

GEOCHEMISTRY OF FLUORINE IN OIL SHALE LEACHATES

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ABSTRACT

Fluorine is an important minor component in oil shale from the Mahogany Zone, in the Piceance Creek Basin in Colorado. It occurs in concentrations up to 2100 ppm in the fresh shale, and it is largely retained in the solid phases of retorted shale. Leachates generated by passing distilled water through retorted shales commonly contain concentrations of dissolved fluorine up to about 30 mg/L, more than an order of magnitude greater than the EPA standard for drinking water. Computer modelling of the aqueous chemistry of such leachates shows that the dissolved fluorine occurs chiefly in the form of free fluoride (F^-) ion, with lesser amounts of dissolved complexes of fluorine with magnesium, calcium, sodium, and other cations. The dissolved fluorine can be removed by exchange on a synthetic anion-exchange resin.

Electrophoresis measurements show that the surfaces of both fresh and retorted oil shale are negatively charged, with a point of zero net charge as low as $pH = 2.7$. The negative surface charge precludes ion-exchange as a major control on the solubility and mobility of fluoride ion in leachates from oil shale, but specific chemisorption is not precluded. The major control on the solubility of fluorine in the leachates seems to be the abundance of dissolved calcium, with a strong inverse relationship existing between the concentration of dissolved fluorine and dissolved calcium. It is likely that the precipitation of solid fluorite (CaF_2) limits the solubility of fluoride.

INTRODUCTION

The disposal of solid waste poses a serious environmental problem in connection with commercial extraction of hydrocarbon fuels from oil shales of the Green River Formation (Eocene) in the Piceance Creek Basin of northwestern Colorado. Natural waters (precipitation, irrigation, ground water) which may percolate through the piles of spent shale will form leachates with a high concentration of total dis-

solved solids. Fluorine is a minor element in oil shale which is associated with the ubiquitous clay minerals present in samples from the Mahogany Zone (Saether and others, 1979). The concentrations of fluorine measured in leachates generated from spent oil shales are in general approximately one order of magnitude higher than the recommended concentrations given in the current standard for drinking water (Stollenwerk and Runnells, 1977; EPA, 1975). In contrast to the concentration of other potentially toxic contaminants present in the alkaline leachates, the concentration of F does not rapidly rinse out after passage of a few pore volumes; instead, dissolved F remains at a high level in the leachates after the passage of over 30 pore volumes (Stollenwerk and Runnells, 1977).

We are interested in the chemical reactions and species of aqueous fluorides present in leachates generated from different types of spent oil shale. The ultimate objectives are to determine the controls on the solubility and mobility of F when spent shale is brought in contact with water. We are also interested in possible methods of large-scale defluoridation of leachates.

The principal purpose of this paper is to report on results of studies on the chemical form of fluorine in leachates generated from spent oil shales, the mechanisms of release and uptake of fluorine at the shale/water interface, and the electrochemical properties of oil shale particles as a function of pH.

MATERIALS AND METHODS

The materials used in this study include fresh and retorted oil shales from the TOSCO II and Paraho retorting processes (Sladek, 1975). The samples from the TOSCO II pilot retort operation at the Colony Development site near Grand Valley, Colorado, are unretorted (OS-1) and retorted spent shales (SS-1, SS-2, and SS-3). The

OS-1 material represents feedstock used to generate SS-2. Spent shale SS-1 was generated from feedstock mined from a lower stratigraphic interval in the Mahogany Zone at the Colony site. The retorted SS-3 material is virtually identical to SS-2 in terms of grain size and reactivity. The shales from the Paraho process are labeled POS-1 (fresh) and PSS-1 (spent). The fresh POS-1 is feedstock from the Paraho retort operation at Anvil Points west of Rifle, Colorado. The retorted Paraho spent shale (PSS-1) was collected from plots constructed on site near Anvil Points by Colorado State University. Physical data on the materials used here are given in Table 1.

Table 1. Grain-size and specific surface area of oil-shale samples. Area measured by B.E.T. method, using nitrogen gas.

Matrix	% clay	% silt	% sand	% 2-10 mm	M ² /g
POS-1 (Paraho-Raw)	2	10	75	13	1.2
OS-1 (TOSCO-Raw)	4	17	79	0	1.8
SS-2 (TOSCO-retorted)	4	86	10	0	6.1
PSS-1 (Paraho-retorted)	2	15	66	18	14.5

Leachates were generated by mixing different amounts spent oil shale with 25 milliliters of water, 0.01M Na₂SO₄, or 0.1M Na₂SO₄ in 125 milliliter polyethylene flasks. The slurries were mixed on a wrist-action shaker for different periods of time before the samples were removed. Each sample was filtered through a 0.1 micrometer Millipore[®] filter prior to measurements of pH, specific conductance and chemical analysis. Leachates were also generated by passing deionized water through cylindrical columns which were allowed to equilibrate for 46 days before the first pore volume was displaced (Runnells and others, 1980a). Fluorine in the leachates was analyzed by the method of molecular absorption (Meglen and Krikos, 1979) and is accurate to $\pm 10\%$ within the 95% confidence level.

