EPA 600/7-80-181

RECONNAISSANCE STUDY OF LEACHATE QUALITY FROM RAW MINED OIL SHALE - LABORATORY COLUMNS

by
David B. McWhorter

Agricultural and Chemical Engineering Department
Colorado State University
Fort Collins, Colorado 80523

Grant No. R806278

Project Officer
Edward R. Bates
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory-Cincinnati, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names of commercial products constitute endorsement of recommendation for use.

FOREWORD

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

This report presents the results of the chemical characterization of leachates generated from laboratory columns of several unretorted mined oil shales, unmined shales, and soils. The findings are indicators of the levels of common and trace species that can be expected to occur in field generated leachates. For further information contact the Energy Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

CONTENTS

Foreword	iii
Abstract	iv
Figures	vi
Tables	vii
Acknowled	lgements
ı	
Section	
1.	Introduction
2.	Conclusions
3.	Recommendations
4.	Materials 6
	Designation and source of samples 6
	Particle size analysis
	Leaching methods
	Methods of chemical analysis
	Leaching experiments conducted
5.	Results
	Range of concentrations observed
	Leaching of common species
	Trace elements
Riblinar	aphy
2.2.1091	27

ACKNOWLEDGEMENTS

The cooperation of Rio Blanco Oil Shale Company, Occidental Oil Shale Corporation, Union Oil Company, Colony Development Operation and the US Bureau of Mines in providing permission to obtain materials and assisting in their collection is greatly appreciated. We also wish to thank the personnel from these organizations that have reviewed and commented upon this report.

FIGURES

Number		Page
1	Schematic diagram of leaching apparatus	. 8
2	Leaching characteristics of USBM raw shale	15
3	Leaching characteristics of Colony raw shale	17
4	Leaching characteristics of Colony naturally leached shale	18
5	Leaching characteristics of Union naturally retorted shale	19
6	Leaching of Boron from raw shale	23
7	Leaching of Fluoride from raw shale	24
8	Leaching of Fluoride from raw shale	25
A-1	Particle size distribution for USBM raw shale	28
A-2	Particle size distribution for Colony raw shale	28
A-3	Particle size distribution for C-a composite raw shale	29
A-4	Particle size distribution for C-a R-5/Mahogany raw shale	29
A5	Particle size distribution for Union naturally retorted shale .	30
A-6	Particle size distribution for C-b soil	30
A-7	Particle size distribution for Colony naturally leached shale .	31
A-8	Particle size distribution for Colony soil	31

INTRODUCTION

The modified in-situ method of oil shale retorting and the various surface methods require that quantities of raw (unretorted) shale be mined from shafts and drifts that provide access to the retorts. Raw shale is also mined to provide a void space into which the shale in the retort expands upon rubblization by blasting. The mined shale will be stored on the ground surface for a period of at least a few years and possibly even permanently. The placement of the unretorted shale on the surface places it in an environment with which it is no longer in geochemical equilibrium, and the precipitation on the pile creates the potential for the release of a variety of chemicals into percolating waters at elevated levels relative to the base line conditions.

There is no single generally accepted method by which the effect of solid waste upon the chemistry of percolating waters can be assessed. Most of the comparative studies of leaching methods have been oriented toward landfill problems (Löwenbach, 1978; Ham et al., 1979). It is not practical to simulate in the laboratory the wet and dry cycles, the freeze and thaw sequences, the microbial activity, the aerobic and anaerobic conditions, temperature fluctuations, and variable residence times that will be experienced in the field.

Futhermore, the chemical and physical properties of raw mined shale cannot be expected to be uniform. This natural heterogeneity imposes an additional constraint on the extrapolation and generalizations of laboratory results.

This report contains the results of a laboratory based reconnaissance study of potential water quality problems associated with leachate from surface storage of raw shale. In view of the fact that laboratory tests are not capable of simulating field conditions, the results of this study must be viewed only as a general indicator of the water quality that can be expected in leachates from raw shale. A major purpose of the study was to investigate whether or not more realistic and comprehensive field tests are warranted.

Eight different materials were subjected to leaching. Four of the materials were raw mined shales obtained at different locations in the Colorado oil shale region. The other four materials were samples of shales and soils that had been exposed to natural leaching processes. The four previously exposed materials provide a background or baseline that assisted in

placing the results for the mined shales in an appropriate perspective. No attempt was made to establish statistical distributions of the concentrations of the various chemical constituents. Because the laboratory conditions do not adequately simulate those in the field, rigorous establishment of the ranges of variation for various confidence intervals was not warranted.

Leaching was conducted by passing de-ionized water through columns of each material. Both saturated and unsaturated tests were conducted. Samples of the effluents were collected and subjected to chemical analyses. The electrical conductivity of the effluent from the columns was measured at small time intervals by means of a flow-through probe and a data logger. Grain size analyses were made for each material. The results of these experiments are summarized in the body of the report. All of the data generated from the chemical analyses are contained in the appendices. Graphical representations of the grain-size distributions are also included in the appendices.

CONCLUSIONS

Raw mined shales of the type tested in this study can be expected to result in leachate containing dissolved solids at elevated concentrations relative to the background. The major contributors to the dissolved solids content are calcium, magnesium, sodium, bicarbonate, chloride and sulfate. Using the electrical conductivity (EC) as an indicator of the dissolved solids concentration, it was found that the dependence of the EC on the throughput volume could be satisfactorily described by

$$EC = EC_{m} \left(\frac{PV}{PV_{m}} \right)^{-\alpha}$$
, $PV \ge PV_{m}$

where PV is the effluent volume expressed in pore volumes, EC $_m$ is the maximum EC observed and PV $_m$ is the corresponding effluent volume. The exponent α is an indicator of the leachability; large α representing a more rapid decline in EC than for small α , other factors being equal. This equation does not hold at large PV where the EC is approaching a stable value.

The leaching index α for the mined shales ranged between 0.4 and 1.1. The USBM, Colony, and C-a composite materials exhibited remarkably similar values of α that ranged between 0.8 and 1.1. The C-a, R-5/Mahogany material had a leaching index of 0.4-0.5. For the materials tested, the leaching index did not depend upon whether the test was conducted under saturated or unsaturated conditions. Futhermore, nearly identical values of α were obtained for the mined shales on a second leaching cycle following a period of drainage and aeration.

In contrast to the mined shales, the values of α obtained for the soils and previously exposed shales on the second leaching cycle were markedly reduced from the values obtained on the first cycle. It is likely that the readily leachable precipitates in the previously exposed materials are largely deposits on the surface of the grains left by evaporating waters. Once the deposits were leached away in the first cycle, they could not be readily replaced because leaching by precipitation over many decades has removed the source. In the case of the mined shales, diffusion of dissolved solids and capillary flow from the interior to particle surfaces during the drainage/aeration period is proposed as the cause of the observed recovery.

The concentrations of Al, B, F and Zn were found to be significantly greater in the leachates from some of the mined shales than in the corresponding samples from the previously exposed materials. The levels of all other trace elements produced by the mined shales were comparable to those observed from the soils and previously exposed shales. Elevated concentrations of Al, B, F and Zn were measured in leachates from the USBM raw shale. The largest values of Al concentration were produced from the unsaturated leaching tests and the second cycle of saturated leaching. No consistent relation between Al concentration and the volume of effluent was found.

The largest concentrations of B were also found in the leachates from the USBM shale columns. A trend toward decreasing concentration of B with increasing leachate volume was observed for all of the mined shales. Concentrations of B did not increase significantly during the period of drainage/aeration.

Fluorine concentrations in the leachates from the mined shales was generally greater than from the previous exposed materials. Concentrations of F decreased rapidly with the first pore volume of effluent from the USBM and C-a R-5/Mahogany mined shales and then approximately stabilized. A similiar leaching effect for the soils was observed, but the concentration of F in leachate from the other materials did not decline significantly. After the concentration was approximately stable, the range of F concentrations for the mined shales was 1-25 mg/l. Only the USBM shale yielded F concentrations consistently greater than 10 mg/l.

The concentration of Zn in the effluent from the USBM shale was consistently greater than for any of the other materials tested. The other mined shales yielded Zn concentrations comparable to those obtained in the background materials.

From comparisons of the maximum observed concentrations of various parameters with drinking water criteria, it is concluded that even the worst leachate from the columns does not exceed 100 times drinking water standards for measured parameters. The maximum concentrations of Cr, F, Fe, Hg, Mn, $\rm NO^3$, Pb, $\rm SO^4$, TDS, and Zn were found to exceed drinking water criteria, however. After leaching, the minimum concentrations generally fell well below the standards with the exception of F.

RECOMMENDATIONS

It is recommended that the chemical constituents of the leachates generated under field conditions be determined. The present study indicates that particular emphasis should be placed upon the total dissolved solids and the trace elements Al, B, F and Zn, although only B and F were found at significantly elevated levels in all of the mined shales tested. There was some indication that Mo concentrations in leachates from the C-a R-5/Mahogany mined shale are significantly above background values. It is recommended that this element be given additional study. It is recommended that the sulfur chemistry be given additional attention. There is a need to determine the levels of sulfur species other than sulfate in the leachates.

At the present time, little is known about the geochemical and biological processes that result in the release of these trace elements to the percolating waters. An understanding of these processes would assist in projecting long term consequences and might suggest methods or practices that would minimize the degradation of the quality of waters contacting the materials.

MATERIALS AND METHODS

A variety of samples of raw shale and soils was obtained from the Piceance Basin of Colorado for use in this study. The purpose of extending the study to selected soil samples was to provide a background and perspective from which the results on the raw shale can be viewed. A total of eight different materials were tested; four raw shales, two soils, one sample of naturally leached outcropping shale, and one sample of naturally retorted shale from a surface fire of unknown age.

DESIGNATION AND SOURCE OF SAMPLES

Two samples of raw shale were obtained from federal lease tract C-a with the cooperation of Rio Blanco Oil Shale Company. One of these is a sample of mixed ore from the R-5 and Mahogany zones and is designated C-a R-5/Mahogany in the remainder of this report. The second sample from this site is designated C-a composite and represents a sample of the trimmings from the service shaft.

A sample of unretorted shale from the Mahogany zone was obtained with the cooperation of Colony Development Operation from the mine on Parachute Creek. This sample was extracted from a stock pile of minus 1/2 inch material that was mined approximately 6 years ago. The sample was collected from well beneath the surface of the pile but has, undoubtedly, been subjected to some weathering and leaching prior to testing. This sample is called Colony raw shale throughout the report.

The fourth raw shale sample was obtained from the United States Bureau of Mines site in Horse Draw. This material is from a drift at 4208 MSL elevation in the saline zone and had been stockpiled outside for approximately 6 weeks.

Soil samples were collected from two locations. The sample designated Colony soil was obtained in the vicinity of the crusher and stockpile at the Colony site on Parachute Creek and was scraped directly from the surface. The second sample was obtained from the B-horizon exposed in a small cut in Cottonwood Gulch on the C-b federal lease tract. These samples are designated Colony soil and C-b soil, respectively.

