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SHALE OIL FROM THE LLNL PILOT RETORT: METAL IONS AS MARKERS FOR WATER AND DUST

by

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Abstract

A metal ion found primarily in one of the three phases (oil, water, or dust) can serve as a marker for that phase. Emulsified water contains most of the magnesium detected in a shale oil. Extraction with saturated salt solution removes most of that Mg. The Mg content of retort water and the percentage of water in the oil (by ASTM D-4006) provides a good estimate of an oil's Mg content. Mineral matter elements with poorly water soluble carbonates (or oxides) at pH 8 (calcium, for example) serve as markers for dust. When the water is separated from the main and light oil fractions before adding the heavy fraction containing dust, a much drier oil can be obtained. However, when done in this way, a powder containing Ca and Si remains in the oil; it cannot be completely removed even by filtering through a 0.24- μ frit. Iron, and certain other transition metal ions, is quite oil soluble. Extraction with dilute nitric acid to remove basic amines reduces the Fe content of shale oil. Unlike carboxylate-complexed metal ions in crude oils, the iron in shale oil does not extract efficiently into an aqueous EDTA solution (pH 5.9). Distillation of shale oil leaves most of the iron and other metals behind in the vacuum residuum. Shale oil corrodes the hottest condenser's steel interior; this is the chief source of iron in the oil.

Introduction

The Lawrence Livermore National Laboratory's (LLNL) Oil Shale Project produces shale oil in a hot-recycled-solids (HRS) pilot retort.¹ The goals of the Project are to develop this retorting methodology while gaining a better understanding of oil shale pyrolysis and shale oil chemistry. Increasingly, oil characterization has become the focus of the chemistry effort.

Shale oil from the LLNL retort, like most shale oils, ordinarily comes well mixed with water and dust. A representative oil must be obtained quickly for characterization, while avoiding air contact and volatile loss. Requiring quick turn-around forces a compromise, and some water and dust remain with the oil. These substances in oil influence analytical data, impart inhomogeneity with associated sampling problems, and possibly, speed aging. With dust and water slowly separating, metal analysis by inductively coupled plasma, atomic emission spectroscopy (ICP-AES), in particular, shows poor repeatability.

Analytical data collected to date force the conclusion that HRS shale oils produced in a standard way are very similar to Colorado shale oils produced by other heat-and-collect processes. Table 1 compares an LLNL shale oil (shale oil A) with bulk shale oils analyzed at Gulf by Stauffer and Yanik 15 years ago.² Figure 1 shows D-2887 simulated distillations of some recently prepared oils, including shale oil A. The remarkable similarity of these oils is testimony to the uniformity of Green River Formation kerogen. Yet, the data hide important details of the oils, such as unsaturation and aromaticity. The simulated distillation curves need to be adjusted for residuum content and relative response factors of compounds eluting at each temperature if they are to provide an accurate comparison. Nevertheless, the generalization that all simple thermal processes produce the same Colorado shale oil seems correct.

Table 1. Whole Shale Oil Properties.

Source: Retort:	Dow ² Tosco	Paraho ² Paraho	LLNL HRS A
Gravity, °API	20.7	20.1	20.5
Viscosity, SUS: @130°F	85.7	121.4	87.0
Pour Point, °F	+75	+85	+15
Carbon, wt%	84.52	84.83	84.78
Hydrogen, wt%	11.14	11.51	11.36
Sulfur, wt%	0.70	0.58	0.69
Nitrogen, wt%	1.99	2.04	2.36
Oxygen, wt%	1.32	1.24	1.63
Arsenic, ppm	13.9	20.9	24.8
Ash, wt%	0.20	0.03	0.05
Vac Resid, vol% 960°F ⁺	26.84	30.97	30.5

Figure 1. ASTM D-2887 simulated distillations.

