

SIMULATED GROUND WATER LEACHING OF IN SITU RETORTED OR BURNED OIL SHALE

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INTRODUCTION

Many social, political, ecological and economic factors combine to make predictions regarding the date of significant commercial shale oil production very uncertain. Although the actual date for commercial shale oil utilization is unknown, scientists and engineers have a responsibility to develop factual information regarding oil shale utilization in order that technical information will not be the delaying factor in utilization of oil shale when required by our nation. This paper is one addition to the technical data base needed for sound utilization of oil shale.

After oil shale has been retorted in situ, the long term hazard to the surface environment will be the possibility of ground water movement through the oil shale to leach various soluble salts from the spent shale. The possible environmental hazard divides itself into two major aspects. One aspect regards the geological details of the particular in situ retorting site, in particular the amounts and quality of ground water which might flow into the previously retorted zone and subsequently have an opportunity to reach the surface. These site dependent factors can be evaluated best by hydrologists, if they have available information regarding interactions between previously retorted oil shale and the invading ground water.

The present research is aimed at a systematic development of information describing the leaching of soluble salts from retorted oil shale by ground water. The total study includes determining the amounts of material made available for leaching by the retorting process, and also the rates at which leaching may occur. The present paper primarily considers the amounts of material made available for leaching as a result of retorting oil shale under varied conditions. Work now in progress is evaluating the rates at which leaching may occur.

EXPERIMENTAL PROCEDURES

One sample of oil shale was employed in this investigation so that the total data set regarding quantities of materials to be leached from the oil shale, and leaching rate studies to be conducted in future work will be on a consistent basis. The slab of oil shale was first drilled to remove cores for future leaching rate studies, and the remainder of the slab was crushed for use in the tests reported here. The slab was from the Rifle, Colorado, mine, but it was not identified further. Data regarding the shale sample are given in Table I.

The shale was retorted in a randomized experiment with factorial treatment combinations. The factors were temperature (4 levels: 430, 483, 630, and 780°C) and retorting time (2 levels: 15 and 30 hours). Two replications were made. These retorting temperatures represent a range of temperatures from a low temperature at which kerogen begins to decompose at a reasonable rate to high temperatures at which carbonates decompose and other reactions in the mineral matter may occur. Actual in situ retorting may employ very long retorting times; however, experimental

expediency necessitated rather short retorting times in this initial set of experiments.

Two extremes of gaseous environment were employed. One sequence of tests as described above was conducted with a slow purge of air through the oil shale to burn carbon from the spent shale and provide an oxidizing environment. In addition, the air flow purged carbon dioxide from the oil shale as carbonates decomposed to facilitate further carbonate decomposition. This test partially simulated the portions of oil shale which might have been burned by air to energize the in situ retorting process. In a second series of tests, no gas purge was used during retorting of the shale which resulted in residual carbon on the spent shale, and reducing atmosphere about the spent shale during retorting. These two series of tests are distinguished as Air-Yes and Air-No in the tabular data.

Retorting of the shale was accomplished in a vertical stainless steel tube 43 cm long and 1.4 cm ID. The central portion of this tube contained 50 g of oil shale. A 1/16 inch swaged magnesia Type K thermocouple was centered inside the tube. A horizontal screen attached to the thermocouple supported the shale in the central portion of the retorting apparatus. For one series of experiments, air was purged into the top of the apparatus at a rate of 0.25 l/hr. Gases and oil were produced from the bottom of the tube into a container with a water leg seal so air could never contact the shale in those tests conducted in the absence of air. A close-fitting electric furnace was placed around the tube. Power input to the furnace was adjusted by a PID type controller actuated by the internal thermocouple. Approximately 0.5 hours was required to heat the apparatus to the desired operating temperature.

After retorting, the shale was allowed to cool to room temperature, then transferred to a 250 ml polyethylene bottle and 200 ml of demineralized and deionized water added. The retorted shale and water were mixed together for 15 hours by revolving the bottle at 160 RPM while tilted at a 45 degree angle. The samples were allowed to settle for 5 hours and the clear water decanted from the shale. Prior to analysis by atomic absorption spectroscopy the samples were filtered through Whatman No. 42 filter paper, and measurements made of the pH and conductivity. These results are reported in Table III.

The 15 hour time used for extraction of the oil shale with water was thought to be generous for extraction of the oil shale fragments which were less than 2 mm in diameter. To confirm this assumption, oil shale was retorted in the absence of air for 15 hours at 483°C and extracted by the previously stated procedure except the pH and conductivity were measured as a function of time. These results are shown in Figure 1. Most of the solids were extracted prior to the first observation after one hour of leaching. Additional solids were extracted during the 24 hour period of the test. The rapid extraction of solids followed by a slow increase in dissolved solids indicated the complexity of the total problem which is being addressed in the leaching rate studies now in progress. The additional variable of extraction time was not considered further in this paper.