The other two materials tested are designated Colony naturally leached and Union naturally retorted. The first is talus slope material collected near the mine on Parachute Creek. This material has been exposed to

weathering and leaching and is presumed to be in approximate equilibrium with the surface environment. The material designated as Union naturally retorted shale is shale that has burned under natural conditions and was obtained near the portal of Union's mine on Parachute Creek. The age of the burn is unknown but probably occurred many decades ago.

PARTICLE SIZE ANALYSIS

Quantities of each material sufficient to fill the leaching columns were separated from the samples collected. These quantities were quartered and samples were taken for particle size analysis. These samples were prepared for analysis in accordance with the standard method for "Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants" (ASTM D421-58). The distribution of particle sizes was determined in accordance with the standard method for "Particle-Size Analysis of Soils" (ASTM D422-63).

LEACHING METHODS

Columns constructed of PVC pipe, 15 cm in diameter, were used to contain the materials during leaching. The columns were capped on the lower end and an outlet was provided as shown in Figure 1. The effluent was forced to pass through an electrical conductivity probe that was connected to an automatic data logger. Below the sample, a layer of glass beads and silica sand was placed to prevent the movement of fines into the outflow. The length of the sample was 107 cm.

Two sets of experiments were performed. In one set, the flow through the columns was controlled so that the sample remained saturated. In the second set, the flow was controlled so that the major portion of the column was unsaturated. The inflow to the columns in the saturated flow experiments was controlled by means of a Mariotte siphon placed on a platform whose position could be adjusted to any desired elevation. A small depth of ponded water was maintained on the surface of the sample at all times during the experiments with saturated flow. The elevation of the outflow tube was adjusted to maintain the desired flow rate.

The inflow to the unsaturated column experiments was provided by means of positive displacement, constant rate pumps. In these runs, the elevation of the outflow tube was maintained near the level of the bottom of the sample, and inflow was provided at a rate per unit area less than the value of saturated hydraulic conductivity. This procedure insured that the pressure of the water in the column was less than atmospheric everywhere except in the immediate vicinity of the bottom of the column. The degree of aeration in the upper portion of the column was not quantified.

With the exception of the soils, the saturated hydraulic conductivities of the materials were rather large. Therefore, during the saturated runs, the differences in elevation between the water surface in the columns and the outflow had to be maintained at a small value to insure reasonable residence times in the columns. Small changes in the difference in head were

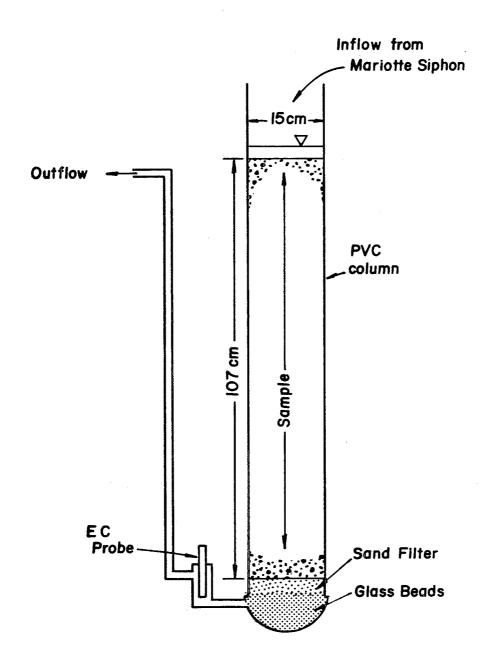


Figure 1. Schematic diagram of leaching apparatus.

thus large relative to the total difference and this caused the inflow rate to be somewhat variable.

The inflow rate per unit area during the unsaturated runs was maintained below the value of saturated hydraulic conductivity. The fact that the hydraulic conductivity was large made it possible to maintain unsaturated conditions with inflow rates that were substantially greater than those used in the saturated runs. Therefore, the residence times for the unsaturated columns were actually less than for the saturated columns. Quantitative residence times for the unsaturated columns could not be calculated because the water content (degree of saturation) was not known. However, the residence times in the unsaturated columns is less than the column length divided by the inflow rate per unit area.

Effluent was collected from the columns continuously and the cumulative volume was measured. The electrical conductivity of the effluent was recorded automatically every two hours. At least daily, the effluent was sampled and the pH and EC measured. Samples of the effluent were collected periodically and subjected to a chemical analysis described subsequently. Influent in all experiments was deionized water.

METHODS OF CHEMICAL ANALYSIS

Chemical analyses were performed at the analytical laboratory in the Chemistry Department at Colorado State University under the direction of Dr. Rodney Skogerboe. Table 1 summarizes the methods utilized. The degree of accuracy decreases from those listed in Table 1 when the concentration approaches the determination level.

LEACHING EXPERIMENTS CONDUCTED

All of the materials described previously were subjected to saturated leaching testing and most were also subjected to unsaturated leaching. In addition, several of the materials were allowed to gravity drain and stand in an aerated condition for several weeks and were then subjected to saturated leaching a second time. Funds available for chemical analysis did not permit a complete chemical analysis in all cases. Table 2 contains a summary of the tests conducted. In those runs for which a chemical analysis is indicated, between one and seven samples were analyzed.

TABLE 1. SUMMARY OF ANALYTICAL METHODS AND LEVELS OF ACCURACY

Constituent		Level of Accuracy
В	Eschelle Multi-element Plasma Spectrometer	+ 20%
Cd	11	
Be	H	11
Mg	II	11
Sť	II	11
Мо	II	11
Mn	II	11
Ni	II	11
Na	11	11
Cu	ıı .	. 11
A1	II	11
Ca	II	11
Ba	II	11
K	II	. 11
Cr	11	11
Sr	II	. 11
Pb	II	11
Sn	Eschelle Single-element Plasma Spectrometer	. 11
F	Dionex Ion Chromatograph	<u>+</u> 10%
C1	II	- "
NO3	II .	H
S0 ₄	· II	#1
As	Atomic Absorption-Hydride Gen.	11
Se	II.	11
Hg	Atomic Absorption-Cold Vapor	11
Fe	Atomic Absorption-Flame	
Li	1)	11
Zn	II	11
HCO ₃	Calculated	11
CO3	· ·	

TABLE 2. SUMMARY OF THE TESTS CONDUCTED

MATERIAL		SATURATED	АТЕD		UNSA.	UNSATURATED
	Ini	ıitial	After	After Aeration		
	# of Runs	# w/Chem Anal	# of Runs	# w/Chem Anal	# of Runs	# w/Chem Anal
USBM Raw Shale	2	2	2 ,	-	↔	
Colony Raw Shale	2	. 2	2	-	, 1	0
C-a R-5 Mahogany	2	П	2	0	H	П
C-a Composite	2	1	2	0	.	г
Colony Naturally Leached	₩	П		Н	H	0
Union Naturally Retorted	, -	1	1	0	⊷	П
Colony Soil	П	H	 -1		0	0
C-b Soil	1	-	0	0	0	0
	12	10	11	4	9	4

RESULTS

The leaching characteristics of the materials studied are presented in this section. The results are divided into three categories; the first being a summary overview of the range of concentrations observed in leachates. The observations relative to the leaching of the common elements that make up the majority of the dissolved solids are presented, and finally the results obtained for selected trace elements are summarized. The chemical analyses for each individual sample of leachate are tabulated in the appendices.

RANGE OF CONCENTRATIONS OBSERVED

Raw shale disposed above ground in the field will be subjected to a variety of weathering processes that probably cannot be adequately simulated in the laboratory. There will be wet and dry cycles, freeze and thaw, microbial activity, periods in which percolation from precipitation is rapid and others in which the contact time will be great. Superimposed upon this variability will be the inherent spatial heterogeneity of the geochemical properties of the materials placed in the embankment. The concentrations of various chemical species in leachates is expected to be highly variable. The results contained in this subsection should be viewed as indicators of the possible range of concentrations that can be anticipated in field disposal.

The range of concentration variation observed in leachates from each material are presented in Table 3. The values in this table were obtained by searching all data for the maximum and minimum values without regard to the cumulative volume of throughput, whether the material was saturated or unsaturated, or the residence time. Thus, this table represents an overview of the magnitudes observed for each species. In most cases the maximum values were obtained early in the leaching process and the minimum values were obtained after several pore volumes of throughput.

As an aid to assessing the significance of the concentrations of several parameters, drinking water criteria are also listed in Table 3. The maximum concentrations of Cr, F, Fe, Hg, Mn, ${\rm NO^3}$, Pb, ${\rm SO^4}$, TDS, and Zn exceed their respective recommended maximum drinking water concentrations. The minimum concentrations obtained after substantial leaching are generally well below the drinking water criteria. Fluoride is a major exception to this statement. The ratios of the maximum observed concentration to the respective drinking water standard were calculated. In no case did the ratio

