,700 primary-jobs personnel, plus their families, and the associated service personnel (THK Associates et al., 1974). Actual population increases from oil shale development will depend on the retorting technology employed, the rate of construction of facilities, and the ultimate production rate for the region (i.e., the size of the oil shale industry).

The increase in water consumption as the result of population growth will cause stream quality degradation from flow reduction. Domestic waste disposal poses additional environmental problems. There are many indirect environmental consequences accompanying oil-shale-associated population growth that are related to the water quality and availability in this area. Potential problems include modified runoff patterns and availability of recreational facilities. Detailed consideration of these factors is beyond the scope of this discussion but a summary is provided by ERDA (1976).

Water Rights

A major factor in water availability for energy development in the Western States is the role of the Federal Government—both as a claimant to the water and as an institutional disburser of water. The Federal Government has the authority to develop, regulate, and allocate all water resources. Of related importance is the large amount of federally owned land in the Colorado River Basin (U.S. Public Land Law Review Commission, 1970). In the oil shale region of the upper Colorado River Basin, 72 percent of the land is federally owned. Reservations have been made on the Federal land for future Navy fuel needs (U.S. Government, 1916 and 1924) and for the purposes of investigation, examination, and classification (U.S. Government, 1930). Conflicts for water among the various alternative uses are expected to be of key importance to future western energy development. The role of the Federal Government, States rights, Indian water rights, and existing compacts and treaties make this an extremely complex legal-economic problem area.

Interstate Allocation of Water

In addition to the aforementioned problem of basic water rights and conflicts between alternative water uses, there are energy development water problems related to water allocation among the basin states. Allocations for the Upper Colorado River Basin are as follows:

	billion m^3	acre-ft
Arizona	0.06	50,000
Colorado	3.82	3,183,000
Utah	1.69	1,414,000
Wyoming	1.03	861,000
New Mexico	0.83	692,000

All of the states in the Colorado River Basin have their own energy development, irrigation, and municipal growth water requirements. These issues are further complicated with regard to energy development since intrastate water is needed for recovery of energy for out-of-state use. It may be necessary to reexamine the allocation of the already limited Colorado River water supply as western energy development accelerates. This is true for both interstate and intrastate allocations.

WATER REQUIREMENTS

Water requirements for synfuel production arise mainly from the need for cooling water to dispose of waste heat, the chemical need of hydrogen in the conversion process, and the need for moisturizing processed shale. The cooling requirement is variable, depending on whether wet cooling or dry cooling is used. Other uses of water in the plant systems include the quenching of gaseous products to remove oil and particulates, dust suppression, solid waste disposal, and, potentially, the generation of steam to drive turbines or gas compressors.

A summary of water consumption from oil shale development is given in Table 7-1. According to the maximum credible scenario, there will be 20 large (16,000 m^3 per day [100,000 bbl per day]) oil shale plants by the year 2000. The total water supply required will be 384 million m^3 per year (320,000 acre-feet per year) using a water-scaling factor of 19.2 million m^3 per year per plant (16,000 acre-feet per year per plant) (U.S. Energy Research and Development Administration, 1976). Table 7-2 shows the projected increase in water demand for the Upper Colorado River Basin by the year 2000. The total water supply required for oil shale development is about 12 percent of the total demand increase (U.S. Department of the Interior, 1974).

Mining

The water requirements for mining operations on Oil Shale Tracts U-a and U-b are shown in Table 7-3 (WRSP, 1976). Potable water will be piped into the mine and distributed to the work force. The nonpotable water for dust suppression and fire control will come from mine drainage and the wastewater ponds associated with surface operations on U-a and U-b. Mine drainage is expected to be small but adequate for dust suppression within the mine, thus reducing freshwater or treated wastewater requirements. In situ mining is expected to have a mining water requirement of about one-fourth that of surface mining.

Retorting and Upgrading

Retorting units, shale oil upgrading units, and power plants require cooling water. Approximately 4.6 million m^3 per year (3,800 acre-feet per year) of water are expected to be consumed for evaporative cooling on Tracts U-a and U-b. This quantity could be reduced significantly if dry cooling were utilized to a greater extent.

The type of cooling system selected has a significant impact on the water resource requirements. The principal types of cooling system alternatives are: once-through, cooling ponds, and wet and dry cooling towers (Jimeson and Adkins, 1971). The once-through cooling system is used with adequate water supplies and has no significant adverse effects on water quality. When the water supplies are limited, cooling ponds can be constructed if suitable sites are available. Heat is dissipated through natural surface evaporation. In the wet cooling tower, warm water is in direct contact with air flow (developed by natural draft or fan assisted). Because of the construction and pumping costs, wet cooling towers may be more expensive than ponds or once-through systems. They also have the highest rate of water consumption. The dry cooling towers use no water but are substantially more expensive than the wet cooling towers.