For a series of HRS retorting experiments, certain oil properties reflected processing variables such as condenser efficiencies, yield loss by coking or cracking, and introduction of chemically active reagents (including steam and burnt shale).³ However, trace metal analyses of HRS shale oils did not vary in a logical way with processing changes but wandered widely and unpredictably. This is not a unique observation. For at least 25 years, unpredictable metal analyses have been a recurring complaint.⁴ The most notable feature of an extensive shale-oil metal-content data base is the wide range of analysis data.⁵ This report addresses factors that influence the metal content of shale oil with the goal of better understanding the chemistry.

Experimental

Samples

Shale oil was prepared in the HRS pilot retort.¹ Dust was filtered off and water separated after freeze-warm cycles. An 8-gal sample of each oil was obtained for characterization. Homogeneous shale oil samples were prepared by mixing on a shaking tray for 0.5 hour. A valved spigot extending to the midpoint of the oil was used for transfers; oil was driven out of the brown glass bottle via the spigot by applying an argon head pressure. Dried shale oils were obtained by adding 10 wt% activated 4Å molecular sieve. After intermittent shaking for one day and then standing over the sieve for a week or more, the dried oil was decanted.

Certain shale oils were extracted with the following aqueous solutions (1:1 v/v): a) saturated NaCl, b) half-saturated dibasic ethylenediaminetetraacetic acid (EDTA), c) 0.35% HNO₃, and d) 1.4% HNO₃. Acid extractions were

carried out in centrifuge tubes under argon. After warm centrifuging, the oil was separated, dried over a K_2CO_3/Na_2SO_4 mixture, and filtered. Extractions with salt solutions were carried out in separatory funnels; after shaking for 0.5 hour, the mixtures were warmed to 50°C to speed separation and were allowed to stand overnight.

Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP-AES)

Following a recommended method,⁶ 2 g of shale oil (or the 1050°F+ vacuum residuum) was ashed in an open Pt crucible at 500°C for 2 hours. After ashing, HCl (5 ml, conc.) was added. The solution was heated to 150°C on a hot plate and held for 20 min. ICP-AES metal determinations were made after transferring the solution to a 50-ml Teflon volumetric flask with deionized water. A xylenes solution containing acetonilacetate complexes of Co, Cu, Fe, Ni, V, and Zn mixed with NIST metal-in-oil standards for Ca, Mg, and Na was prepared so each element was present at near its concentration in shale oil. This and NIST's standard fuel oil #1634b were ashed and run as controls (both neat and spiked into shale oil). Sc was always added as an internal standard. A Fison (formerly ARL) model 3560 simultaneous ICP-AES measured Al, Ca, Fe, Mg, Na, and Si. Other elements (Co, Cu, Ni, V, and Zn) were determined with a Jobin Yvon Instruments sequential ICP-AES, model JY-38. Shale oil samples also were sent to commercial laboratories for ICP-AES analysis where they were diluted with *o*-xylene or kerosene and were aspirated into the instrument.

Retort water was separated from shale oil and filtered. The water always contained a few percent of the more water-soluble oil components. It was diluted 5:1 and 25:1 to adjust the ion concentrations for best accuracy and to prevent extinguishing the plasma flame.

Water Analyses

Water in oil was determined by a Karl Fischer procedure, by an ^{17}O -nmr method, and by azeotropic distillation following ASTM D-4006 with certain modifications. Results by the last two methods agreed well, and the D-4006 procedure with toluene as solvent proved to be the most reliable and convenient technique, provided the sample size was large (i.e., 250 g of oil). Generally, shale oil was sampled for water and ICP-AES metal analysis during the same transfer operation. Certain samplings and water analyses were done after an oil had stood for a time following shaking.

Oil Inspection Data

A LECO SC132 Sulfur Determinator was used for sulfur analysis. Organic elemental analysis (C,H,N,O) was provided by Midwest MicroLab and verified in-house using a LECO CHN-600 Micro-CHN Determinator. A Mettler

model DA-300 density meter measured specific gravity. The ASTM D-4530 method was used to determine viscosity. Simulated distillation followed the ASTM D-2887 method. The National Institute of Petroleum and Energy Research (NIPER) provided petroleum tests to ASTM specifications or by other standard methods. These included the following: pour point (D-97), distillation (D-2892), vacuum distillation (D-1160), total nitrogen (D-4629 Mod.), basic nitrogen (UOP 269), ash content (D-482), wax (UOP 46), and arsenic (ICP-AES in kerosene).