TABLE 3 - SUMMARY OF THE RANGE OF OBSERVED CONCENTRATIONS

Parameter	Units	USBM Raw Shale	Colony Raw Shale	C-a R-5/Mahog. Shale	C-a Composite	Colony Nat. Leached	Union Nat. Retorted	Colony Soil	C-b Soil	Drinking Water Criteria
Al	mg/1	0.34 - 7.54	<0.05 - 0.75	0.3 - 3.53	< 0.05 - 0.69	<0.05 - 0.17	<0.05 - 0.1	<0.05 - 0.37	<0.05	ł
As	=	<0.005	<0.005	<0.005	<0.005	<0.005	<0.00>	<0.005	<0.005	0.05
∞	=	0.24 - 43	<0.025 - 2.75	<0.025 - 0.59	<0.025 - 1.97	0.12 - 0.365	0.165 - 0.39	0.47 - 0.76	0.65 - 0.985	į
88	=	0.061 - 0.17	0.07 - 0.48	0.088 - 0.27	0.027 - 0.22	0.088 - 0.495	0.028 - 0.35	0.12 - 0.57	0.038-0.240	1.0
9e	=	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	:
ొ	£	36 - 750	40 - 1550	180 - 1510	18 - 970	25 - 500	10 - 49	40 - 960	6.5 - 330	1
5	=	<1.0 - 560	1.1 - 22	1.9 - 300	0.3 - 130	0.8 - 71	1.1 - 15	0.1 - 200	1.8 - 520	
60	2	0.1 - 1.1	0.03 - 1.6	<0.1 - 346	0.3 - 0.7	0.12 - 1.03	<1.0 - 22	0.17 - 2.9	1.0-8.8	-
່ວ	-	<0.025 - 0.68	<0.025 - 0.04	0.022 - 0.034	<0.025 - 0.043	<0.025	<0.025 - 0.71	<0.025	<0.025 - 0.069	0.05
3	=	<0.025 - 0.30	<0.025 - 0.41	<0.025 - 0.69	<0.025 - 0.44	<0.039 - 0.31	<0.025 - 0.33	0.075 - 0.38	<0.025 - 0.28	1.0
23	umhos/cm	280 - 13000	240 - 5400	1900 - 37000	125 - 8200	240 - 4200	300 - 1300	370 - 9000	840 - 3000	;
LL	mg/1	9.5 - 75	4.0 - 7.2	0.8 - 65	<0.5 - 3.0	4.0 - 8.7	5.4 - 6.6	1.2 - 10	4.5 - 25	1.8
Fe	=	0.01 - 1.8	<0.03 - 0.89	<0.1	<0.1	<0.03 - 0.08	<0.0>	<0.01 - 0.52	0.1 - 0.42	0.3
HCO,	=	83.1 - 321	50 - 558	3.0 - 403	82 - 1026	136 - 233	168 - 585	152 - 480	481 - 846	!
, 도	5	<0.0001 - 0.0035	<0.0005	<0.0001	<0.0001	<0.000>	<0.0001	<0.0005	<0.0001	0.002
¥	=	1.1 - 22	1.7 - 59	8.2 - 640	0.4 - 34	0.83 - 57	9.2 - 74	25 - 270	1.3 - 22	;
ŗ	2	0.02 - 3.1	0.02 - 0.151	0.02 - 0.11	<0.02 - 0.79	<0.004 - 0.02	0.14 - 0.51	0.03 - 0.47	0.02 - 0.08	;
₽	=	6.7 - 1050	5.5 - 140	0.675 - 108	4.9 - 820	17 - 365	30 - 108	17 - 1450	2.6 - 145	:
ñ	=	0.075 - 3.2	0.074 - 2.74	<0.05 - 0.35	<0.05 - 0.40	<0.05 - 0.11	<0.05	<0.05 - 0.97	<0.05 - 0.16	0.05
웃	E	0.09 ~ 0.87	0.09 - 0.65	0.10 - 5.18	0.10 - 2.2	0.075 - 0.74	0.065 - 0.45	<0.05 - 0.84	<0.05 - 0.43	1
Na	z ·	<25 - 1430	5.8 - 145	27 - 7710	4.3 - 1240	14 - 350	12 - 75	3.8 - 340	210 - 2050	:
ž	=	<0.025 - 0.60	<0.05 - 0.10	0.047 - 0.085	<0.05 - 0.16	<0.05 - 0.05	<0.05	<0.05 - 0.07	<0.05 - 0.075	:
K03	=	<1.25 - 40	0.9 - 25	4 - 172	<0.5 - 140	<0.3 - 245	0.5 - 8	<0.2 - 180	1.4 - 30	10
2	=	<0.04 - 1.9	<0.05 - 0.64	<0.05 - 0.83	<0.05 - 0.77	0.12 - 0.35	0.05 - 0.16	0.12 - 0.38	0.07 - 0.31	0.02
Ħ	1	6.8 - 8.06	7.06 - 8.18	6.93 - 11.98	7.03 - 7.99	6.93 - 8.11	7.20 - 8.81	7.1 - 8.2	7.43 - 8.49	:
Se	[/6m	< 0.01	<0.01	<0.005	<0.005	<0.01	<0.005	<0.01	<0.005	0.01
Sŧ	=	1.65 - 9.7	2.12 - 10.58	1.2 - 23.28	5.8 - 19.58	6.71 - 14.72	8.8 - 19.06	8.0 - 16.8	11.0 - 20.7	:
S	=	<0.025 - 1.28	0.12 - 0.67	;	:	0.041 - 0.67	i	<0.025 - 1.37	:	;
50 4	=	20 - 5700	28 - 5150	2 - 6600	7.9 - 6100	15 - 2650	9 - 128	60 - 4200	23 - 860	250
. SOT	=	70 - 13300	110 - 7160	610 - 30130	164 - 9450	120 - 4760	460 - 1200	250 - 7450	1050 - 3760	200
uZ	z	0.01 - 6.8	<0.02 ~ 0.68	<0.01 - 0.09	<0.02 - 1.5	0.07 - 0.3	0.02 - 0.15	0.01 - 0.65	0.04 - 0.35	5.0

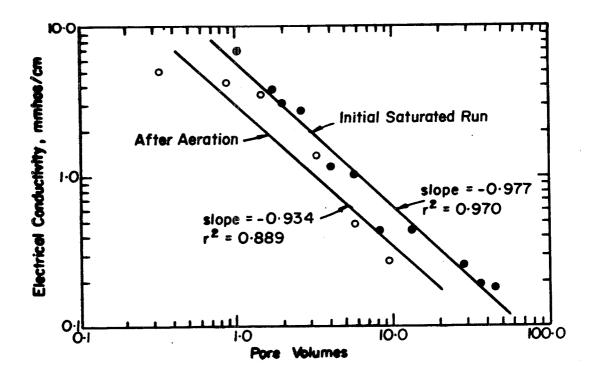
exceed 100. The largest ratio was found to be 64 for Mn in effluent from USBM raw shale in saturated run number 2. This comparison indicates that even the worst of the leachates generated from the laboratory columns do not exceed 100 times drinking water standards for the parameters measured.

The four materials on the right side of the table have all been exposed to natural leaching. The quality of leachate from these materials is useful for establishing a perspective in which the leachates from the raw shale can be viewed. The maximum dissolved solids in the effluent from the raw shales are significantly greater than in that from the previously exposed materials. The increased dissolved solids are almost entirely attributable to increases in Ca, Mg, Na, HCO₃, Cl and SO₄ in some combination. In general, the maximum concentrations of trace elements from the raw shales are low and are not often substantially greater than the values measured for the previously exposed materials. One exception is B, the maximum concentration of which was significantly greater in the raw shale leachate (except for C-a R-5/Mahogany). The minimum values of B from the raw shales are within the observed range for the previously exposed materials, indicating the leachability of this species. Boron, F, and Al concentrations are discussed further in a subsequent section.

Calculation of the quantities of anions and cations for the raw shales showed a substantial deficiency of anions, except for the colony raw shales for which an acceptable balance on every sample was observed. There are at least two possibilities that are presently under investigation. First, there may exist an error in the determination of sulfate. For this reason sulfate concentrations on individual samples have not been reported. It is believed that another probable explanation involves the presence of other sulfur species. For instance, thiosulfate ($S_{20_3}^{2-}$) is a common constituent of oil shale process waters and Wong and Mercer (1979) found that this species accounted for 7-20 percent of the chemical oxygen demand. A few spot checks of the COD of the leachates from the raw shale showed values ranging between 1000 and 1500 mg/l. This is suggestive that substantial quantities of thiosulfate may be present. Stuber, et al., (1978) analyzed four process waters from in-situ production operations for various sulfur species. They found the percentages of total sulfur to range from: 3.9 to 30.2 as sulfate, 34.8 to 55.2 as thiosulfate, 1.0 to 26.3 as thiocyanate, and <0.3 to 3.5 as tetrathionate. It is not likely that these percentages can be extrapolated to leachates from raw shale, but the possible presence of such species seems to warrant investigation.

LEACHING OF COMMON SPECIES

The most convenient indicator of the quantity of the common species Ca, Mg, Na, Cl, HCO $_3$ and SO $_4$ in the leachate is the electrical conductivity (EC) of the solution. A measure of the leachability of these species is the rate at which the EC declines with the volume of throughput. Figure 2 shows such a relationship for the USBM raw shale. The two sets of data in the upper block are those obtained under saturated leaching conditions; the black circles being the initial run and the open circles being the



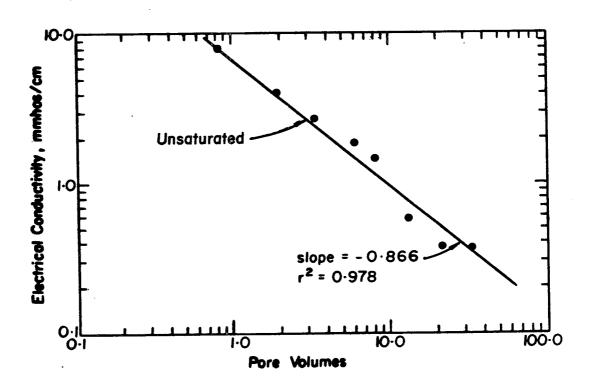


Figure 2. Leaching characteristics of USBM raw shale.

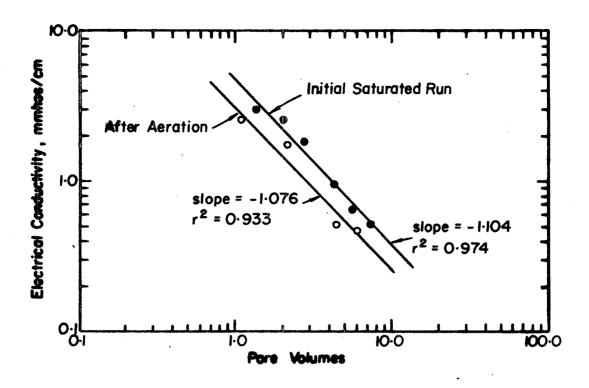
resaturated run. The data in the lower block are those obtained by leaching under partially saturated conditions.

Because the columns were quite permeable and saturated from the top, the residence time of the first few hundred ml of water was much smaller than the mean residence time. This short residence time and probable channeling of flow caused the dissolved solids in the first sample to be less than the maximum. In the preparation of Figure 2 and similar graphs, only values after the maximum were used. This tends to laterally shift the straight line in a rather arbitrary way, but has no affect on the slope of the lines.

The rate of leaching of the common species for the USBM raw shale is practically the same in all three of the experiments. After the initial saturated leaching had been completed, the column was allowed to drain and become aerated for 108 days. Leaching was initiated again and the data indicated by the open circles were obtained. Note that the EC almost completely recovered to its original value and subsequently declined at almost the same rate as in the first run. The mean residence time was 46 hours in these runs. The variation of EC with the volume of throughput during the unsaturated run is, again very similar, even though the residence time during the unsaturated run was less than one-half the residence time for the saturated runs.

Similar results were observed for the other raw shales tested. Figure 3 shows the results for the Colony raw shale. Again the leaching characteristics are practically the same for all three tests. As for the raw shales, the rate of leaching during saturated and unsaturated tests was about the same for the four materials that had been exposed to natural leaching. However, in each of these four cases, the rate of leaching following the drainage/aeration period was markedly less than during the initial run. Examples are shown in Figure 4 and 5 for Colony naturally leached and the Union naturally retorted. Futhermore, the EC did not recover substantially during the aeration period.

In the case of the previously exposed materials, it is believed that the large fraction of the readily leachable materials existed as the result of long term weathering processes and precipitation of dissolved solids caused by the evapotranspiration of soil water. When these materials were leached during the initial run, they were not rapidly replaced. In the raw shales, the percolating waters of the first run removed the readily leachable materials from the surface of the solid particles much as in the case of the previously exposed materials. However, during the aeration period the leachable materials were replenished rapidly to the surfaces, probably by diffusion and capillary flow. The movement of dissolved species to the surfaces of the particles was relatively rapid for the raw shales because no significant leaching on the interior of the particles had occurred and, thus, the concentration gradients were very large. A similar process may still be operative in the other four naturally leached materials, but at a much reduced rate due to the countless number of such cycles experienced previously.