Chemical consumption of water in oil shale processing occurs in the steam reforming furnaces, where hydrogen is produced for use in hydrotreating raw shale oil products. Water consumption for this purpose is approximately 1.8 million m^3 per year (1,500 acre-feet per year).

TABLE 7-1. AVERAGE WATER CONSUMED FOR VARIOUS RATES OF SHALE OIL PRODUCTION

	Underground		Surface mine		In situ		Technology mix		Technology mix	
	50,000 bbl/day (7,945 m^3/day)		100,000 bbl/day (15,890 m^3/day)		50,000 bbl/day (7,945 m^3/day)		400,000 bbl/day (63,560 m^3/day)		1,000,000 bbl/day (158,900 m^3/day)	
	acre-ft/yr	$10^6 m^3$/yr	acre-ft/yr	$10^6 m^3$/yr	acre-ft/yr	$10^6 m^3$/yr	acre-ft/yr	$10^6 m^3$/yr	acre-ft/yr	$10^6 m^3$/yr
Mining and crushing	440	0.53	875	1.05	-	-	3,100	3.72	7,000	8.4
Retorting	650	0.78	1,315	1.58	-	-	4,600	5.52	10,500	12.6
Upgrading	1,825	2.19	3,650	4.38	1,840	2.21	14,600	17.52	36,500	43.8
Spent shale disposal	3,650	4.38	7,295	8.75	-	-	25,650	30.78	58,500	70.2
Power generation	875	1.05	1,750	2.10	1,275	1.53	7,500	9.00	19,000	22.8
Regeneration	350	0.42	350	0.42	350	0.42	2,450	2.94	6,000	7.2
Domestic Use	950	1.08	1,515	1.82	885	1.06	6,950	8.34	17,500	21.0
Total	8,740	10.43	16,750	20.10	4,350	5.22	64,950	77.82	155,000	186.0

TABLE 7-2. PROJECTED INCREASE IN WATER DEMAND FOR THE UPPER COLORADO RIVER BASIN BY THE YEAR 2000

Category of use	Increase in water demand	
	100 million m^3/yr	thousand acre-ft/yr
Municipal	9.0	750
Environmental (fish, wildlife, recreation, water quality)	1.8	150
Agricultural (primary irrigation)	9.6	800
Mineral production	1.38	115
Coal-fired electric generation	5.7	475
Coal gasification	1.68	140
Syncrude from oil shale	3.84	320
Total	33.0	2,750

TABLE 7-3. MINING OPERATION WATER REQUIREMENTS

	10,000 TPCD[a]		160,000 TPCD	
	acre-ft/yr	$10^4 m^3$/yr	acre-ft/yr	$10^4 m^3$/yr
Potable Water	3	0.36	43	5.16
Nonpotable Water	56	6.7	1,100	132

Waste Disposal

During the retorting and upgrading of oil shale, wastewater is generated as excess moisture from the retorting process and the gas recovery unit. Most of these wastewater streams will be used to moisturize the spent shale. Essentially all process wastewater will be reused. An overall water utilization flow diagram from a TOSCO II oil shale plant is shown in Figure 7-1 (U.S. Department of the Interior, 1973).