The raw shale was analyzed for several elements by colormetric procedures in those cases when atomic adsorption was not effective. These data are given in Table I. V, Be, Sn, and Sb were determined by the methods described in Reference 1. As, B, and Se were determined by methods described in References 2, 3, and 4, respectively. Prior to analysis the shale was digested in HF.

EXPERIMENTAL RESULTS

Data for the 32 retorting and extraction experiments are reported in Table III.

These results were analyzed by standard analysis of variance procedures, AOV. A significance level of $\alpha = 0.05$ was selected for interpretation of the AOV results. Significant variations in the results are indicated in the left column in regard to retorting time, T_m , retorting temperature, T_p , and the time temperature interaction, TT .

For the two retorting times examined, 15 and 30 hours, little effect of retorting time was shown on the amounts of each element leached from the oil shale. The total amount of dissolved solids was not influenced by retorted time as determined by the AOV analysis. The results in Table III indicate that the amounts of several elements dissolved were dependent on retorting time by the AOV technique, K, Mg, Sr, Zn, and Cd when retorted in the presence of air. Standard analysis of covariance procedures, ANCOVA were applied to the experiments conducted in the presence of air. When leachate pH was used as the covariant, the apparent dependency on retorting time regarding the amounts of Mg dissolved was eliminated. This set of data indicated that the only significant influence on the amount of magnesium dissolved was pH of the extract. The ANCOVA examination of the data also indicated that pH of the leachate influenced the amounts of Fe and Al extracted, and perhaps the amounts of Zn, as might be expected. The ANCOVA tests indicated that only the amount of K leached was clearly dependent on retorting time.

Retorting temperature was the major variable influencing the amounts of material extracted. The difference in the amounts extracted after retorting at the two highest temperatures was not great. In some cases, retorting at the highest temperature, 780°C for the longest period of time, 30 hours, resulted in less of a particular element being leached from the oil shale, for example Sr and Zn.

The relative amounts of material leached in the absence or presence of air were not examined by statistical methods, but it appears obvious that less material was leached after retorting in the absence of air at the two lower retorting temperatures employed. This effect is not just a function of pH as shown in Figure 2, since the samples retorted in the presence of air had a lower pH, but a larger amount of solids were dissolved. The X-ray diffraction studies shown in Table II show no major alteration of the crystalline material due to retorting at the lower temperatures either in the presence or absence of air. The X-ray diffraction data shown in Table II show the production of a new mineral phase, hydroxalcite, $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$, at the most severe retorting conditions.

DISCUSSION OF RESULTS

These results show the influence of selected retorting conditions on the amounts of material leached from oil shale by pure water. Much of the ground water associated with oil shale deposits already contains large amounts of dissolved salts, up to 40,000 ppm (5), contrasted to the maximum of 1800 ppm observed in these tests. The interactions of these real ground waters with oil shale will be considerably different than observed in these tests with pure water; however, the tests with pure water provide more reproducible and readily interpretable results. Tests are now in progress using ground water.

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TABLE I

Properties of the Oil Shale Investigated

Fischer Assay Yield (gal/ton)

19.1

Principal mineral species present

(Please see Table II)

Analysis for Selected Metals

Metal	Method	Amount Present PPM in Shale	Detection Limit in Shale PPM
Be	Colorimetric	Trace	0.2
V	Colorimetric	Absent	0.5
Cr	AAS	Absent	0.005
Fe	AAS	3.68	0.1
Ni	AAS	Trace	0.01
Cu	AAS	0.16	0.003
Ag	AAS	Absent	0.005
Cd	AAS	Trace	0.003
Hg	AAS	Absent	1.00
B	Colorimetric		2.00
Pb	AAS	0.49	0.04
As	Colorimetric	Absent	8.00
Sb	Colorimetric	Absent	0.05
Se	Colorimetric	Absent	0.04

Screen Analysis of Crushed Oil Shale

Screen Mesh (US Std.)	Wt% Retained	Screen Mesh (US Std.)	Wt% Retained
+16	32.0	60	10.8
24	13.9	115	10.8
32	14.1	250	4.0
42	12.2	Pan	2.5

TABLE II. Mineralogical Phases in Raw and Retorted Oil Shale by X-ray Diffraction