The distribution of aqueous fluorides were calculated using WATEQFC (the University of Colorado version of the computer program WATEQF; Plummer and others, 1976; Runnells and others, 1980b). The results of the theoretical modeling were verified by ion-exchange on synthetic cationic (DOW 50W-X8) and

anionic (DOWEX1-X8) resins.

Isotherms were established by spiking the leachates with fluorine, using reagent-grade NaF. The initial concentrations of F varied from 0 to 200 mg/L and the contact time was from 6 hours to 24 days. Data from 20 hours are presented here.

The electrophoretic mobilities of the various oil shale materials as a function of pH were measured with a Zeta-Meter[®]. Suspensions of a few milligrams of solid per liter water were adjusted to different values of pH with H₂SO₄ or NaOH in the range 2 to 11. Separate suspensions were used for the alkaline and acid range of pH. The exact amount of solid in the aqueous suspension varied from sample to sample, but this factor is not significant. The electrophoretic mobility was also measured as a function of pH with 0.1M Na₂SO₄ as supporting electrolyte. It was observed that there is negligible difference in electrophoretic mobility of the oil shale particles as a function of ionic strength of the supporting solution, and only the results from runs with deionized water are reported here.

RESULTS AND DISCUSSION

Shaker-table experiment

The results of the chemical analysis of a Paraho (PSS-1) leachate, generated by mixing shale and water in a 1:1 mass ratio for 30 days, are shown in Table 2. We have observed that a contact period of 30 days is sufficient time for the system to closely approach chemical equilibrium. The electrical balance calculated from the chemical analysis of cations and anions deviated from neutrality by an amount that is reasonable (14%) for such a complex solution. The leachate comprises a sodium-sulfate water with pH=10.6 and TDS approximately 9,250 mg/L. The concentration of fluorine is 7.6 mg/L.

The chemical analysis of the Paraho leachate was used as input in the computer program WATEQFC. The results of these calculations, which are presented in Table 3, show that the free fluoride ion (F⁻) makes up 95.5 percent of the total dissolved fluorine in this particular leachate. The remainder of the fluorine in solution is present as NaF⁰ (3.1%), CaF⁺ (1.4%) and MgF⁺ (0.03%).

Table 2. Chemical composition of Paraho leachate (Batch experiment with 1:1 solid/liquid ratio and 30 days contact)

Cation	mg/L	Anion	mg/L
Ca	402	HCO ₃	161
Mg	0.6	CO ₃	60
Na	2513	SO ₄	5276
K	472	Cl	302
Mo	3.6	F	7.6
Sr	12	B	1.0
Li	13	PO ₄	0.3
Al	<1	NO ₃	<1
Ba	1	V	0.016
Fe	<1		
SiO ₂	12	pH = 10.60	

Table 3. Distribution of total dissolved fluorine in oil shale leachate generated from Paraho shale (see Table 2).

Total F	7.6 mg/L
F ⁻	95.50%
NaF ⁰	3.12%
CaF ⁺	1.35%
MgF ⁺	0.03%
Total F =	100.00%

The results of the theoretical computations of speciation are verified by the fact that most of the F (94%) in the Paraho leachate can be removed by exchange on a synthetic anion-exchange resin. In a complementary experiment using a synthetic cation-exchanger, 94 percent of the dissolved F in the leachate passed through the exchanger and was classified as negatively charged or neutral species. This work with the Paraho leachate generated by a shaker-table experiment shows that the theoretical calculation of the distribution of aqueous fluorides is probably reliable.

Column experiments

Table 4 shows the calculated distribution of aqueous fluorides in leachates generated in columns in the laboratory (Runnells and others, 1980b). The Paraho (PSS-1) leachate generated in the columns have a chemical composition which is generally similar to the leachate generated from the same material in shaker studies. The dissolved fluorine in leachates generated from fresh and retorted oil shales of the Paraho process is predominantly present as the free fluoride ion (F⁻), as it was in the earlier shaker studies. In contrast, the F species in leachates

Table 4. Concentrations of major ions and the distribution of dissolved fluorine in the first pore volume of large columns equilibrated for 46 days.