Results and Discussion

HRS shale oils had a higher metal content than typical crude oils. Iron, in particular, was present at high levels—often 300-400 ppm. Only a few other shale oils (for example, that from the gas combustion retort³) have had iron in this range. High Fe content has a negative impact on oil quality. Metals poison catalysts and complicate water disposal. Thus, the metal ions in HRS shale oil were of immediate interest and concern. Goals of this study were to provide definitive answers to questions such as the following:

- ◆ If metals in the oil come from retort corrosion, can this be avoided?
- ◆ If metals are extracted from dust that collects with the condensate, can oil-dust contact be minimized?
- ◆ If metals distill as complexes, can they be de-metallated or destroyed in a simple way?

Understanding the nature of metal ion association with shale oil components was necessary information and a first step toward addressing these questions.

ICP-AES analyses of shale oils initially generated by the HRS process agreed poorly from laboratory to laboratory (see results of shale oil A analyses in Table 2).

Table 2. The Effect of Dust and Water Present in Shale Oil A on ICP-AES Reproducibility.

Element	LLNL	Lab I	Lab II
Al	5.6	<0.4	<0.2
Ca	4.4	1.1	<0.1
Mg	5.8	2.2	<0.2
Na	13	10.9	<0.2
Cu	5.4	5.0	3.1
Fe	340	304	435
Ni	16.4	15.1	21.1
V	1.8	2.1	2.4
Zn	8.6	6.6	6.9
Co	6.9	6.5	7.2
Cr	<2	0.24	

units: ppm

Problems with ICP-AES methods were ruled out because controls analyzed correctly in our Laboratory. Typically a xylenes solution containing Ca, Co, Cu, Fe, Mg, Na, Ni, V, and Zn at the level found in shale oil gave results within $\pm 20\%$ of the known concentration for all ions (when concentrations were at least 10 times the detection limit). Sodium often proved most difficult to analyze accurately since its concentration was seldom much above its 3-ppm limit of detection. The spread of results for certain Table 2 metals suggested difficulties in sampling heterogeneous oil-water-dust mixtures. Those elements that showed the worst scatter (Al, Ca, Mg, Na, and Cu) were likely candidates as water and dust markers.

How the oil is prepared and handled can contribute to difficulties in sampling. Shale oils from the LLNL pilot retort condensed in three fractions: i) a heavy cut containing dust but no water, ii) a main oil fraction with most of the water and about half the dust in it, and iii) a light oil cut plus water. Table 3 lists differences in how these three fractions were generated and treated to obtain oils for this study. These differences relate directly to water and dust content and indirectly to sampling difficulties.

Table 3. Work-up Procedures for those HRS Shale Oils Studied.

Oil	Conditions
A	Water distillation: Water distilled from heavy and main cuts during 2 days; then filtered and lights added.
B	Standard method: Mix of heavy and main cuts filtered; freeze/warm cycles to drop off water; lights added.
C	Double filtration: Main cut filtered; water dropped out; heavy cut added and re-filtered; lights added.
D	Heavy cut omitted: Main cut filtered with no heavy oil cut added; otherwise, like B .
E	Heavy cut coked to extinction: Main cut filtered (no heavy fraction obtained); work-up like B and D .
F	Hot vapor filtering experiment: Water removed from main fraction ($<0.02\%$ dust in oil); combined with heavies; filtered and again separated water; lights added.