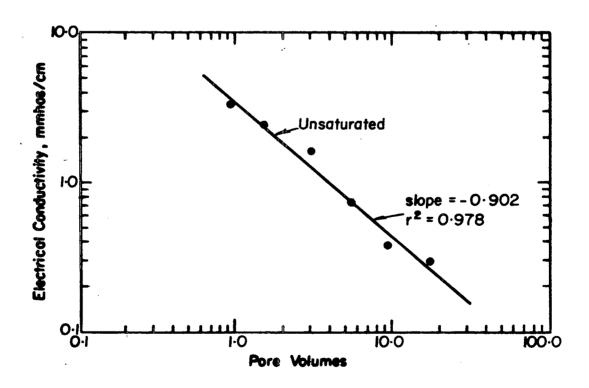
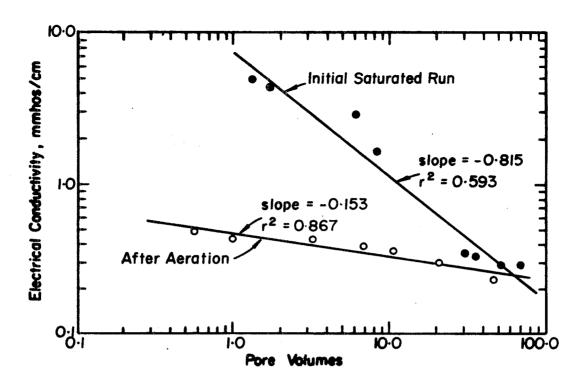


Figure 3. Leaching characteristics of Colony raw shale.



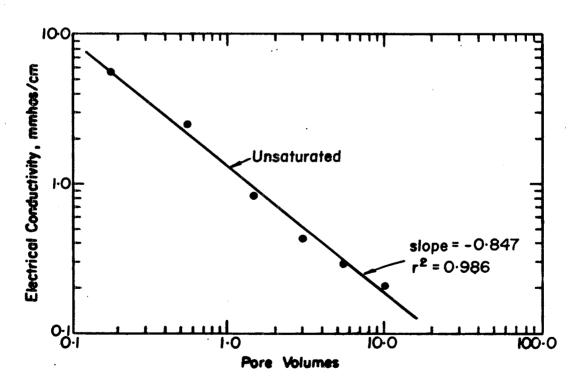
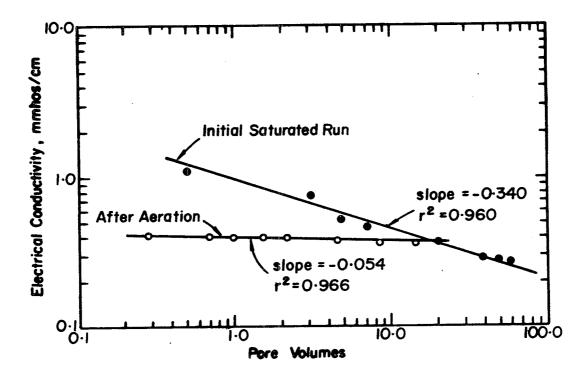


Figure 4. Leaching characteristics of Colony naturally leached shale.



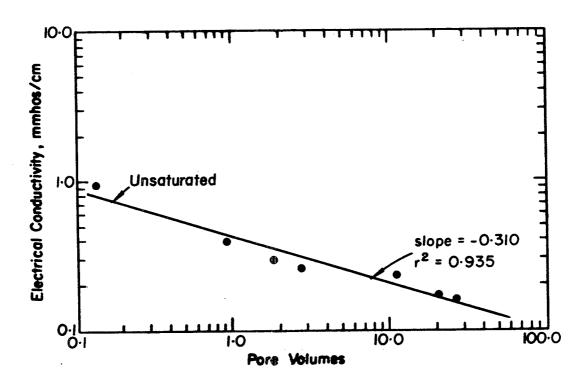


Figure 5. Leaching characteristics of Union naturally retorted shale.

All of the EC versus pore volume data were fit satisfactorily with an equation of the type

$$EC = EC_m \left(\frac{PV}{PV_m} \right)^{-\alpha}, PV \ge PV_m$$

where EC_m is the maximum electrical conductivity observed and PV_m is the corresponding volume of effluent expressed in pore volumes (PV). This equation does not apply after the EC of the leachate begins to stabilize following the removal of the most readily soluble materials. For the USBM, Colony, and C-a composite raw shales, the exponent α varied between 0.8 and 1.1. However, for the C-a R-5/Mahogany shale this leaching index was between 0.4 and 0.5. The chemical composition of the leachate from the R-5/Mahogany shale was also substantially different from that of the other three raw shales; the total dissolved solids being significantly greater, sodium concentrations being disproportionately greater, and a very small quantity of magnesium being present in the leachate.

TRACE ELEMENTS

The results from the eight materials tested were divided into two groups; those for the 4 mined shales and those for the 4 materials that have been exposed to leaching and weathering under natural circumstances. The maximum concentrations of each trace element that were observed for each group are presented in Table 4. This presentation assists in gaining an overview of the degree to which trace element concentrations in leachate from the mined shales differ from those obtained from materials that might reasonably be expected to represent background conditions.

In view of the range of values that results entirely from material variability, variable leaching rates, and analytical error, only the concentrations of Al, B, F, Mo, Pb, and Zn in Table 4 are significantly elevated in the mined shales relative to that in the background materials. In the case of zinc, only the USBM raw shale produced concentrations in excess of the maximum observed in the background materials. The elevated zinc concentrations from the USBM material does not appear to be spurious, as relatively high concentrations were observed in a number of samples.

The maximum concentration of Mo was observed in the initial sample from the unsaturated leaching of the C-a R-5/Mahogany material. The subsequent sample collected at 0.88 PV of effluent contained a much reduced quantity of Mo but still a relatively high value. The Mo concentration in the initial sample from the saturated column of R-5/Mahogany material was not obtained due to analytical difficulties. However, the C-a composite material in both the saturated and unsaturated experiments showed initial Mo concentrations that are approximately twice those obtained in the other materials. It is believed that subsequent leaching studies of raw shale from the C-a site

COMPARISON OF TRACE ELEMENT CONCENTRATIONS FROM RAW MINED SHALES WITH THOSE FROM SOILS AND PREVIOUSLY EXPOSED SHALES TABLE 4.

	Re	Raw Mined Shales	Soils & Pr	Soils & Previously Exposed Shales	Drinking Water Criteria
Element	Max. Conc. Observed mg/l	Test Yielding Max. Conc.	Max. Conc. Observed mg/l	Test Yielding Max. Conc.	
Al	7.54	USBM, Unsaturated	0.37	Colony Soil	1 1 1 1
As	<0.005	1 1 2 1	<0.005	!!!!	0.05
<u>.</u> ထ	43	USBM, #2 Saturated	0.99	C-b Soil	: : : : : : : : : : : : : : : : : : : :
Ba	0.48	Colony Raw, #2 Sat.	0.50	Colony Nat.	1.0
Be	<0.025	1 8 9 9	<0.025	1 1 1	[1
ر د	0.68	USBM, #1 Saturated	0.71	Union Nat. Ret.	0.05
ŋ	0.69	C-a R-5/Mahog., Unsat.	0.38	Colony Soil	1.0
14.	75	USBM, #1 Saturated	25	C-b Soil	1.8
Fe	1.8	USBM, #1 Resaturated	0.52	Colony Soil	0.30
£	0,0035	USBM, #2 Saturated	<0.005	1 1 1	0.002
; <u> </u>	3.1	USBM, #2 Saturated	0.51	Union Nat. Ret.	i 1 1
Æ	3.2	USBM, #2 Saturated	0.97	Colony Soil	0.05
₩ W	5.18	C-a R-5/Mahog., Unsat.	0.84	Colony Soil	E 8 8
. <u>.</u>	0.60	USBM, #2 Saturated	0.075	C-b Soil	\$ 1 1
Pp	1.9	USBM, #1 Saturated	0.38	Colony Soil	0.05
Se	<0.01	1 1 1	<0.01	1 1 1	0.01
Si	23.28	C-a R-5/Mahog., Unsat.	20.7	C-b Soil	1 1 8
.S.	1.28	USBM, #2 Saturated	1.37	Colony Soil	1 1 1
Zu	8.9	USBM, #1 Saturated	. 0.65	Colony Soil	5.0
			,		

should include analyses for Mo to verify or disprove the indications of elevated Mo obtained in this study.

Concentrations of Al in leachate from both saturated runs and the unsaturated experiment on USBM raw shale were significantly elevated relative to the background materials. Elevated concentrations in the C-a R-5/Mahogany leachate were also observed. The greatest concentrations of Al for each material were found in the leachates from either the aerated columns or the unsaturated columns. No consistent relationship between the Al concentration and leachate volume was observed. The average concentration of Al in the USBM saturated runs was 1.76 mg/l, which compares to 3.71 mg/l obtained for the same material by averaging the concentrations from the aerated and unsaturated experiments. These data suggest that Al is produced into the water in the greatest quantites when aerated conditions exist.

The concentrations of F and B observed in this study are of the same order as those measured by others (Runnells, et al., 1979). Boron concentrations in the leachates obtained at small throughput volumes from USBM, Colony, and C-a composite were all substantially greater than the maximum value observed in the background materials that were tested. Boron concentrations in leachates from C-a R-5/Mahogany were all less than the maximum value obtained in the soils and previously exposed materials. The largest concentrations of B were consistently measured in leachates from the USBM raw The other mined shales exhibited B concentrations much less than the USBM material. A trend toward decreasing concentration of B with increasing leachate volume was observed as shown in Figure 6. Because of the large differences in concentrations for different materials, the actual concentrations were divided by the maximum observed value so that all data could be shown conveniently on a single figure. The data in Figure 6 suggest that the Boron concentrations will be reduced to 10 percent of the maximum value by approximately 5 PV of continuous leaching. Aeration following the first leaching did not cause the B concentration to recover significantly.

The maximum concentrations of F were observed in the USBM experiments, but the F concentrations in the background materials are also relatively high. In these leaching tests, the concentration of F was generally greatest in samples obtained at small throughput volumes, although this was not uniformily true. Figure 7 shows the leaching trend for F from USBM and R-5/Mahogany materials. These data show a relatively stable concentration of F of 20-25 mg/l after an initial reduction from a maximum of 75 mg/l for the USBM raw shale. Concentrations of F in leachate from the same column after 108 days of drainage and aeration did not differ significantly from the stable values obtained in the first cycle of leaching.

With the exception of the USBM material, the more-or-less stable concentrations of F obtained in the mined raw shales were between 1 and 10 mg/l. (Figure 8). The stable concentrations in both materials from the C-a site were found to be about equal to that for the soils. The Colony naturally leached shale and the Colony mined raw shale showed approximately equal F concentrations over most of the range of leachate volumes (Figure 8), even though the naturally leached material had previously been subjected to countless leaching cycles in its natural environment.