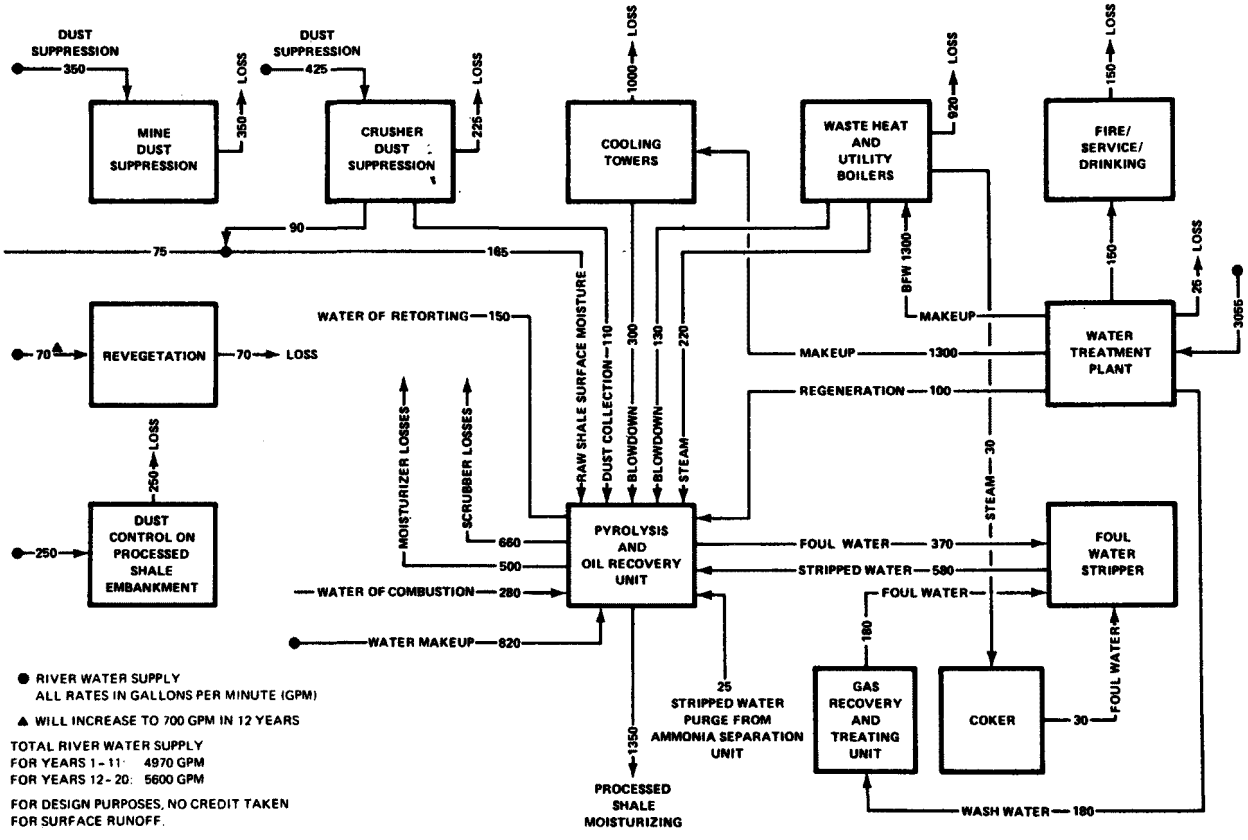


Figure 7-1. River water utilization for 50,000 bbl/day TOSCO II oil shale plant (Colony Development Operation, 1974).

Excess mine water and spent-shale runoff water will be used for spent-shale moisturization. The water used for spent-shale disposal accounts for nearly 40 percent of the total water needed for an oil shale industry.

The prospect of achieving a long-term, stable ecosystem on a massive spent-shale pile remains one of the major problems in oil shale development. It has been indicated that a wide variety of plants can be grown on the spent-shale pile if it is carefully fertilized and watered. However, only a few types of wheat grass can survive on the unattended spent shale (Bloch and Kilburn, 1973). Experimental work has indicated that about 1,200 m^3 per year (1 acre-foot per year) of water is required to reestablish vegetation at a spent-shale disposal for for an 8,000 m^3 (50,000 bbl) per day plant (Hutchins et al., 1971).

Domestic Water Use

The water requirements for sanitary and domestic uses of the work force population are relatively low. They are only about 10 percent of the total water used (U.S. Department of the Interior, 1972).

WATER TREATMENT AND REUSE

The major waste liquid product from oil shale retorting processes is the retort water. It must either be upgraded for reuse in various plant processes or be disposed of in an environmentally acceptable way. Waste treatment may be required to make the water acceptable for reuse.

The original, raw retort water contains small amounts of suspended oil and particles. Most of these suspended materials are removed by filtration. The types of soluble materials that may remain in retort waters are listed in Table 7-4 (Yen et al., 1976b). The soluble organics can be classified as acidic, neutral, and basic fractions (Table 7-5). The high concentrations of organic components, NH_4^+ and HCO_3^-, cause the retort water to behave very differently from conventional wastewater. A comparison of different waste characteristics is shown in Table 7-6. The applicability of state-of-the-art water purification technology to the treatment of retort water is currently the subject of extensive research and testing.

The quantity and quality of the produced retort water depend on the type and the operating conditions of the retorting process and the nature of the oil shale. Several physical and chemical processes have been tested for the treatment of retort water. The main limitation of these methods is the problem of ultimate disposal. They require continuous addition of chemicals, which increases the quantities of contaminants in the environment as well as the operation cost. Since many microorganisms are capable of metabolizing organic compounds, biological treatment may be useful as a waste treatment process, in conjunction with other physical and chemical processes. These physical, chemical, and biological treatment processes are outlined and discussed as follows.