Retorting Conditions			Minerals and their relative percentages						
Air	time (hrs)	temperature (°C)	Quartz	Dolomite	Calcite	Analcite	Hydrocalcite	Illite	Feldspars
(Raw Shale)			25	30	10	15	-	10	10
Yes	15	430	30	30	+	20	-	10	10
Yes	30	430	25	30	+	20	-	10	10
Yes	15	483	30	30	+	20	-	10	10
Yes	30	483	30	35	+	15	-	10	10
Yes	15	630	25	10	20	20	10	+	10
Yes	30	630	20	10	20	10	10	10	5
Yes	15	780	30	15	10	5	10	-	30
Yes	30	780	40	10	10	10	5	-	25
No	15	430	20	30	5	20	-	10	10
No	30	430	20	30	5	20	-	10	10
No	15	483	20	30	5	20	-	10	10
No	30	483	20	30	5	20	-	10	10
No	15	630	25	15	25	15	5	5	10
No	30	630	25	25	20	20	+	+	10
No	15	780	35	10	20	10	5	+	20
No	30	780	35	10	10	10	10	+	25

+ indicates trace quantity; - indicates not detectable

TABLE III Equilibrium Extraction Study-Miscellaneous Data

Retort Temp °C	Retort Time hours	Air Replicate	430		483		630		780	
			A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂
%weight loss after retorting	I		7.21	10.3	11.3	11.3	19.2	18.7	27.4	27.0
	II		7.74	10.1	11.5	11.6	19.0	18.9	27.1	26.9
	AV		7.48	10.2	11.4	11.4	19.1	18.8	27.2	26.9
YES	I		12.1	11.4	13.6	15.2	21.6	24.5	28.6	29.0
	II		12.4	11.6	13.8	14.3	22.0	24.6	28.4	29.2
	AV		12.2	11.5	13.7	14.7	21.8	24.5	28.5	29.1
pH when analyzed (Tp)*	I		9.02	10.28	10.34	9.39	11.84	11.91	11.82	11.51
	II		8.74	9.17	10.76	10.67	12.20	12.11	12.21	11.75
	AV		8.88	9.73	10.55	10.03	12.02	12.01	12.02	11.63
(Tp)*	I		7.48	7.83	11.72	11.96	12.17	12.72	12.16	11.98
	II		8.04	8.93	11.53	12.07	12.49	12.70	12.27	12.00
	AV		7.76	8.38	11.63	12.02	12.33	12.71	12.22	11.99
Total Dissolved Solids via Conductivity in Extract (Tp)*	I		305	195	185	150	1410	1645	1575	945
	II		195	160	245	235	2140	2250	>2500	1275
	AV		250	178	215	193	1775	1948		1110
(Tp; TT)*	I		860	810	1125	1410	1215	1750	1615	1395
	II		915	905	1000	1060	1270	1700	1760	1520
	AV		888	898	1063	1235	1243	1725	1688	1458

*See note at end of Table III.

TABLE III (cont.) Equilibrium Extraction Study--Group I-A Elements
(ppm extracted from oil shale after retorting)

Retort Temp °C		430	430	483	483	630	630	780	780
Retort Time hours		15	30	15	30	15	30	15	30
Element	Replicate	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂
Mg	NO	16.80	0.88	1.25	1.09	0.37	0.32	0.37	0.28
	II	0.80	11.40	0.61	13.38	0.40	0.38	0.43	0.40
	AV	8.80	6.14	0.93	7.23	0.38	0.35	0.40	0.34
Mg (Tp, Tm, Tt)*	I	94.1	36.4	0.16	0.12	0.08	0.014	0.08	0.08
	II	66.0	22.0	0.16	0.14	0.08	0.016	0.08	0.08
	AV	80.0	29.2	0.16	0.13	0.08	0.015	0.08	0.08
Ca	NO	105	92	80	63	596	869	659	370
	II	168	25	105	59	995	693	1113	504
	AV	137	59	92	61	796	781	886	437
Ca	I	924	1008	1680	1722	1814	2100	798	764
	II	1008	939	1327	1424	1147	2058	706	596
	AV	966	974	1504	1573	1481	2079	752	680
Sr (Tp)*	NO	0.088	0.056	0.104	0.064	25.0	19.6	9.0	4.40
	II	0.040	0.024	0.088	0.056	30.2	25.0	28.4	7.60
	AV	0.064	0.040	0.096	0.060	27.6	22.3	18.71	6.00
Sr (Tp, Tm, Tt)*	I	14.0	14.2	19.8	24.2	34.4	84.0	23.6	14.2
	II	14.1	15.8	19.6	24.0	60.0	90.0	24.0	15.8
	AV	14.0	15.0	19.7	24.1	47.2	87.0	23.8	15.0

* See note at end of Table III

TABLE III (cont.) Equilibrium Extraction Study--Group II-B Elements
(ppm extracted from oil shale after retorting)