Magnesium as a Marker for Water in Shale Oil

Shale oils were shaken, sampled, and analyzed for water content by an azeotropic distillation with toluene, a modified ASTM D-4006 procedure. During the same transfer, a sample was taken for metal analysis by ICP-AES. Those

oils with appreciable water content generally contained more Mg, Na, and Cu than did dry oils. Table 4 lists metal ions of interest in two shale oils (**B** and **C**) and the respective retort waters. Ions added to oil by water are calculated and included in the table. Retort water from the main condenser fraction is used for the water metals analysis. This water is not an exact match to the emulsified water, but its ion content should be close. Magnesium in emulsified or dispersed retort water accounts for all the Mg in the oil. Sodium also is largely in water, but as noted, errors in Na analysis make it a poorer marker for water. Copper apparently results primarily from corrosion of new copper gaskets in the condenser train. Copper has both water and oil solubility. Retort waters varied wildly in Cu content, and occasionally water that condensed with lights accounted for most of the copper. Cu does not serve as a useful water tag.

Table 4. Retort Water as a Source of Magnesium in Shale Oils.

I. Element	Retort Water B	Oil B (3.26% H ₂ O)	Ions from H ₂ O in Oil, Calc'd	Dry Oil B (0.1% H ₂ O)
Na	269	5.4	8.8	6.5
Mg	689	21.3	22.4	5.1
Ca	18.4	19.2	0.6	6.8
Fe	49	363	1.6	376
Cu	8.3	7.7	0.3	4.1

II. Element	Retort Water C	Oil C (0.39% H ₂ O)	Ions from H ₂ O in Oil, Calc'd
Na	194	2.9	0.8
Mg	688	2.8	2.7
Ca	18.9	128	0.1
Fe	52	301	0.2
Cu	57	5.3	0.2

units: ppm

Emulsified water separates from shale oil over a few weeks time. Figure 2 shows water separation kinetics (room temperature) for a shaken sample of shale oil **B** that had previously separated. Shaking disperses water, but does not cause all the separated water to again form the stubborn emulsion that was present initially—although, ultrasonic methods were not tried. Dust may well play an important role in making the original water-oil emulsion so stable. Distinct differences in original and subsequent oil-water mixtures have made it difficult to study appropriate methods for solving the emulsion problem. Others have encountered similar difficulties and have been plagued by the availability of only old samples unsuited for emulsion-breaking tests.⁷ HRS shale oils differed in their tendency to emulsify water, both initially and later. Figure 2 cannot be generalized.

Figure 2. Separation of water from shale oil *B* according to a first-order rate law.

Figure 3. Evidence for water-phase Mg: the good correlation of an oil's Mg and water content.

The rate that water separates seems to depend on dust loading, nitrogen content, temperature, viscosity, and a variety of other factors. However, water content correlates with Mg content for each shale oil (see Figure 3 for oil *B* results). The tendency of water to slowly separate from shale oils and resist re-emulsification presents continual sampling problems. Two of the Figure 3 data points (3.26% and 2.67% water) are from analyzing "initial" samplings of a well-shaken shale oil (*B*). In one case, water was determined by ASTM D-4006 and in the other, by ASTM D-2892/1160 distillation (in which case, Mg was determined in the vacuum residue). The difference in water content is typical of the sampling error.

Table 5 shows water solubility data for carbonate mineral cations present in oil shale. Ca, Mg, and Fe carbonates have relative solubilities remarkably similar to

their ratio in retort waters (see Table 4). HRS process water proves to be a dilute ammonium carbonate/bicarbonate solution buffered with a variety of salts to pH 8.5 ± 1 , and it contains water-soluble (polar) oil components. Since MgCO_3 solubility is influenced by pH and enhanced by both CO_2 and NH_4^+ , it (and other carbonates) should have a somewhat higher solubility in retort water than in pure water. Over time, aging and air exposure have an effect on the water. The buffer loses CO_2 and NH_3 , dust contact (and so carbonate mineral saturation) is not maintained, and sulfates with their greater solubilities become increasingly significant. Once dust-free, the oils soon fail to give plots such as Figure 3. Of course, if there is insufficient water, some Mg will remain as part of the dust.

Table 5. Carbonate Salt Solubilities in Water.