TABLE 7-4. ANALYTICAL RESULTS FROM TWO SAMPLES OF IN SITU RETORT WATER

Parameter	Concentration (ppm)	
	Sample No. 1[a]	Sample No. 2[a]
COD	20,000	12,500
BOD	5,500	250
NH_3-N	4,790	-
Organic-N (dissolved)	1,510	-
Phosphorus	0.26	19.0
NO_3-N	38	-
TOC	3,182	19,000
Chloride	-	1,560
Iodide	0.003	1.3
Bromide	0.46	0.01
Sulfate (S)	59	930
Phenols	169	2.2
Bicarbonate ($CaCO_3$)	16,000	4,200
Sulfide (S)	16.1	15.4
Potassium	3.5	-
Sodium	312	-
Magnesium	48.4	16.4
Calcium	14.9	4.63
Iron	3.3	3.75
Zinc	1.6	2.8
Copper	5.6	0.94
Silica (Si)	-	78.3

[a]No. 1 retort water is from the 1-bbl lot and No. 2 retort water from the 5-bbl lot; both were sent from LERC.

TABLE 7-5. TOTAL SOLUBLE MATERIALS IN RETORT WATER

Inorganics 67-75 (% wt)	Cations 15-25 (% wt)	Na^+	1000 ppm
		Mg^+	100 ppm
		K^+	50 ppm
		Ca^+	10 ppm
		NH_4^+	8000 ppm
	Anions 40-55 (% wt)	HCO_3^-	20,000 ppm
		CO_3^-	5,000 ppm
		Cl^-	4,000 ppm
		SO_4^-	1,000 ppm
		NO_3^-	---
		S^-	---
		F^-	---
	Trace metals	Pb, Zn, Cu, U, Cr, Fe, Mo, As, etc.	
Organics 25-33 (% wt)	Acidic organics 10-15 (% wt)	Short-chain carboxylic acids C_1 - C_{11}	
		Long-chain carboxylic acids C_{16} - C_{24}	
		Phenols	
	Neutral organics 3 - 5 (% wt)	Substituted benzenes n-alkanes	
	Basic organics 7-10 (% wt)	Nitrogen base organics (quinolines, pyridines, maleimides, succinimides, etc.)	
		Organic-sulfur compounds (thiophenes, sulfides, disulfides, etc.)	

TABLE 7-6. COMPARISON OF DIFFERENT WASTE CHARACTERISTICS

Waste	COD/TOC	BOD_5/TOC
Domestic	4.15	1.62
Chemical	3.54	-
Refinery-chemical	5.40	2.75
Petrochemical	2.70	-
Retort water (filtered)	6.28	1.73

Physical and Chemical Processes

Activated carbon and resinous adsorbers have been evaluated for the reduction of high organic concentrations in retort water (Harding et al., to be published). The treatment data are shown in Table 7-7. They also investigated the removal of ammonia and carbon dioxide gases by thermal stripping. The performance of column experiments indicates that these gases can be stripped simultaneously from the retort water (Table 7-8). Weak-acid ion exchange appears to affect the removal of ammonia, carbon dioxide, and bicarbonates. The interference by organics remains an unsolved economic problem.

TABLE 7-7. ACTIVATED CARBON ADSORPTION DATA

Parameter	Influent (mg/l)	Effluent (mg/l)	Percent reduction
COD	12,544	1,418	88.7
Alkalinity	38,300	36,700	4.2
Phenol	31	0	100.0
NH_3-N	10,690	9,540	10.8
Organic N	654	161	75.4

TABLE 7-8. THERMAL STRIPPING COLUMN RESULTS

Parameter	Before treatment	After treatment	Percent reduction
pH	8.65	8.44	2.4
NH_4^+ (mg/l)	10,000	5,700	43.0
Alkalinity (mg/l)	24,300	16,300	32.9
COD (mg/l)	14,064	15,328	-

Many refractory organic compounds (i.e., those that cannot be utilized by microorganisms) are sensitive to photo-oxidation (including nitrogen heterocyclics, phenol, and benzenoid and aromatic heterocyclic compounds) (Spikes and Straight, 1967). Most of these substances are found in retort water (Wen, 1976), which therefore should be susceptible to photochemical oxidation. The decrease of the peak intensity of polar components on the right side of the liquid chromatographic spectrum (Figure 7-2) shows the effectiveness of photo-oxidation on water treatment (Yen et al., 1976a). The breakdown of high molecular weight components in the retort water by a DuPont Size Exclusion Column after ozone treatment has been reported (Yen et al., 1976a). Extensive investigation has been undertaken to explore the electrolytic treatment for the purification and recovery of valuable materials from retort water (Yen et al., 1976a; Wen, 1976). The results of this treatment method are shown in Table 7-9.