	TOSCO II		Paraho	
	INOS * (raw)	SS-3 (retorted)	POS-1 (raw)	PSS-1 (retorted)
pH	7.4	8.0	8.4	9.5
Na(mg/L)	310	4,730	1,660	4,000
Mg(mg/L)	640	1,740	7.6	33.0
Ca(mg/L)	560	470	5.6	480
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F(mg/L)	3.4	26.7	82.0	6.4
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F ⁻ (%)	67.7	57.0	97.1	92.8
NaF ⁰ (%)	0.3	3.0	2.4	4.4
MgF ⁺ (%)	30.0	39.2	0.5	1.4
CaF ⁺ (%)	2.0	0.8	0.03	1.4
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Total F(%)	100.0	100.0	100.0	100.0

* A second sample very similar to OS-1.

generated from columns of fresh and retorted TOSCO II shales are primarily distributed between the free fluoride ion (2/3 of the total F) and the monovalent positively charged magnesium complex (1/3 of the total F as MgF⁺). This is a result of the high concentration of magnesium present in the leachates from TOSCO II material. This is probably a result of the lower pH of the TOSCO II leachates compared to the pH of leachates generated from spent shales of the Paraho process. The lower pH hinders Mg from precipitating either as magnesite (MgCO₃) or brucite (Mg(OH)₂).

Release of F as a function of solid/liquid mass ratio

The release of an element from a solid in contact with water may follow one of two principal mechanisms. The first type of mechanism is illustrated by the desorption of the element from surface sites. Because of the number of surface sites exposed to the liquid increases with the amount of solid present, the concentration of the element in solution increases with increasing solid/liquid ratio. The second type of release mechanism takes place when an element is dissolved from a mineral phase. If there is enough solid to saturate the solution and to remain present in excess, the concentration of the element in solution should be dependent on the solubility of the mineral and independent of

the solid/liquid ratio. Small deviations from the latter rule are expected as a result of complexing agents in solution or the mineral having an ion in common with other solid phases present.

The concentration of F in shaker-type leachates from fresh and retorted shales is presented as a function of solid/liquid ratio in Figure 1. Both

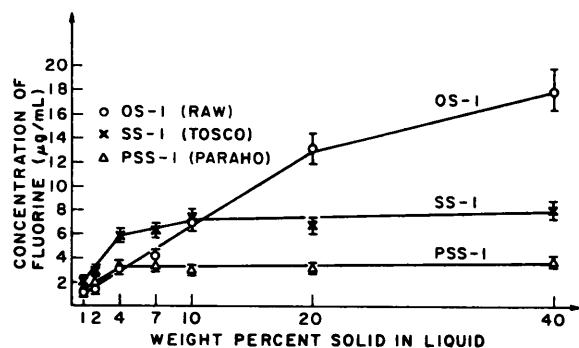


Fig. 1. The concentration of fluorine in slurries plotted as a function of weight percent solid in liquid. The error is $\pm 10\%$ at the 95% confidence level.

TOSCO II (SS-1) and Paraho (PSS-1) retorted oil shale show a leveling-out of dissolved F, when the amount of solid in the slurry increases above 4 weight percent. This suggests that after a certain concentration of F is reached, precipitation occurs and hinders further increase. Similar trends are evident from other experiments where the ionic strength of the solution is modified by 0.01M and 0.1M Na_2SO_4 . The fresh oil shale (OS-1) releases F in a manner which is proportional to the solid/liquid ratio (Fig. 1). The concentration of F is 18 mg/L when 40 percent of the slurry is fresh (OS-1) oil shale. This release pattern for F can best be interpreted as being a result of desorption, either from the clay minerals or from other surfaces in fresh oil shale.

Uptake of F on oil shales in contact with water

Important questions regarding possible removal of dissolved fluorine by oil shale can be elucidated by studies of isotherms. An isotherm is a partition diagram in which the concentration of an element on a solid in contact with a liquid is plotted versus the concentration of the element in solution. Data for an isotherm is obtained by spiking slurries which contain the same weight percent solid, with different concentrations of the element of interest. The spiked solutions are shaken for the same period of time.

The isotherms observed for OS-1, SS-2, and PSS-1 during 20 hours of contact are plotted in Figure 2. Two weight-percent of oil shale material was used in 25 mL 0.01 M Na_2SO_4 . Sodium sulfate was chosen as supporting electrolyte because Na^+ and SO_4^{--} are the predominant ions in actual leachates from oil shale.