Cation	Salt	Solubility @25°C	
		in g/100 cc	in ppm
Ca	Calcite	0.0014	6
Mg	Nesquehonite	0.1790	314
Fe	Siderite	0.0067	32

As a wet oil stood and separated, dust also slowly settled. Consequently, several metals that fail to track water decrease just as do the water markers. This makes the results of drying studies ambiguous. A shale oil's Mg content changes insignificantly during the early stages of drying with 4Å molecular sieve. Apparently a supersaturated solution is generated, or perhaps, precipitated salts remain suspended in the oil for some time. Dust from molecular sieve increases the oil's Na, Al, and Si content. Eventually much of this dust and salt settle from the oil. A dry oil analysis (*B* with <2 ppm Al remaining suspended) has been included in Table 4. Problems associated with heterogeneity leave some uncertainty as to the form of Mg in dried shale oil.

Calcium as a Marker for Solids in Shale Oil

Magnesium is transported into the product collection region as dust. Solubility of its carbonate salt makes it a water marker. Salts with poor water and oil solubility are good candidates for dust markers. Major mineral elements of insoluble rock grains are the best choice. High solid-phase dilution complicates the use of trace elements (Ba, for example) as markers. Calcium should be a particularly good indicator of solids, and it has the characteristics expected of a dust marker. Given the low water solubility of its carbonate salt (see Table 5), less than 10 ppm Ca is found in retort water. The large scatter of results, when oils containing very little Ca (~1 ppm) were analyzed in kerosene (no ashing), could be attributed to dust's granular nature. Ashed dissolved samples gave better short-term repeatability.

Association of calcium with the water phase is ruled out, since for a set of HRS shale oils, Ca content fails to correlate with water (see Table 4). Shale oil *C*, with quite a low water content (0.23%), has a particularly high Ca and Si content (93 ppm), for example (see Table 6). Oil *C* was prepared by first filtering the main condenser fraction and separating away water. Then this main oil fraction was mixed with the heavy oil and re-filtered through a 0.24- μ frit. It was intended that dust in the heavy fraction function as a drying agent, but it is possible that water simply separates more easily from the main cut than from the main-plus-heavy cut. Nevertheless, the resultant oil was low in water but high in Ca. The Ca content of this oil failed to decrease on standing 6 months—when sampled without shaking. Remaining calcium-compounds either are exceedingly fine, or have some oil solubility.

Table 6. An Elevated Ca Content of Shale Oil *C*, a Relatively Dry Oil Prepared by Double Filtration.

Element	Metal Content
Ni	8.0
V	1.4
Fe	187
Ca	76.7
Mg	1.6
Cu	3.5
Zn	2.8
Co	3.3
Na	3.5
Si	94

units: ppm

Si and Al also are expected to be good markers for solids in shale oil (see Table 6). However, our study of these elements was less extensive and is incomplete.

Iron as an Oil Component

Transition metal ions were chiefly oil soluble, apparently complexed by organic ligands native to shale oil. Iron is representative of this group of metal ions, and as the metal present at the highest level in most HRS shale oils, it is of major interest. Good repeatability and reproducibility of analyses provide evidence that iron is primarily an oil component and is not associated with dust or water phases. Iron content of shale oil is affected very little by filtration, settling, aqueous extraction, or sample preparation for ICP-AES (ashed/aqueous or in an organic matrix, not ashed).

Table 7 shows ICP-AES data obtained after extracting shale oil *D* with a saturated salt solution or half-saturated disodium EDTA. Saturated aqueous NaCl partially dries oil.

The original crude shale oil contained 1.1% emulsified water; after washing with the brine, 0.6% water is left (based on the Na content of the brine and assuming the oil sodium was all from emulsified salt solution). Saturated NaCl replaces the water that was originally present and removes water soluble ions (Mg and Cu) in the oil; it partially eliminates solids (and hence, Ca) as an emulsion at the oil-water interface. Polar ligands have some slight water solubility (pH of the salt solution was 8.2 after oil contact), and removal of these ligands may have decreased the oil's Fe content very slightly. Aqueous EDTA competes for carboxylate-complexed metals and removes them from crude oil at pH 5.9.⁸ However, EDTA captures Fe (and Ca) from HRS shale oil inefficiently (only a bit better than brine). Apparently few metal ions in this shale oil are carboxylate-complexed, as they often are in crude oils.