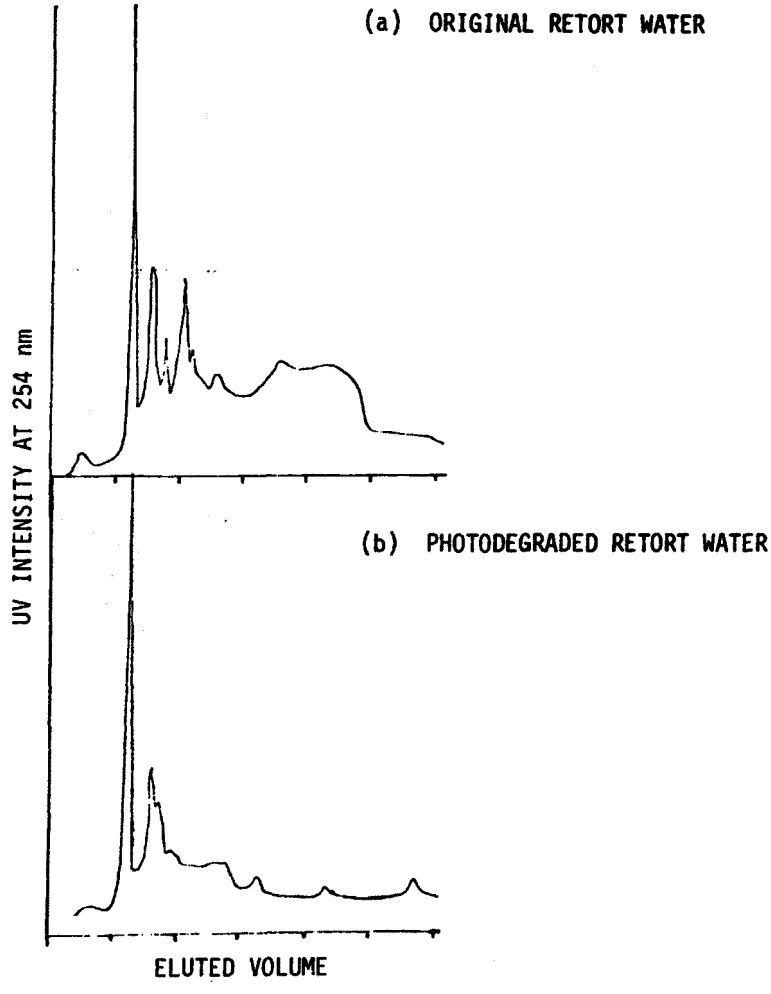


Figure 7-2. High-pressure liquid chromatography spectra of highly polar constituents (Kwan and Yen, unpublished data).

TABLE 7-9. SUMMARY OF ELECTROLYTIC TREATMENT OF RETORT WATER[a]

Portion	Organic carbon[b] (% wt)	Nitrogen[b] (% wt)	Total solid residue[c] (% wt)	COD (mg/l)	Benzene-soluble material (% wt)	Color intensity[d]
Original retort water	9.16	19.48	1.68	16,600	0.45	3441
Processed solutions						
Anodic solution	0.42	1.88	1.05	6,283	0.05	255
Cathodic solution	4.04	22.98	2.01	9,991	0.24	1214

[a] Treatment in U-type membrane cell at current density of 20 mamp/cm^2, cell voltage of 15 volts, and 10-hour treatment time.

[b] Elemental analyses of the lyophilizing solids (ELEK Microanalytical Lab., Torrance, California).

[c] Values for waters subject to lyophilization.

[d] Color intensity = $\int_{250\ nm}^{750\ nm} A\, d\lambda$, where A is adsorbance and λ is the wavelength.

Biological Processes

The low operating cost of biological treatment processes makes them attractive for organic removal. Results from activated sludge treatment of retort water show a 37 to 43 percent COD reduction (Yen et al., 1976b). The refractory components in biodegradation have been determined to reside in the basic and residual (highly polar) fractions (Table 7-10).

