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Project Summary

Reconnaissance Study of Leachate Quality from Raw Mined Oil Shale—Laboratory Columns

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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. Since 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.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In this study, leaching was conducted by passing de-ionized water through columns of each material. All of the materials described previously were subjected to saturated leaching testing, and most were also subjected to unsaturated leaching. Samples of the effluents were collected and subjected to chemical analyses, which were performed at the analytical laboratory in the Chemistry Department at Colorado State University under the direction of Dr. Rodney Skogerboe. The electrical conductivity of the effluent from the columns was measured at short time intervals by means of a flow-through probe and a data logger. Grain size analyses were made for each material. Samples for the experiments were obtained through the cooperation of the Rio Blanco Oil Shale Company, the Colony Development Project, the U.S. Bureau of Mines, Occidental Oil Shale Corporation and Union Oil Company. Funding for this study was provided through EPA Grant No. R806278.

In one set of tests, the initial saturated leaching was followed by a second saturated leaching after a period of drainage and aeration. The tests on the soils and previously exposed shales were conducted to provide a basis for comparison of the results from the raw mined shales. The results indicate that leachates from mined shales will contain dissolved solids at levels substantially greater than the background levels as indicated by the soils and previously exposed shales. This study indicates that the trace elements Al, B, F, Zn, Pb and possibly Mo occur in the leachates from some of the mined shales in quantities significantly greater than in the leachates from the background materials. All other trace elements considered in this study were present in the effluents from the mined shales in about the same concentration as observed in the leachates from the soils and previously exposed shales.

Description 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 is the trimmings from the service shaft.

A sample of unretorted shale from the Mahogany zone was obtained with the cooperation of Colony Development Operations from the mine on Parachute Creek. This sample was extracted from a stockpile of minus 1/2 inch material that was mined approximately 6 years ago. This sample is called Colony raw shale through the report.

The fourth raw shale sample was obtained from the U.S. 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.

Results

A summary of the range of observe concentrations for all parameter measured is presented in Table 1. Tabl 2 compares the maximum concentra tions of some of the more significan trace elements in raw shale leachate with maximum concentrations fron naturally occurring materials. The con centrations of Al, B, F, Mo, Pb, and Zr were found to be significantly greater ir the leachates from some of the mine shales than in the correspondin samples from the previously expose materials. The levels of all other trac elements produced by the mined shale were comparable to those observe from the soils and previously expose shales. Elevated concentrations of Al, B F, and Zn were measured in leachate from the USBM raw shale. The larges values of Al concentrations were produced from the unsaturated leachin tests and the second cycle of saturate leaching. No consistent relation between Al concentration and the volum of effluent was found.

Fluorine concentrations in the leachates from the mined shales wer generally greater than from the previously exposed materials. Concentrations of F decreased rapidly with the firs pore volume of effluent from the USBM and C-a R-5/Mahogany mined shale and then approximately stabilized. A

Table I. *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	----
As	"	<0.005	<0.005	<0 005	<0.005	<0.005	<0.005	<0.005	<0 005	0 05
B	"	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	----
Ba	"	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
Be	"	<0 025	<0 025	<0 025	<0 025	<0 025	<0 025	<0.025	<0 025	----
Ca	"	36-750	40-1550	180-1510	18-970	25-500	10-49	40-960	6.5-330	----
C1	"	<1 0-560	1 1-22	1.9-300	0.3-130	0.8-71	1 1-15	0.1-200	1 8-520	----
CO_3	"	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	----
Cr	"	<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
Cu	"	<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
EC	µmhos/cm	280-13000	240-5400	1900-37000	125-8200	240-4200	300-1300	370-9000	840-3000	----
F	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	<0.05	<0.01-0.52	0.1-0.42	0.3
HCO_3	"	83 1-321	50-558	3 0-403	82-1026	136-233	168-585	152-480	481-846	----
Hg	"	<0.0001-0.0035	<0 0005	<0 0001	<0.0001	<0 0005	<0.0001	<0 0005	<0.0001	0.002
K	"	1 1-22	1 7-59	8.2-640	0 4-34	0.83-57	9 2-74	25-270	1 3-22	----
Li	"	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	----
Mg	"	6 7-1050	5 5-140	0 675-108	4 9-820	17-365	30-108	17-1450	2.6-145	----
Mn	"	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
MO	"	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	----
Na	"	<25-1430	5 8-145	27-7710	4 3-1240	14-350	12-75	3.8-340	210-2050	----
Ni	"	<0.025-0.60	<0 05-0 10	0.047-0 085	<0 05-0 16	<0.05-0 06	<0 05	<0 05-0 07	<0 05-0 075	----
NO_3	"	<1 25-40	0.9-25	4-172	<0.5-140	<0.3-245	0.5-8	<0.2-180	1 4-30	10
Fb	"	<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 05
pH	---	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	mg/1	<0 01	<0 01	<0 005	<0 005	<0.01	<0.005	<0.01	<0 005	0 01
Si	"	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	----
Sn	"	<0.025-1.28	0.12-0 67	----	----	0.041-0 67	----	<0.025-1 37	----	----
SO_4	"	20-5700	28-5150	5-6600	7 9-6100	15-2650	9-128	60-4200	23-860	250
TDS	"	70-13300	110-7160	610-30130	164-9450	120-4760	460-1200	250-7450	1050-3760	500
Zn	"	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