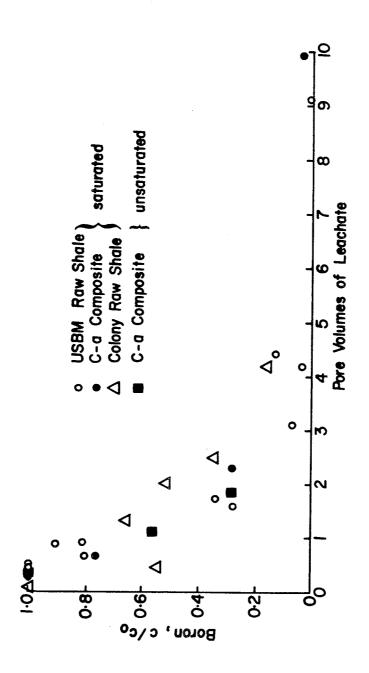


Figure 6. Leaching of Boron from raw shale.

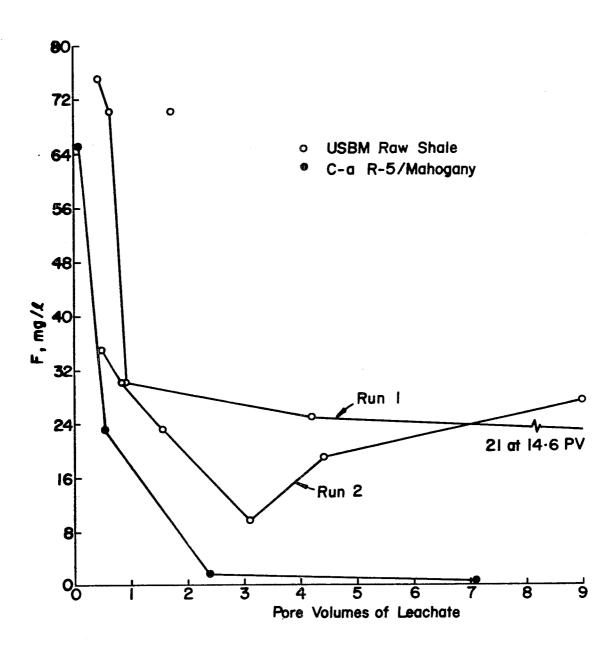


Figure 7. Leaching of F from raw shale. (Saturated columns)

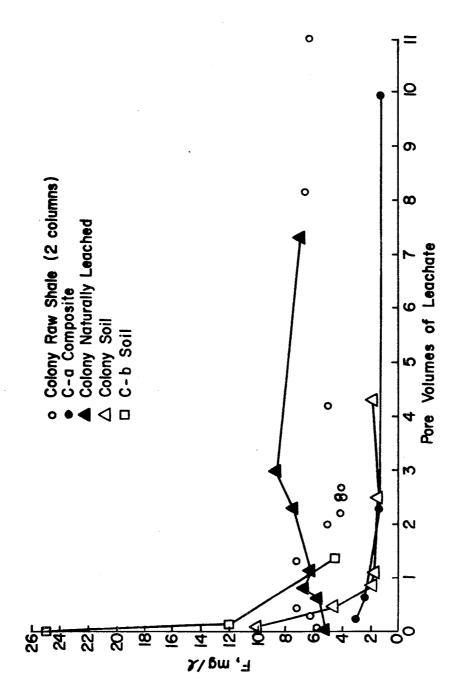


Figure 8. Leaching of F from raw shale. (Saturated columns)

BIBLIOGRAPHY

- Ham, R. K., M. A. Anderson, R. Stagmann, and R. Stanforth. 1979. Comparison of Three Waste Leaching Tests. EPA-600/2-79-071. Municipal Environmental Research Lab, Office of Research and Development, USEPA, Cincinnati, Ohio.
- Löwenbach, W. 1978. Compilation and Evaluation of Leaching Test Methods. EPA-600/2-78-095. Municipal Environmental Research Lab, Office of Research and Development, USEPA, Cincinnati, Ohio.
- Runnells, D. D., M. Glaze, O. Saether, and K. G. Stollenwerk. 1979.
 Release, Transport, and Fate of Some Potential Pollutants in Water
 Associated with Oil Shale. In Trace Elements in Oil Shale, Progress
 Report: 1976-1979, Contract No. EY-76-S-02-4017. Department of Energy
 by Center for Environmental Sciences, University of Colorado, Boulder,
 Colorado.
- Stollenwerk, K. G., and D. D. Runnells. 1977. Leachability of Arsenic, Selenium, Molybdenum, Boron, and Flouride from Retorted Oil Shale. Proc. Chem. Engr. Congress, AICHE, New York. 2:1023-1030.
- Stuber, H. A., J. A. Leenheer, and D. S. Farrier. 1978. Inorganic Sulfur Species in Waste Waters from IN-SITU Oil Shale Processing. Journal of Environmental Science Health. A13(9):663-675.
- Wong, A. L., and B. W. Mercer. 1979. Contribution of Thiosulfate to COD and BOD in Oil Shale Process Waste Water. ASTM Symposium on Analysis of Waters Associated with Alternate Fuel Production. Pittsburgh, PA.

APPENDIX TABULATED CHEMICAL DATA AND GRAIN SIZE DISTRIBUTIONS

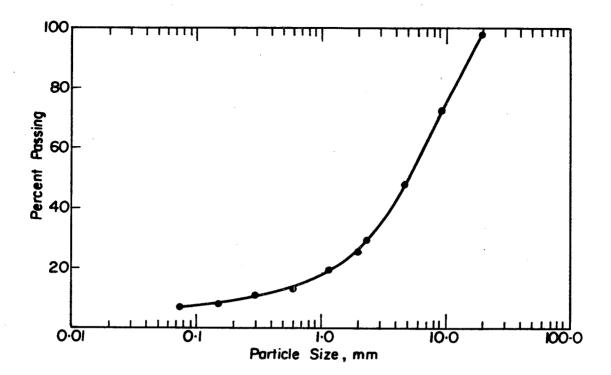


Figure A-1. Particle size distribution for USBM raw shale.

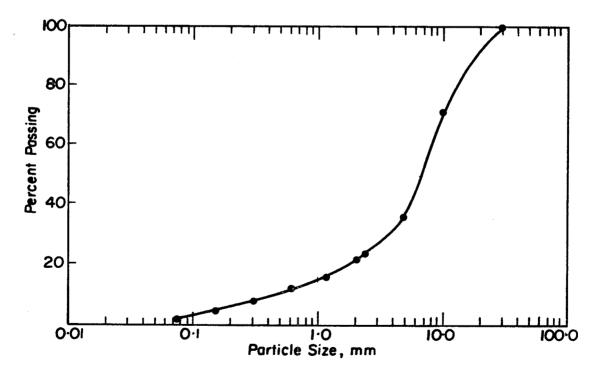


Figure A-2. Particle size distribution for Colony raw shale.

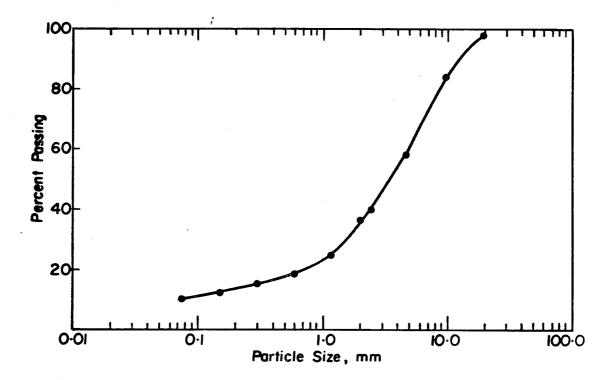
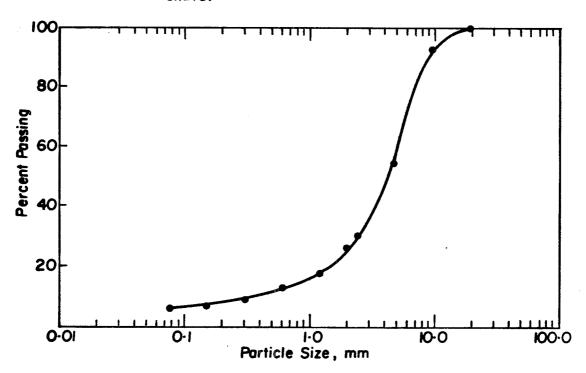


Figure A-3. Particle size distribution for C-a Composite raw shale.



-Figure A-4. Particle size distribution for C-a R-5/Mahogany raw shale.

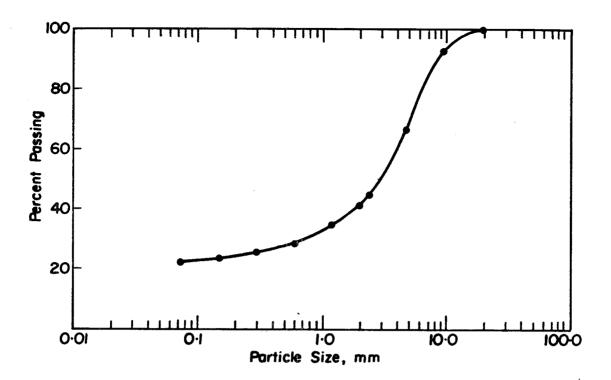


Figure A-5. Particle size distribution for Union naturally retorted shale.

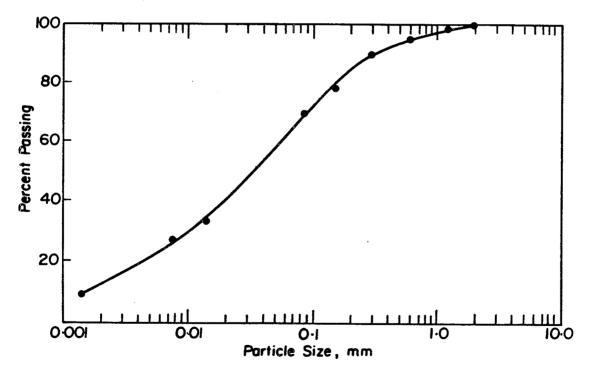


Figure A-6. Particle size distribution for C-b soil.

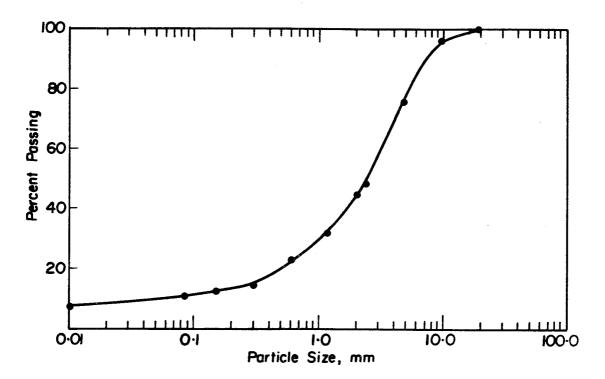
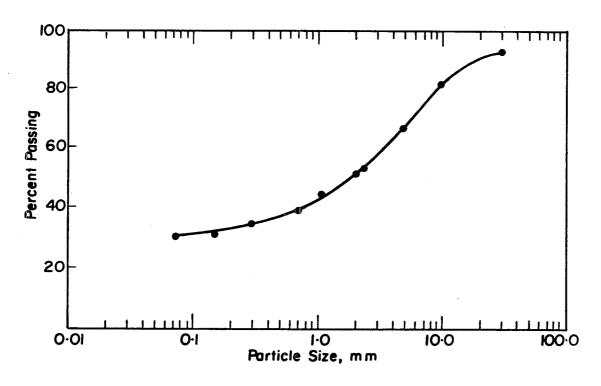


Figure A-7. Particle size distribution for Colony naturally leached shale.