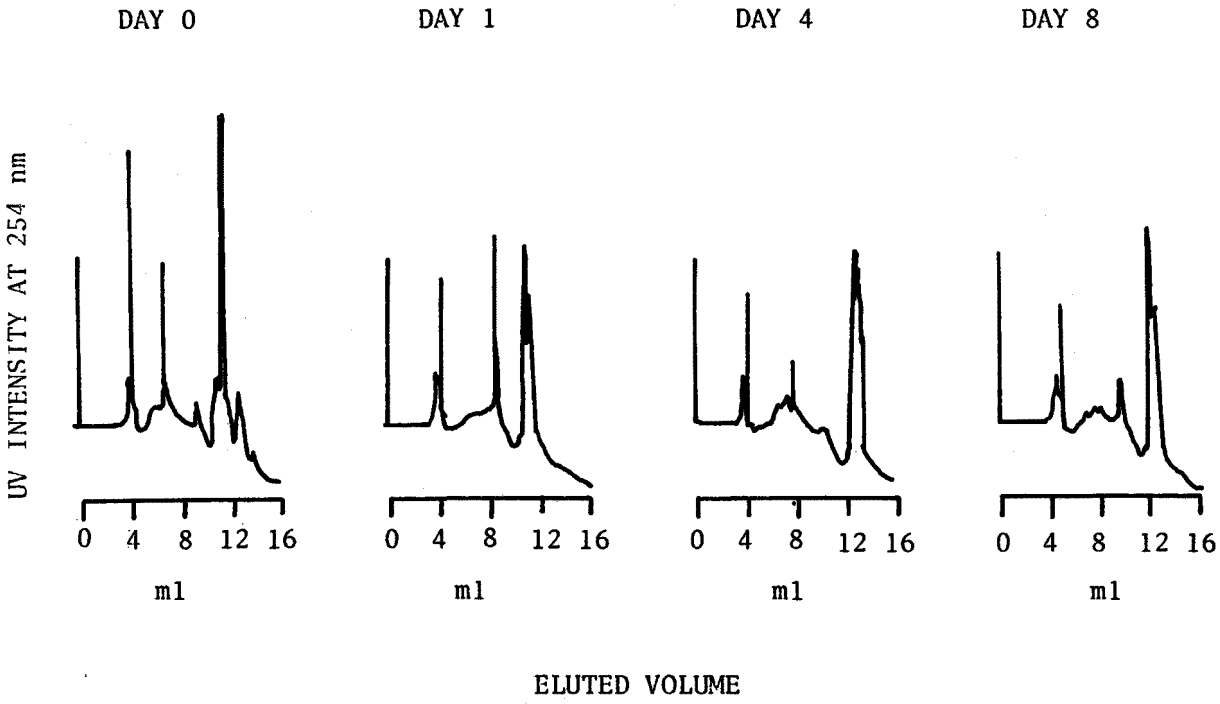
TABLE 7-10. RESULTS OF AEROBIC TREATMENT OF FRACTIONATED RETORT WATER

	COD			TOC		
Fraction	Initial	Final	Percent reduction	Initial	Final	Percent reduction
Acidic	1000	345	65	295	105	65
Neutral	991	452	54	251	116	54
Basic	1349	930	31	324	235	27
Residual	1958	1740	11			

The aerobic treatment of retort water with mutant bacterial species (Phenobac and Polybac) has been investigated to study the effects of mutant bacteria on the reduction of organics in retort water (Yen et al., 1977). The TOC results indicate that further organic reduction can be achieved by mutant species.

Recently the rotating biological contractor system has been recognized as an effective biological process for wastewater treatment (Antonie, 1976). The preliminary data on retort water treatment show that the TOC reduction is a function of the concentration of retort water (Yen et al., 1977).

Toxicity is of major concern in the operation of the biological treatment. The development of effective biological processes for removing persistent organic components depends on the identification and monitoring of the organic components during the biological treatment processes. The TOC and COD data give no information on the alternative paths the organic matter may take, other than being completely decomposed in gaseous form and leaving the system. Monitoring of the intermediate products will help select the appropriate treatment method and improve the overall process. The application of high-pressure liquid chromatography (HPLC), mentioned previously, will provide more detailed information on treatment intermediates. The liquid chromatography spectrum shows a dynamic change of intermediates (Figure 7-3), in which the TOC or COD data of the residual fraction show no decrease under biological treatment. It is understood that the bacteria do break down some of the polar components. The data also provide information on the



Sample: 20 μl Residual Fraction under Aerobic Digestion

Column: μ Bondapak NH_2

Solvent: THF: CH_3CN (1:1) —— H_2O: CH_3CN: THF (2:2:1)

Program: Curve #4 Time: 10 min

Chart: 0.25 cm/min

Flow: 1.0 ml/min

U.V.: 1.0 at 254 nm

Figure 7-3. Changes in HPLC spectrum over time with biological treatment (Kwan et al., 1977).

improvement of process control and treatment efficiency (Kwan et al., 1977).