Element	Air	Replicate	430		483		630		780	
			A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂
Retort Temp °C			430	430	483	483	630	630	780	780
Retort Time hours			15	30	15	30	15	30	15	30
Zn	NO	I	0.220	0.022	0.005	0.032	0.200	0.160	0.096	0.040
		II	0.005	0.008	0.008	0.008	0.200	0.149	0.400	0.080
		AV	0.112	0.015	0.006	0.020	0.200	0.154	0.248	0.060
Zn (Tp, Tm, TT)I	YES	I	0.190	0.160	0.110	0.120	0.160	0.220	0.170	0.080
		II	0.200	0.160	0.100	0.120	0.160	0.208	0.160	0.080
		AV	0.195	0.160	0.105	0.120	0.160	0.214	0.165	0.080
Cd	NO	I	X	X	X	X	X	X	X	X
		II	X	X	X	X	X	X	X	X
Cd (Tm)*	YES	I	X	X	X	X	X	T	X	X
		II	X	X	X	T	X	T	X	X
Hg	NO	I	X	X	X	X	T	T	X	X
		II	X	X	X	X	T	T	T	X
YES	I	X	X	X	X	X	T	T	X	X
	II	X	X	X	X	X	T	T	X	X

*

See note at end of Table III.

TABLE III (cont.) Equilibrium Retorting Study--Transition Elements
(ppm extracted from oil shale after retorting)

Retort Temp °C		430		430		483		483		630		630		780		780	
Retort Time hours		15		30		15		30		15		30		15		30	
Element	Air Replicate	A ₁	A ₂	A ₂	A ₂	B ₁	B ₂	B ₂	C ₁	C ₁	C ₂	D ₁	D ₂	D ₁	D ₂	D ₁	D ₂
Cr	NO	I	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
		II	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cr	YES	I	0.400	0.360	0.360	1.20	0.80	0.80	2.40	2.40	T	7.20	19.2	7.20	19.2	7.20	19.2
		II	0.600	0.040	0.040	1.20	1.80	1.80	0.04	0.04	X	4.00	16.0	4.00	16.0	4.00	16.0
	Av		0.500	0.200	0.200	1.20	1.30	1.30	1.22	1.22		5.60	17.6	5.60	17.6	5.60	17.6
Fe	NO	I	0.004	0.005	0.005	0.004	0.005	0.005	0.006	0.006	0.006	0.008	0.006	0.008	0.006	0.008	0.006
		II	0.003	0.004	0.004	0.004	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
	Av		0.004	0.004	0.004	0.004	0.005	0.005	0.005	0.005	0.006	0.006	0.006	0.006	0.006	0.006	0.006
Fe (Tp)*	YES	I	0.400	0.360	0.360	0.080	0.032	0.032	0.036	0.036	0.200	0.036	0.032	0.036	0.032	0.036	0.032
		II	0.400	0.480	0.480	0.200	0.040	0.040	0.040	0.040	0.080	0.040	0.036	0.036	0.040	0.036	0.036
	Av		0.400	0.420	0.420	0.140	0.030	0.030	0.038	0.038	0.140	0.038	0.034	0.034	0.038	0.034	0.034
Mo	NO	I	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
		II	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
Mo	YES	I	0.120	0.100	0.100	0.100	0.140	0.140	T	T	0.120	0.120	T	0.120	T	0.120	T
		II	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T

*See note at end of Table III.

TABLE III (cont.) Equilibrium Retorting Study--Group III-A and IV-A
(ppm extracted from oil shale after retorting)

Retort Temp °C	430	430	483	483	483	630	630	780	780
Retort Time hours	15	30	30	15	15	30	15	30	15
Element Air Replicate	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂	D ₂
Al	N0	4.40	4.00	10.0	14.0	18.0	18.4	28.0	32.0
	II	3.60	3.60	8.8	14.0	14.0	18.0	3.8	24.0
	Av	4.00	3.80	9.4	14.0	16.0	18.2	15.9	28.0
Al (Tp)*	I	15.0	1.10	X	X	X	X	X	X
	II	12.0	0.80	X	X	X	X	X	X
	Av	13.5	0.95						
Pb	N0	X	X	X	X	0.152	0.192	X	X
	II	X	X	X	T	0.120	0.144	X	X
	Av					0.136	0.168		
Pb	YES	X	X	X	X	X	X	X	X
	II	X	X	X	X	X	X	X	X

* The symbols enclosed in parentheses indicate that the factor made a significant contribution to observed result at the 95% confidence level over the range of variables investigated by standard AOY techniques.
T_m=time, T_p=temperature, T_l=time-temperature interaction