A-8. Particle size distribution for Colony soil.

TABLE A-1 USBM RAW SHALE - RUN #1 (SATURATED)

				Volume of	Effluent		
Parameter	Units	0.43 PV	0.65 PV	0.90 PV	1.73 PV	4.18 PV	14.61 PV
A1	L/Bm	1.85	0.75	1	1.55		0.34
As	= =	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
ئ م	: \$	23.5	23.5		10.0		0.24
eg d	: =	71.0	0.15		0.10		/0°0
ag O	: =	<0.02	670.05		670.05		czn.u>
. 5	: =	029	550 250		200		36
3 5	=	430	200		130		^I.U
۳ ع 3	=	0.10	0.30		0.4/		0.1/
3 3	=	0.23	0.17		<0.025		<0.025
EC	umhos/cm	11000	0006		4500		280
ഥ	mg/1	75	70		70		21
Fe	,=	0.75	0.31		0.39		90.0
HCO3	E	243	247		270		83.1
β.	= :	<0.0905	<0.0005		<0.0005		<0.0005
× :	= ;	19	16		10		1.1
: בי	= :	2.4	2.5		1.6		0.02
Đ.	= :	1050	370		220		6.7
€ :	= :	2.9	2.6		1.68		0.075
운 :	= :	0.87	0.83		0.475	0.17	0.09
Na	= :	1430	009		400		<25
Z:	= :	0.48	0.48		0.33		<0.025
N03	= :	<25	<25		<25		<1.25
P	=	0.57	0.41		0.21		<0.04
H	1	æ.	.3		ر. ک		7.5
s S	mg/1	<0.01 	<0.01 0.01		<0.01	0.01	<0.01
Si	= :	7.5	ۍ ش		6.2	3.4	1.65
Su	= =	1.1	1.18		0.51	0.038	<0.025
504 196	= =	0000	7000	. 00101	***	0001	
25	: =	12600	13300	10500	00611	1300	103
Zn Zn	=	5.2	4.9	103 6.8	83 3.0	0.39	0.02
					ł		
Source: S	Saline Zone	of the Green	ı River Formation	tion - Bull	< Volume:	18700 cm ³	
hing	olution:	De-ionized Wa	iter	Meal	Leaching	₹	per hour
D ₅₀ Partic	le Size:	5 mm		Mea	n Residence	Time: 46 hours	٠,٠

TABLE A-2 USBM RAW SHALE - RUN #2 (SATURATED)

				Volume of	Effluent		
Parameter	Units	0.48 PV	0.86 PV	1.56 PV	3.08 PV	4.41 PV	9.11 PV
A1	L/gm	1.7	1.8	3.72	1.30	1	1.05
As	= :	<0.005	<0.005		<0.005		<0.005
с	= :	43.0	39.0		2.7		0.37
Ba G	= :	0.16	0.14		0.10		0.11
Be G	= :	<0.025	<0.025		<0.025		<0.025
g;	= ;	750	200		460		40
<u>.</u> :	: :	560	410		8.0		3.8
	= =	0.10	0.17		0.77		0.19
ئ ځ	: =	0.45	0.46		<0.025		<0.025
35	:	12000	0.30		<0.025		0.070
ח ני	mo/sommi	13000	11000		2/00		420
۵.	- }=		38		, c		6.73
HCG	=	287	321		172		60.00
Hg	=	0.0035	<0.0005		<0.0005		20 <0 0005
<u>'</u> ×	=	22	10		, r.		2000
ב	=	3.1	2.9		0.34		0.02
₩g	=	1350	1350		40		8.0
돌	= :	3.2	3.02		0.7		0.13
€:	= :	0.85	0.00		0.27		0.19
es :	: :	2100	2000		130		25
Ę	= =	0.60	0.50		0.11		<0.025
N03	: :	40	1		5.0		5.0
2 7	=	0.47	0.47		0.15		90.0
ī. 6	1	0.0	0.7		۲.۶		9./
e c	- /6m	<0.01 5.05	.0.0 .0.0		<0.01		<0.01
	=	1.28	1.12	0.47	4./5	0.0	2.6/
S04	=)	;		***		17.0
ZE S	= :	14850	13000	5050	2700	1950	70
10C	. =	41	130	109	42	95	15
117		0.0	7.0	3.1	0.55	0.02	0.01
Source: Sa	Saline Zone	of the Green Draw Site	River Formation	tion - Bulk	volume:	18700 cm ³	
hing	Jution:	onized	Water	Mean	Leaching	Rate: 0.014 PV	per hour
USO rartici	e Stze:	O IIIII		Mear	n Residence	Time: 74 hours	

TABLE A-3 COLONY RAW SHALE - RUN #1 (SATURATED)

				Volume	Volume of Effluent			
Parameter	Units	0.061 PV	0.45 PV	1.32 PV	1.99 PV	2.48 PV	4.20 PV	11.00 PV
A1	L/gm	<0.05	<0.05	<0.05		<0.05	<0.05	<0.05
AS &	= =	<0.005 0.75	<0.005 1.48	<0.005 1 79	<0.005	<0.005	<0.005	<0.005
a R	=	0.34	0.29	0.38		0.22	0.16	0.30
Be	=	<0.025	<0.025	<0.025		<0.025	<0.025	<0.025
ca :	= :	1110	1510	830		530	200	11
ចទ	= =	2.2	22.0	ເຄືອ		3.7	3°0	1.3
င်း	=	<0.025	<0.025	<0.025		<0.025	<0.025	<0.025
3	= .	0.16	0.34	0.12		<0.025	<0.025	<0.025
ည ယ	umhos/cm	4200 F 7	4600	3100		2300	900	460
با ـ	- /6	<0.03 <0.03	<0.03 <0.03	0.89		0.47	0.15	<0.03 <0.03
HCO,	=	• 266	304	558		385	250	178
£	-	<0.0005	<0.0005	<0.0005		<0.0005	<0.0005	<0.0005
∠ :	= =	19	18	11		4.9	2.3	3.1
- B	=	72	120	140		50.143	18	14
둔	= :	0.24	0.28	1.64		1.91	0.82	0.17
Q <u>2</u>	= =	0.16	0.11	0.27		0.31	0.36	0.65
g .c	I	0.087	0.080	00.02 <0.02		0.07	13 <0.05	1/ <0.05
NO,	=	25.0	25.0	<2.5		<2.5	<2.5	<2.5
P _b	=	0.12	<0.05	0.20		0.19	0.095	0.08
E.9	 	, ć	7.34	7.62		, 85 5	7.83	7.23
	- }=	2.95	9.47	10.58		5.89	4.54	4.22
rs s	= =	0.24	0.48	0.47		0.27	0.17	0.12
201 104	: =	4590	0009	3250	2860	2400	770	400
T0C	=							
Zn	=	0.29	0.62	0.58	0.50	0.31	90.0	0.04
Source: Mi Leaching So	ne Stock Jution:	Pile - Parach De-ionized Wa	ute Creek iter		Bulk Volume: Pore Volume:	18700 cm ³ 4290 cm ³		
U ₅₀ Partici	e Size:	D./ mm			Mean Leaching	g Rate: 0.0	10 PV per ho	ur
					Mean Kesidenc	ce ilme: IU	3 nours	

TABLE A-4 COLONY RAW SHALE - RUN #2 (SATURATED)

				Volume	Volume of Effluent			
Parameter	Units	0.13 PV	0.30 PV	2.21 PV	2.48 PV	2.69 PV	8.14 PV	12.54 PV
A1	ma/1	<0.05	<0.05	<0.05		<0.05	<0.05	<0.05
As	;=	0.002	0.005	0.005		0.005	0.005	0,005
B	=	0.44	2.2	1.25		1.08	0.2	0.2
Ва	= :	0.48	0.32	0.25		0.10	0.21	0.19
Be •	= ;	<0.025	<0.025	<0.025		<0.025	<0.025	<0.025
್ಷ ಕ	= =		1550	730		640	51	44
58	= =	8.7	8.0	8.0		4.0	1.3	1.4
35	: =	0.11	0.03	0.60		1.1	0.49	0.94
53	=		0.025	960.0		<0.020 <0.025	<0.025	<0.029 <0.025
	umhos/cm		5400	2900		2500	290	330
	L/gm		6.2	4.0		4.0	9.9	ນີ້
я. Э	,= :	<0.03	<0.03	0.03	0.02	0.04	<0.03	<0.03
HCO3	= =	150	50	234		223	111	105
g,	: =	<0.0005	<0.0005	<0.0005		<0.000	<0.0005	<0.0005
∠ <u>"</u>	: =	59 0 068	18	8.0 0.0		3.1	1./	2.3
υŒ	=	40.000 40.000	140	85.003		55.00	7.02	50.7
Σ	=	0.093	0.26	1.16		1 26	2.0	0 125
Q.	=	0.13	0.29	0,23		0.24	0.23	0.45
Na	=	06	145	93		09	10	14
Z	Ξ ;	0.064	0.10	<0.05		<0.05	<0.05	<0.05
NO3	= :	3,5	<2.5	<2.5		<2.5	<0.4	6.0
- -	=	0.14	0.27	<0.05		<0.05	0.052	<0.05
E.		7.09 6.09	7.06	7.64		7.92	7.87	8.18
ς υτ	- / <u>B</u>	<0.01 4.75	0.0I			<0.0I	40.0J	<0.0I
- V	=	0.26	0.67	0.02		0.41	0.13	0.12
20 7	=	•				÷.	2	
ZOT.	= :	3660	7160	3380	3140	2840	310	230
Zu	: =	0.10	0.52	0.68	0.54	<0.04	<0.04	0.53
Source: M Leaching So D ₅₀ Partic	Mine Stock Solution: cle Size:	Pile - Parach De-ionized Wa 6.7 mm	ute Creek ter		Bulk Volume: Pore Volume: Mean Leaching Mean Residenc	18700 cm ³ 4290 cm ³ 1 Rate: 0.01	11 PV per hour hours	£

TABLE A-5 C-a COMPOSITE - RUN #1 (SATURATED)