Since the organic components in retort water have been recognized to be extremely complex, various combinations of unit processes are necessary to reduce organic contaminants to a level that is acceptable to both reuse and discharge. The effectiveness of converting high-molecular polar refractory compounds into biodegradable low molecular species by ozone, photo- or electro-oxidation, could be used as a pretreatment. The biological treatment will still be used to remove gross organic contaminants for economic purposes. Processes such as activated carbon adsorption, ion exchange, and electrolytic oxidation might be chosen for tertiary treatment.

CONTROL TECHNOLOGY AND ABATEMENT

The preceding paragraphs provide a discussion of oil shale wastewater treatment technology. Environmental control technology for abatement of air quality emissions from oil shale development is discussed in sections of this document dealing with mining (Section 2), retorting processes (Section 3), and shale oil upgrading processes (Section 4).

The development of control technologies is necessary for future oil shale operations because of the great potential for environmental impact. Many techniques are available for environmental control. However, many of these approaches remain to be tested on commercial-scale operations. Water treatment and reuse were discussed in the preceding paragraphs. To summarize some of the available or proposed control approaches, the following sections present technologies initially proposed for use on Colorado Tract C-a (initially proposed as a surface mining operation [Rio Blanco Oil Shale Project, 1976]) and Utah Tracts U-a and U-b (an underground mine [White River Shale Project, 1976]). Other available technologies are also listed.

Control of Water Pollution

On Tract C-a, mine water problems would have been mitigated by collection of surface runoff, mine seepage, and dewatering well discharges at a centralized collection point for reuse. On U-a and U-b, water is to be stored in a collection pond for use in dust control within the mine.

Various methods were proposed for control and treatment of process waters (retort water, condensates, sour water, and cooling tower and boiler blowdown waters) on Tract C-a:

- Boiler and cooling tower blowdown used for moisturizing processed shale
- Retort and sour water treated with API separator, stripping system, retention pond
- Surface runoff collected in a conventional storm sewer system and conveyed to an effluent lagoon

- Sewage treatment plant for wastewater from processing and discharge into the effluent lagoon for reuse.

Tract U-a and U-b systems include the following:

- All clean condensates generated in the processes segregated and reused in boilers and cooling towers
- Sour water stripped and reused in hydrotreating units
- Process wastewater streams collected in storage tanks for further treatment.

The use of chemical treatment (such as liming to reduce carbonates and ammonia), ion exchange resins (Hubbard, 1971), and electrolytic methods (Wen, 1976) have also been discussed.

Control of water pollution from spent-shale disposal requires a variety of approaches:

- Surface runoff collected by a series of lined ditches, then conveyed to a lined collection pond at the edge of the pile; water evaporates or is returned to the pile
- Disposal pile constructed to minimize the discharge of leachate by surrounding the main body of processed shale on all sides with an impermeable layer of highly compacted processed shale (ERDA, 1976; Prien, 1974)
- If some leachate is discharged, it will be conveyed to a lined collection pond
- Effluent lagoons will be lined with impermeable material as will the water collection ponds and ditches.

Control of Air Pollution

Control of air pollution during surface mining may include the following measures:

- Prewatering and wetting for dust control
- Treating with dust palliatives, such as oil emulsions, polymers, and soil stabilizers
- Restricting the construction and mining vehicle activity
- Proper drill patterns and quantities of explosives to minimize fugitive dust.

Underground mining, such as proposed on Tracts U-a and U-b, may include the following for air pollution control:

- Application of water and wetting agents applied during drilling
- Muck pile of blasted shale wetted before and during rock loading
- Conventional road wetting and chemical stabilization techniques use for haulage roads
- Catalytic converter or wet scrubber used to control emissions from mining equipment.

Dust suppression during shale preparation (crushing and sorting) may be accomplished by several techniques. Developers of Tract C-a initially proposed the following:

- Primary and secondary crushers enclosed with fabric filter dust collector baghouse
- Dust collected from baghouse slurried to the processed shale moisturizer
- Conveyor covered
- Transfer points equipped with dust suppression systems.

The following methods are proposed for Tracts U-a and U-b:

- Primary and secondary crusher units equipped with water sprays or wet scrubber
- Fully enclosed belts and wet scrubbers at transfer points in disposal system.