Table 2. *Comparison of Trace Element Concentrations from Raw Mined Shales with Those from Soils and Previously Exposed Shales*

	Raw Mined Shales		*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*	*----*
As	*<0.005*	*----*	*<0.005*	*----*	*0.05*
B	*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*	*----*	*<0.025*	*----*	*----*
Cr	*0.68*	*USBM, #1 Saturated*	*0.71*	*Union Nat. Ret.*	*0.05*
Cu	*0.69*	*C-a R-5/Mahog., Unsat.*	*0.38*	*Colony Soil*	*1.0*
F	*75*	*USBM, #1 Saturated*	*25*	*C-b Soil*	*1.8*
Fe	*1.8*	*USBM, #1 Resaturated*	*0.52*	*Colony Soil*	*0.30*
Hg	*0.0035*	*USBM, #2 Saturated*	*<0.0005*	*----*	*0.002*
Li	*3.1*	*USBM, #2 Saturated*	*0.51*	*Union Nat. Ret.*	*----*
Mn	*3.2*	*USBM, #2 Saturated*	*0.97*	*Colony Soil*	*0.05*
Mo	*5.18*	*C-a R-5/Mahog., Unsat.*	*0.84*	*Colony Soil*	*----*
Ni	*0.60*	*USBM, #2 Saturated*	*0.075*	*C-b Soil*	*----*
Pb	*1.9*	*USBM, #1 Saturated*	*0.38*	*Colony Soil*	*0.05*
Se	*<0.01*	*----*	*<0.01*	*----*	*0.01*
Si	*23.28*	*C-a R-5/Mahog., Unsat.*	*20.7*	*C-b Soil*	*----*
Sn	*1.28*	*USBM, #2 Saturated*	*1.37*	*Colony Soil*	*----*
Zn	*6.8*	*USBM, #1 Saturated*	*0.65*	*Colony Soil*	*5.0*

similar 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 do not exceed 100 times drinking water standards for measured parameters. The maximum concentrations of Cr, F, Fe, Hg, Mn, NO_3, Pb, S_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.

Leaching of Common Species

The most convenient indicator of the quantity of the common species Ca, Mg, Na, Cl, HCO_3, 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 1 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 resaturated run.

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 maximun. In the preparation of Figure 1 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. The full report contains similar figures for leaching characteristics of USBM and Colony raw shales, Colony naturally leached shale, and Union naturally retorted shale under both saturated and unsaturated conditions.

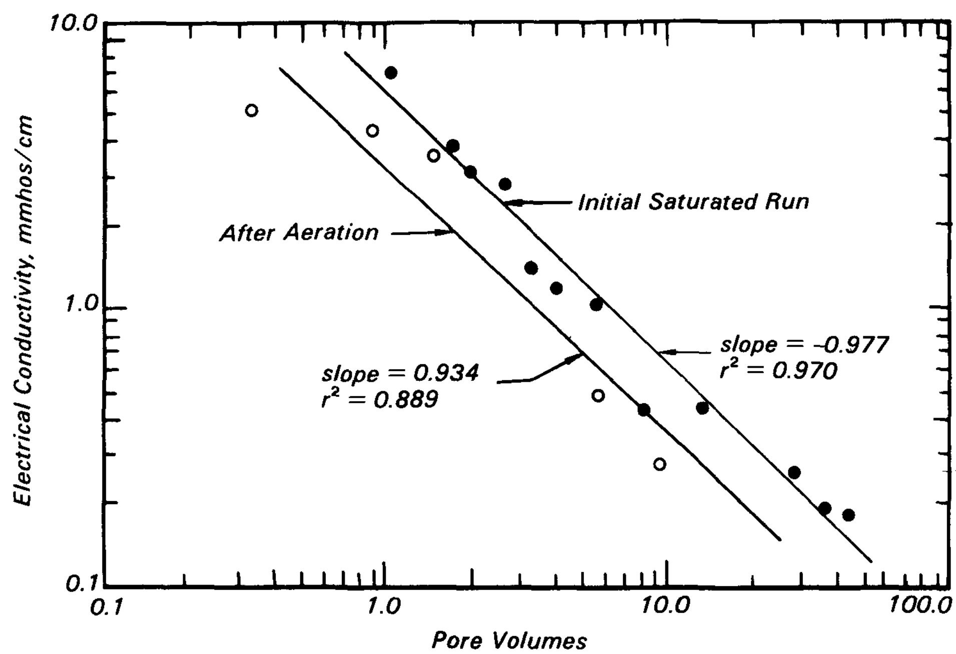

Figure 1. Leaching characteristics of USBM raw shale.

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Recommendations

It is recommended that the chemical constituents of the leachates generated under field conditions be determined. (Such a study is now being conducted by Colorado State University under the sponsorship of EPA and with the active assistance of the Area Oil Shale Office (USGS), Rio Blanco Oil Shale Company, Cathedral Bluffs Oil Shale Company, and DOE). The completed laboratory study indicates that particular emphasis should be placed upon the total dissolved solids and 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.

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The complete report, entitled "Reconnaissance Study of Leachate Quality from Raw Mined Oil Shale—Laboratory Columns," (Order No. PB 81-129 017; Cost: $8.00, subject to change) will be available only from:

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