			Volume of	Effluent	
Parameter	units	0.25 PV	0.64 PV	2.29 PV	9.96 PV
Al	ma/1	<0.05	<0.05	\$0 O \$	-0 05
As	5=	<0.005	<0.005	<0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	20.0>
· —	=	1.45	1.10	0.40	90.0
Ba	=	0.093	0.046	0.051	0.02
Be	=	<0.025	<0.025	<0.025	<0.025
Ca	=	425	370	100	18
2	=	38	6.8	0.3	0.3
Š	=	<1.0	<1.0	4.0	<1.0
ິນ	=	<0.025	<0.025	<0.025	<0.025
3	=	<0.025	090.0	<0.025	<0.025
ည္	mmhos/cm	8200	2600	820	170
اجا	mg/1	3.0	2.4	1.4	1.3
e :	= :	<0.05	<0.05	<0.05	<0.05
HC03	= :	239	180	165	87
오:	= =	<0.0001	<0.0001	<0.0001	<0.0001
∠:	= :	34	10	2.0	0.4
: ت	= =	0.68	0.42	0.08	0.03
Ē,	: =	16	415	48	6.9
Ē	= =	<0.05 0.05	0.24	0.062	<0.05
2	: =	2.2	6.0	0.475	0.100
5 Y	=	0.47	000	ک بر	٠ د د د د
- S	=	.0.05 140	60.03		.05 .05
100	: =	140	7,	\$0.5 0.5	0.5
2 2	:	7.25	0.20	0.0/5	
<u>.</u>	[/ bm	67.7	7.09	96.7	26.00
	- - - -	10.003	10.00	10.003	, vo.003
Š	=	2 !	2 !		
20%	=				!
SOT	=	9150	6410	1580	440
10 C	=		!	1	•
Zn	=	0.50	1.5	0.30	0.05
Source:	Composite of Rai From G Level In	sed Bore R-5 Zone	Cuttings Bulk to Pore	Volume: 18700 cm ³	
Loaching	Surface - Lease	ease Tract C-a	Mean	Ď.	0.015 PV per hr.
Dsn Particle	Size:	ושש	меап	Kesidence ime:	67 hours

TABLE A-6 C-a R-5 / MAHOGANY - RUN #1 (SATURATED)

			Volume of Effluent	Effluent	
Parameter	Units	0.062 PV	0.519 PV	2.38 PV	7.10 PV
A1	mg/1	:	0.70	0.30	2.00
As	=	<0.005	<0.005	<0.005	<0.005
m (= :	0.59	0.035	<0.025	<0.025
gg G	: :		0.11	0.088	0.16
ge G	: :	<0.025	<0.025	<0.025	<0.025
35	: =	1430	375	006	240
<u>.</u> 5	=	175		χ. γ.	1.9
ું કુ	=	c/1 .	312	346	1/4
5 G	=	33	<0.025 0.16	<0.029	<0.025
2	umhos/cm	2000	0096	3400	3400
Ŀ	mg/1	65	23	1.9	0.8
Fe	. =	<0.05	<0.05	<0.05	<0.05
HCO3	= :	22	9.4	7.7	3.0
훈:	= :	<0.0001	<0.0001	<0.0001	<0.0001
∠.	= :	280	180	20	16
: ت	= :	0.11	0.07	90.0	0.03
ω.	= :	; ; ;	<0.7	<0.7	<0.7
Ē:	: :	0.35	<0.05	<0.05	<0.05
<u>ا</u> ع	= =	1 2	0.20	0.225	0.10
۳	: :	3600	1700	310	9
- C	= =	: ;	0.085	<0.05	<0.05
	= =	95	40	0.6	4.0
5 :	•	1 ;	0.15	<0.05	0.12
Ξ,	1 :	11.14	11.75	11.88	11.98
s e	l/gm	<0.005	<0.005	<0.005	<0.005
	: =	;	5.94	1.65	1.20
Z 0	: =	•	! !	:	! !
TDS TDS	=	1000	6880	1340	1160
1 2 2 2 3 2 3 3	=	20061	0000	7340	0911
Zn	=	<0.01	<0.01	0.03	0.08
Source: R-	R-5/Mahogany Zo	Zone -	Bulk Vo	Volume: 18700 cm ³	
Le:	Lease Tract C-a	B		: 7463 cm ³	
	Size:	06-1011250 Maler 4.2 mm	Mean Le	Leaching Kate: U. Residence Time: I(.UU93 PV per nr. 108 hours

TABLE A-7 C-6 SOIL - RUN #1 (SATURATED)

			Volume of Effluent	יות בור	
Parameter	Units	0.0084 PV	0.13 PV	0.46 PV	1.35 PV
A1	1/gm	<0.05	<0.05	<0.05	<0.05
As R	= =	<0.005 0.65	. <0.005	<0.005	<0.005
. e	=	0.169	0.240	0.030	0.070
Be a	=	<0.025	<0.025	<0.025	<0.025
ီဒီ	=	330	75	11	5.5
5	=	520	23	2.4	. 8.
°03	=	1	1.3	1.0	80
ر ر	= :	0.069	<0.025	<0.025	<0.025
3	=	0.28	0.25	0.075	<0.025
<u>ස</u>	mhos/cm	;	3000	006	840
u. 1	mg/1	52	12	4.6	4.5
ē.	= :	0.17	0.42	0.38	0.10
£03	= :	!!	846	203	481
£	= :	<0.0001	<0.0001	<0.0001	<0.0001
∠:	= =	22	21	2.5	1.3
5 :	= =	0.08	0.05	0.02	0.05
ğ	: :	145	35	ω. Θ.	2.6
E S	: =	0.0/5	0.16		0.05
2 =	: =	0.175	0.43	01.0	40.05
ρ.: .:	=	0007	040	730	017
E \$: =	cn.05	0.0/5	د٥٠.٥٠	.0°.
NO3		30	13	٥.٠	P. 1
ם י		0.31	07.0).IC	0.0
E G		8.0I	7.43	7.54	8,49
S.E	- /Bш	c00.05	<0.005	c00.0>	c00.05
<u>,</u> 5	: =	11.0	7.07	11.8	711./
E 6	=	:	:	1 1	:
50¢	: =		0010	•	
201	: =	:	3/00	1200	ncnī
2 2	=	0 04	7.	000	ט
117		to•0	0.00	0.50	60.0
Source: Cot	Cottonwood Gulch	:h- -h-	Bulk Volume:	18700 cm ³	
Leaching Solu	tion:	യ	Leaching	Rate: 0.0018 PV	V per hour
TOTAL CHE	140.		Most Conference		

TABLE A-8 COLONY NATURALLY LEACHED - RUN #1 (SATURATED)

				Volume of	of Effluent			
Parameter	Units	0.028 PV	0.61 PV	0.81 PV	1.13 PV	2.29 PV	2.97 PV	7.30 PV
Al	mg/1	<0.05	0.08	0.076	0.050	<0.05	<0.05	<0.05
As B	= =	<0.005 0.365	<0.005	<0.005	<0.005	<0.005 0.190	<0.005 0.170	<0.005
Ba Ba	=	0.495	0,53	0.29	0.22	0.15	0.088	0.120
Be	=	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Ça	= :	500	320	170	110	31	25	27
	= =	/1	7.7 7.7 7.7	15 0 20	0°2	1.5	7.3 0.63	9. 0.
35	=	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
3	=	0.31	0.23	0.18	0.15	0.08	0.05	0.039
ដ	nmhos/cm	4200	2900	1600	1300	380	310	240
- H	1/BW	2.5 0 03	5.7 <0.03	\°0.03 <0.03	0.03 <0.03	0.08	0.08	6.03 0.03
HG3	=	233	209	209	192	214	189	136
Hg.	= :	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
⊻:	= =	57	11	3.9	1.9	0.93	0.83	0.99
_ 2	: =	0.012 366	0.0I	120	73	\$0.00 \$0.004	17	10.004
Đ S	=	203	11	0.11	0.11	0.082	0.068	0.070
2	=	0.74	0.63	0.64	0.59	0.20	0.11	0.075
Na	=	350	210	160	120	48	33	14
Z	= :	90.0	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
803 1	= =	245	. 15	5.0	5.0	1.3	8.0	×0.3
운 :	=	0.22	0.315	0.320	0.350	0.140 7.81	0.130	0.1/0
Ξú			7.7	, c,	4.6	7.01		
y ve	- - - - - - - - - - - - - - - - - - -	14 72	12.01	10.01	38.38	6.71	6.78	7.61
. S	=	0.67	0.44	0.25	0.16	0.054	0.047	0.041
504	=				,	,	į	,
TDS	= =	4760	3160	2090	1180	300	220	120
Zu Zu	: =	0.11	0.22	0.21	0.30	0.12	0.24	0.07
Source: T Leaching S D ₅₀ Partic	ailus Slo olution: le Size:	Slope Material - nn: De-ionized Wa e: 2.5 mm	Parachute Creel ater	ek	Bulk Volume: Pore Volume: Mean Leachin Mean Residen	18700 cm ³ 7090 cm ³ 19 Rate: 0.00	064 PV per ho 5 hours	our

TABLE A-9 UNION NATURALLY RETORTED - RUN #1 (SATURATED)

			Volume of Effluent	Effluent	
Parameter	Units	0.05 PV	0.39 PV	1.33 PV	5.23 PV
A1	mg/1	<0.05	<0.05	<0.05	<0.05
As	,= :	<0.005	<0.005	<0.005	<0.005
න 1	= :	0.37	0.24	0.210	0.165
Ba	= :	0.12	0.053	0.037	0.028
g,	= :	<0.025	<0.025	<0.025	<0.025
డ్డ్ క	= =	45		13	10
58	: :	15	5.8	1.0	
	= :	1.1	<1.0	=	1.3
క్ క	= =	0.40	0.21	0.031	<0.025
35	:	0.16	0.06	<0.025	<0.025
יו ני	umnos/cm ma/1	1300	740	420	300
_ <u>U</u>	- /fill	4.0	4.0	o. c.	χ, ς,
יים ביים	=	50.03	60.05	50.05	<0.05 150
H	=	50 000 V	234 40 000	747	100
	=	7.	15,0001	11	000.00
: "5	=	0.38	0.25	0.18	0.14
Mg	=	103	62	09	30
M	=	0.05	<0.05	<0.05	<0.05
Q ∶	= :	0.32	0.25	0.125	0.065
S.S.	= :	44	22	16	12
Z	= :	<0.05	<0.05	<0.02	<0.05
803 2.03	: :	4.0	0.8	2.8	0.5
2 7	•	0.10	0.10	0.105	0.05
E.	: 5	7.54	7.20	68.7	8.12
o ce	- /BIII	<0.005	.00.005	<0.005	.0.03 0.03
- <i>5</i>	=	11	OŦ	7.1	x. x.
0.000	=	!	!	!	!
10\$	=	1200	620	460	560
T0C	=		<u>;</u>	}	
Zn	=	0.08	0.15	0.10	0.02
Source: Near Leaching Solu D ₅₀ Particle	Union I ution: Size:	ortal ized W	- Parachute Creek ater		.8700 cm ³ 330 cm ³ tate: 0.007
				Mean Kesidence	e ilme: 133 nours