As shown in Figure 2, more F is taken up on the surface of the oil shale as the concentration of F in the spiked leachate increases. The

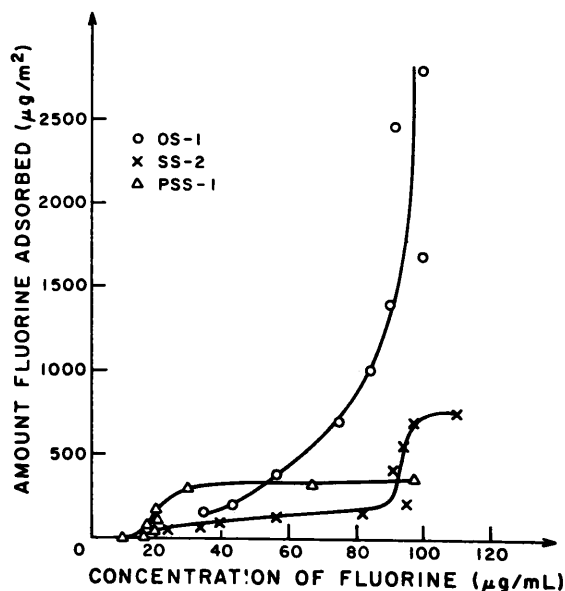


Fig. 2. Adsorption isotherms for F in leachates. Contact period is 20 hours. Weight ratio solid/liquid is 0.02 and 0.01M Na_2SO_4 is used as electrolyte. Initial spike of F as NaF range from 20 to 200 mg/L.

isotherms for fresh (OS-1) and retorted (SS-2) TOSCO II shales do not, however, follow a distinct path of adsorption. On the contrary, the isotherms become vertical at a concentration of about 90 mg/L F, suggesting that more F is taken up on the surface without increasing the concentration of F in solution. The most probable interpretation of this phenomenon is that F precipitates as a solid phase, without permitting the concentration of F in the leachate to increase. The difference in the shape of the isotherms of the fresh (OS-1) and retorted (SS-2) TOSCO II shales is primarily due to the difference in specific surface area (Table 1).

The Paraho oil shale (PSS-1) behaves quite differently from the other two oil shale materials when spiked with F. The isotherm becomes vertical at a relatively low concentration of F of 15 mg/L. This means that precipitation of F occurs and hinders further increase. The concentration of F in the leachate increases only after the concentrations of the co-precipitating major ions are reduced.

The amount of precipitate which eventually forms in leachates spiked with F is too small to be detected by x-ray diffraction. It can be proven indirectly, however, that fluorite (CaF_2) probably precipitates by evaluating the change in the concentration of F relative to the concentration of Ca. We have found that the relationship between the concentration of Ca and F in the leachate fits the solubility product of fluorite (CaF_2):

$$(a_{\text{Ca}^{++}})(a_{\text{F}^-})^2 = 10^{-10.96}$$

$$\log a_{\text{Ca}^{++}} + 2\log a_{\text{F}^-} = -10.96$$

$$Y = -2X - 10.96$$

Electrophoretic mobility of oil shale materials

Information concerning the electrical charge of a solid as a function of pH forms the basis for predicting the mechanisms of adsorption of ions in solutions in contact with the solid. In conjunction with studies on the reaction mechanisms which govern the concentration of dissolved fluorine in oil shale leachates, the electrochemical properties of spent shale were investigated. It is particularly important to know if the surface of the oil shale materials is positively or negatively charged in the range of pH measured in the leachates. Knowledge of the charge of the predominant fluorine species in solution reveals information on how coulombic forces may affect their

affinity to the surface of the particles of oil shale.

The electrophoretic mobility (EM) was determined for raw and retorted oil shale using the Zeta-Meter[®] (Fig. 3). The procedure used in these measurements was standardized by measuring the electrophoretic mobility of four

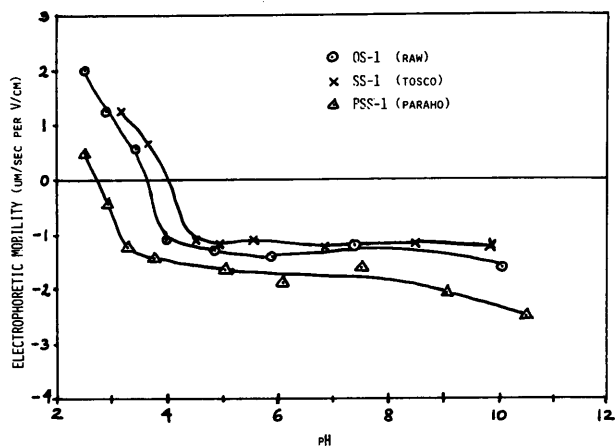


Fig. 3. Electrophoretic mobility of OS-1, SS-1, and PSS-1 as function of pH. The error for the point of net zero charge is ± 0.5 for OS-1 and PSS-1 and ± 1.0 for SS-1.