Air pollutant emissions from proposed Tract C-a retorting and refining facilities included the following:

- Purified gas used to minimize emissions of particulates
- Desulfurization in sulfur recovery plant for untreated gas
- High energy venturi scrubber used to remove entrained shale dust in flue gas and vapors from shale moisturizing system
- Steam stripping used to remove hydrogen sulfide and ammonia in sour water
- The ammonia containing gas treated with special burner in the thermal oxidizer.

Tract U-a and U-b systems include:

- Feed hoppers and processed shale moisturizer scrubbed to remove dust
- Retorts and refining plants provided with clean fuels
- Vent gas from processed shale moisturizer scrubbed to remove dust
- Exhaust gases from the ball elutriators and the shale preheater cleaned in the wet scrubbers; sulfur plants will recover sulfur from crude shale oil and off-gases will be treated by the tail gas treatment unit.

Solid Waste Disposal

Pollution control for spent-shale disposal, the largest solid waste problem from oil shale operations, includes drainage control, compaction, and stabilization. Some of the approaches for disposal and control are as follows:

- Processed shale dumped, spread, and compacted in disposal areas to form a stable disposal pile
- Processed shale kept at a moisture content of 11 to 19 percent by adding water to aid compaction and stabilization
- Excess construction overburden or local material used to cover the material in order to minimize rainwater percolation through the spent shale
- A catchment dam constructed downstream of the pile to collect runoff or leachate from the disposal area
- Drainage ditches located around the pile prevent surface water from percolating through the spent-shale pile
- The processed shale pile graded and revegetated.

Spent catalysts are another important solid waste problem. Disposal requires special handling, such as transfer in airtight containers. Spent catalysts will be disposed of in landfills or in the spent-shale pile, or they may be reclaimed.

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APPENDIX

METRIC CONVERSION TABLE

Symbol	When you know	Multiply by	To Find	Symbol
ac-ft	acre-feet	43,560	cubic feet	ft^3
ac-ft	acre-feet	325,850	gallons	gal
atm	atmospheres	14.7	pounds per square inch	psi
cm	centimeters	0.3937	inches	in.
°C	Celsius	9/5 + 32	Fahrenheit	°F
*g, gm	grams	0.002,21	pounds	lb
ha	hectares	2.47	acres	ac
Kcal	kilocalorie	3.96	British thermal unit	Btu
kg	kilograms	2.2	pounds	lb
km	kilometers	0.6214	miles	mi
l	liter	0.2642	gallons	gal
m	meters	3.281	feet	ft
m	meters	39.37	inches	in.
m	meters	1.09	yard	yd
m^2	square meter	10.76	square feet	ft
m^3	cubic meter	6.28	barrel	bbl
m^3	cubic meter	264.2	gallons	gal
Q	Quad	10^{15}	British thermal unit	Btu
tonne	metric tons	1.1	ton	short tons
tonne	metric tons	2.2×10^3	pounds	lb

* Used interchangeably in text.

Abbreviations for Units of Measure

atm	atmospheres
bbl	barrel
bblD=BPD	barrel per day
gpd	gallons per day
gpm	gallons per minute
kg/hr	kilograms per hour
LPM	liters per minute
mmhos/cm	millimhos per centimeter
MSCF/D	million standard cubic feet per day
MSCM/D	million standard cubic meters per day
*μgm, μg	microgram
nm	nanometer
ppm	parts per million
Psi	pounds per square inch
Psig	pounds per square inch gage
Q	quad
standard ft^3	standard cubic foot
standard m^3	standard cubic meter
TmPD	tonne per day
TPD	ton per day
wt. %	percentage of weight

* Used interchangeably in text.

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16. ABSTRACT
The development of western oil shale resources has been an evolutionary process in which production and environmental control technologies have evolved from current mining and petroleum industry practices. In addition, new technologies are being developed which are specific to shale oil recovery. The compendium or summary reports included in this document consider the various production processes (mining, retorting, and oil upgrading) and key environmental factors (organic and inorganic characterization, environmental control, and limitations) related to oil shale development. This state-of-the-art survey supports a study designing groundwater quality monitoring program for oil shale operations such as that proposed for Federal Oil Shale Lease Tracts U-a and U-b located in northeastern Utah. Hence, the reports emphasize technologies applicable to this development while also providing a general overview of oil shale technology.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Oil shale	Utah	08G
Mining	Organic pollutants	08H
Waste disposal	Inorganic pollutants	08I
Groundwater	Pollutant identification	13B
Retorts	Groundwater pollution	13H
Waste water		
Refining		

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