TABLE A-10 COLONY SOIL - RUN #1 (SATURATED)

	4.30 PV	 <0.05 <0.055 <0.025 <0.025 <0.025 <0.025 <0.025 <0.025 <0.025 <0.075 <0.075 <0.075 <0.075 <0.075 <0.075 <0.01 <0.01 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.07 <0.07 <0.05 <0.05 <0.05 <0.05 <0.01 <l< th=""><th></th></l<>	
	2.49 PV	0.07 <0.005 0.12 <0.025 200 1.4 1.04 <0.075 2000 1.4 0.18 1.4 0.18 1.92 0.09 1.40 0.09 1.40 0.09 0.09 1.4 0.09 1.40 0.09 0.09 0.04 <0.005 0.04 <0.05 0.04 <0.05 1.40 0.09 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.04 <0.05 1.40 0.17 6.2 0.09 1.40 0.17 6.2 0.04 <0.05 1.40 0.04 <0.05 1.40 0.04 <0.05 1.40 0.05 1.40 0.07 1.40 0.07 1.40 0.07 1.40 0.08 1.40 0.09 1.40 0.00 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.5	
	1.50 PV	<pre><0.05 <0.055 0.68 0.22 <0.025 450 0.1 0.46 <0.025 0.05 175 0.52 175 0.52 175 0.05 170 0.9</pre>	
of Effluent	1.11 PV	5 Summer commercial control of the c	
Volume	0.83 PV	 <0.05 <0.005 <0.005 <0.020 <0.025 <0.015 <0.01 <0.05 <0.05 <0.05 <0.05 <0.01 <0.05 <0.01 <0.05 <0.01 <0.05 <0.05 <0.01 <0.05 <0.05	
	0.47 PV	0.15 <0.005 0.69 0.20 <0.025 650 10 0.48 <0.025 0.16 7500 4.5 0.03 270 0.03 0.04 0.06 0.06 0.06 0.07 0.07 0.07 0.07 0.07	
	0.10 PV	<pre><0.05 <0.005 0.70 0.40 0.40 <0.025 960 200 0.17 <0.025 0.38 9000 10 0.01 233 <0.005 270 0.47 1450 0.84 340 0.06 180 0.27 7.1 <0.01 7.33 <0.025 0.65 Portal - Parach De-ionized Wat 1.8 mm</pre>	
	Units	mg/1 mg/1 mg/1 mg/1 mg/1 cle Size: 1	
	Parameter	A1 As As Ba	

TABLE A-11 USBM-RAW SHALE - UNSATURATED

		Volume	ne of Effluent	
Parameter	Units	0.31 PV	14.5	₽
A1		4 15	7 5.1	
As	· =	•	#C. C.	+ C
B	=	10.08	0.00	3 ~
Ва	=	0.065		7. 15.
Be .	± :	<0.025	Q.025 △0.025	: 22
Ca	=	400	9)
5	=	100	61	
දි	=	0.4	0.2	
ູ່ບໍ	= :	<0.025	<0.025	25
38		0.26	0.04	4
ם נ	munos/cm	9009	250	
<u>. L</u>	I/gm	24	<0.5	
E C	: =	. <0.1 223	<0.1	
。 至	=	<0.0001	133	101
· '~	Ξ.	14	,	5
::	Ξ	1.7	0.05	ın
ğ.	= :	420	13	
Ę.	= :	2.5	0.19	0
O N	: =	0.48	0.06	
ž	=	060 ·	40	
N03	=	17.		•
Pb	=	0.29		,
표	1	7.45	7,35	
S. Se	mg/1	<0.005	<0.00	5
2 5	= =	3.05	<0.05	
<u>ج</u> د	= =	!	!	
304 TNA	: =		700	
10C	=	! !	304	
Zn	=	2.5	0.11	
Source: Saline Fermat	Zone of tion-USBM,	en River Draw Site	870	0 dd 3
	Size: 5 mm	בם רבו. בי	0.052 PV per	٦. ايا

TABLE A-12 C-a R-5 / MAHOGANY - UNSATURATED

			Volume of Effluent	ent
Parameter	Units	0.051 PV	0.88 PV	14.4 PV
Al	1/ Dm	3 53	1 43	0
Δc	}=		£. ¢	71.1
2 0	=	00.00	000.05	c00.0>
	=	0.10	<0.025	<0.025
g 6	=	0.27	0.2/	0.17
e 6	: :	<0.025	<0.025	<0.025
<u>s</u> :	= ;	1510	704	180
<u>.</u>	=	300	22	7.5
දි	=	<0.1	246	241
် င	=	0.029	0.034	0.02
3	=	0.69	0.032	<0.025
2	umhos/cm	37000	6500	7
LL.	I/bm	208 22	<55.0	
Fe	;=	<0.1	0.0	`
HC03	=	403	: [
, E	=	<0.0001	<0.001	•
,×	=	640	140	
ij	=	0.0	90.0	
₩	=	108	9.7	•
M٩	=	<0.05	<0.05	
æ	=	5.18	1.76	
Na	=	7710	820	
Z	=	0.35	0.047	
NO3	=	. 172	70	9.6
Pb.	=	0.83	0.74	<0.05
돐	:	6.93	11.58	11.65
Se	mg/1	<0.005	<0.005	<0.005
Si	= :	23.28	7.05	2.7
Sn	= :	1 1 1	!	1 1
204	= :			
T05	= :	30130	6365	610
20	=		1	!
Zu	=	0.02	0.09	<0.02
ce: hing	/Mahogan ution:	y Zone-Lease Tract G-a De-ionized Water	Bulk Volume: Pore Volume:	18700 cm ³ 7463 cm ³
uso rarticle	Size: 4.2 mm		Mean Leaching	Rate: 0.036 PV
				חסוו ושלו

TABLE A-13 C-a COMPOSITE - UNSATURATED

Parameter	Units	0.13 PV	1.13 PV	1.84 PV	19.54 PV
A.	l/gm	<0.05	0.69	0.31	0.058
As	;=	<0.005	<0.005	<0.005	<0.005
മ	=	1.97	1.1	0.56	<0.025
ga	=	0.22	0.157	0.16	0.075
Be	=	<0.025	<0.025	<0.025	<0.025
ဗ ဗ	= :	970	536	230	21
5	= =	130	ω.	1.1	0.83
65	: =	0.7	0.5	0.4	
5 3	=	0.44	0.057	0.031	0.052
B B B	umhos/cm	7500	2000	2900	
LL.	L/gm	<0.5	2.4	1.4	
F.	;=	<0.1	<0.1	.0.1	
HCO3	= :	1026	452		
훈:	= =	<0.0001	<0,0001		
∠ ≟	: =	63 0 70	16 0 33		
_ \$	=	820	210		
e E	=	0.40	0.30		•
운	=	1.68	1.25		
S.	=	1240	211		
ž	= :	0.16	0.11		
2 2	= :	52	II 'II		
<u>.</u>	•	0.77	0.79	0.4/	0.055
핊		7.03	30.00	•	
. ve	- " "	19.58	24.7		8,12
	=		: !		•
20,	=				
105	= :	9450	3710	764	164
100	= :	i		6	ç
Zn	-	0.31	0.42	0.09	ZU.U>
Source:	ite of	Raised Bore Cuttings -5 Zone to Surface -	tings From		ᆼᆽ
Leaching	Lease Tract C-d Solution: De-i	L-d De-ionized Water		Mean Leaching	Kate: 0.043 FV per hour
•					-

TABLE A-14 UNION NATURALLY RETORTED - UNSATURATED

		Volume of Effluent
Parameter	Units	0.09 PV
Α1	mq/]	0.10
As	5=	<0.005
	=	0.39
Ba	=	0.35
Be	=	<0.025
Ca	=	49
15	=	9.5
ිට්	=	22
ر ت	=	0.71
ŋ	=	0.33
监	umhos/cm	1200
u.	1/gm	6.6
Fe	= :	<0.0001
HC03	= :	585
- Rg	= :	
ᅶ	= :	/4
Ľ	= :	0.51
Mg	= :	108
¥:	= =	<0.05 0.05
Q:	: =	75
ر د د د د د د د د د د د د د د د د د د د	=	20 C
- G	=	
F03	=	0.16
2 =	;	8.81
9	ша/1	<0.005
Si	; }=	19.06
Sn	=	!
504	= ;	
TOS	± :	1085
70C Zn	: =	0.04
Source: Near Union Mine	Mine Portal-	Bulk Volume: 18700 cm ³ Pore Volume: 9330 cm ³
Leaching Solution:	De-ionized Water	Leaching Ra
D ₅₀ Particle Size:	1.9 mm	0.051 PV per hour
2		

Source: Near Union Mine Portal-Parachute Creek Leaching Solution: De-ionized Water D₅₀ Particle Size: 1.9 mm

TABLE A-15 LEACHATE QUALITY AFTER AERATION

		USBR Raw Shale After Drainage	w Shale rainage	Colony Nat. Leached After Drainage	Colony R After D	Raw Shale Drainage	Colony Soil After Drainage
Parameter	Units	0.33 PV	6.02 PV	0.06 PV	0.093 PV	7.89 PV	0.15 PV
A1	mg/1	2.75	0.40	0.17	0.75	0.11	0.37
As	;= :	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
~	= :	3.9	0.34	0.16	0.87	<0.025	0.76
Ba	=, ·	0.061	0.075	0.19	0.11	0.0	0.57
Be	= :	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
ල	= :	458	47	42	400	40	190
58	= =	22	4.1	1.4	11	1.1	2.2
۳ ک	: :	0.3	0.9	0.5	0.2	0.4	2.9
క్ శ	: =	0.033	0.038	<0.025	\$.	0.014	0.022
3 5	: 1	czn.0>	<0.025	0.064	0.11	<0.025	0.190
3.	pullos/cm	0400	9	460	2500	240	1/00
. <u>.</u>	- /Bm	19	21	0.4	4.2	4.4	1.2
a S	=	175	138	20¢	<0.1 123	111	780 780
Hg .		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
<u>~</u>	=	19	1.1	4.0	10	1.0	80
Ξ:	= :	0.22	0.05	0.02	0.0	0.02	0.18
Mg:	= :	>460	16	28	140	5.5	110
Ē	= :	0.33	0.14	<0.05	0.95	0.074	<0.05
운	= =	0.86	0.19	0.13	0.44	0.0	<0.05
ر د ج	: =	310	31.	16	50	9.0 0.0	18 18
E S	: =	0.51 14	<0.05	\$0.05 40.05	0.059	<0.05 2 = 2	<0.05
	=	<0.05	0.073	0.12	0.53	0.088	0.23
舌	i	7.51	8.06	7.60	7.50	7.83	8 5
Se	mg/1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Si	<u>,=</u>	4.7	4.09	10.03	6.15	2.12	16.8
s.	= :	:	;	:	:	!!	1 1
204 405 405	: : :	6130	230	350	2685	110	1470
Zu	: =	3.0	0.02	0.02	0.44	<0.02	<0.02