reference materials (calcite, dolomite, activated alumina and quartz), each with known points of zero charge. The EM-pH curve for the raw oil shales OS-1 and POS-1 both show a similar trend. The surface of the OS-1 material has a net surface charge of zero at $\text{pH} = 3.7 \pm 0.5$, whereas the POS-1 material has a net surface charge at $\text{pH} = 3.0 \pm 0.5$. At pH greater than 4.0, the POS-1 material is more negatively charged than the OS-1 material. The EM of raw oil shale particles increase slightly with increasing pH. Measurements of the EM of these materials with 0.01M Na_2SO_4 as supporting electrolyte do not deviate significantly as a function of pH from those obtained with distilled water. This suggests that no significant amounts of sulfate ions are specifically adsorbed on the surface of the raw oil-shale materials studied.

The retorted oil shale materials investigated are PSS-1, SS-1, and SS-2. Only results of

PSS-1 and SS-1 are plotted in Figure 3. The retorted oil shales seem to be less homogeneous than the raw oil shales. It was therefore more difficult to obtain a unique EM-pH curve for the retorted oil shales. Because the Paraho material (PSS-1) is coarser than any other oil shale material used in this study, this material had to be crushed to form smaller particles of more uniform size before the electrophoretic mobility could be measured. Repeated measurements of the electrophoretic mobility of the crushed Paraho material gave a point of zero net charge which was reproducible within the pH range 2.7-3.2. The materials from the TOSCO II process behave less uniformly than spent oil shale from the Paraho process.

Oil-shale materials from the TOSCO II process do not exhibit a cross-over which is reproducible within the error of ± 0.5 pH-units. The SS-1 gave a point of net zero charge of 4.0 ± 1.0 . A singular point of net zero charge could not be obtained from EM-measurements of the SS-2 material. Rather, there is a broad pH-range from about 2.5 to 6.5 in which particles move in both directions. This suggests that the SS-2 material consists of both negatively and positively charged particles within a significant portion of the pH-range. It is possible that the small portion of positively charged particles within this range of pH are dolomite grains which have lost their organic coating during retorting. Most of the dolomite found in the oil shale breaks down during retorting by the Paraho process and there does not seem to be a problem with positively charged particles for this material at pH greater than 3.5.

The results obtained on the point of net zero charge for TOSCO II retorted shale differ from those obtained in a previous study. Cowling (1978) has indicated that the point of net zero charge for the TOSCO II shale is at pH of 8.5. However, the method of electrophoresis is a standard technique and our determinations of the point of net zero charge on standard materials (calcite, dolomite, activated alumina, and quartz) are closely similar to published values. We feel that our measurements are quite reliable and subject to far fewer possible errors than the methods of acid-base titration and adsorption of organic dyes used by Cowling (1978).

CONCLUSIONS

Computer modeling of the aqueous chemistry of

leachates generated from spent oil shales shows that the dissolved fluorine occurs chiefly in the form of the free fluoride ion (F^-). Smaller amounts of fluorine are complexed with magnesium, calcium, and sodium. Leachates from raw and retorted TOSCO II shale have significantly higher concentrations of magnesium which form a strong complex (MgF^+) with fluorine over the Paraho shale, probably due to the lower pH of the TOSCO leachates. The results from the theoretical calculations of the distribution of dissolved fluorine in an oil shale leachate were confirmed experimentally by ion-exchange on synthetic ion-exchange resins. Dissolved fluorine in leachates with a high percentage of free fluoride ions can be removed by exchange on a synthetic anion-exchanger.

Fluorine in oil shale is released by desorption during leaching with water. The amount of dissolved fluorine in the leachates are determined by the abundance of calcium and a strong inverse relationship exists between the concentrations of dissolved calcium and dissolved fluorine. It is likely that the precipitation of fluorine as fluorite (CaF_2) limits the concentration of dissolved fluorine in oil shale leachates. The high concentrations of fluorine measured in some oil shale leachates may be removed by addition of lime (CaO).

Measurements of the electrophoretic mobility show that raw and retorted oil-shale particles are negatively charged in the alkaline range of pH. The point of net zero charge obtained for the various types of oil shale materials studied are as low as 2.9 ± 0.5 . This is probably due to the organic matter present in all the oil shale materials studied. This means that significant adsorption of free fluoride ions by ion-exchange is not likely to occur during leaching of spent oil shale.

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