Table 7. Shale Oil *D* Extracted with Salt Solutions (1:1 v/v).

Element	Raw Shale Oil	pH = 8.2 Sat. NaCl Extracted	pH = 5.9 EDTA Extracted
Ni	5.5	5.5	5.6
V	<0.7	<0.7	<0.7
Fe	61.5	56.	49.
Ca	14.9	6.4	5.8
Mg	9.4	2.7	3.1
Cu	9.0	3.4	4.4
Zn	5.7	5.1	4.0
Co	1.8	1.8	1.8
Na	<1	884.	44.

units: ppm

Table 8. Shale Oil *E* Extracted with HNO₃ (1:1 v/v).

Element	Raw Shale Oil	0.35% Acid Extracted	1.4% Acid Extracted
Ni	2.7	2.9	1.7
Fe	42.5	22.1	7.1
Ca	2.5	3.1	2.5
Mg	3.0	1.2	0.6
Co	0.9	1.3	<0.8

units: ppm

Table 8 shows the effect of extracting shale oil *E* with aqueous acid. This shale oil had a base number of 42 mg KOH/g (or 1.1% basic nitrogen). Basic nitrogen compounds, including some capable of complexing iron, can be removed by strong acid extraction. Incomplete extraction

(0.35% HNO₃, 1:1 v/v) removes some iron; even more is extracted when sufficient acid is available to protonate all shale oil bases (1.4% HNO₃, 1:1 v/v). Since a volume reduction of about 25% accompanied acid extraction, the decrease in an oil's total Fe content was 25% greater than the Table 7 data might suggest.

The perception that heavy polar compounds act as emulsifying agents may well have merit.⁹ Coincidentally, some of these polar compounds are excellent ligands. The somewhat lower iron content of oil *C* might have been due to activated solid acting as an adsorbant for polar compounds. Certainly, the data in Tables 7 and 8 implicate nitrogen heterocycles as iron complexing agents. Zn was similar to Fe in its response to brine, EDTA, and acid.

The behavior of iron can be contrasted with that of nickel. Nickel in crude oils associates strongly with heterocycles (including petroporphyrins) and is unaffected by an aqueous EDTA or acid treatment.⁸ In shale oil, Ni, and also Co, seem to form tight complexes that decrease ligand basicity (and aqueous solubility) to a greater extent than Fe and Zn. As a result, Ni and Co are particularly difficult to remove from shale oil by acid washing. Iron seems to complex more loosely, at least in part, so it can be largely acid extracted.

Table 9. Characterization Data for Shale Oil *E* and Other HRS Shale Oils, Showing the Beneficial Impact of Secondary Processing Conditions.

Test	Shale Oil <i>E</i>	Shale Oil <i>D</i>	Average Oils <i>A, B, C</i>	St.Dev.
Gravity, °API	26.4	21.8	20.7	±0.8
H/C Ratio	1.57	1.62	1.60	±0.01
% Water	0.42	1.09		
1050°F+ Resid	7.9	14.5	22.3	±0.7
Wax, wt%	0.02	0.60	2.11	±1.27
%N	2.00	2.10	2.85	±0.72
%N(tot)	1.75	1.66	2.12	±0.19
Basic N	0.95	1.09	1.16	±0.19
As, ppm	22.9	23.6	30.7	±5.3

When the metal content of crude HRS shale oils *A* to *E* (see Tables 2, 4, 7, 8) are compared, shale oil *E* stands out as the highest quality oil. Acid extraction of metal and nitrogen compounds result in a further improvement. Table 9 collects some crude shale oil inspection data for the series of oils analyzed here. HRS shale oils *A, B*, and *C* were prepared in the pilot retort under slightly different conditions, but they are similar. Shale oil *E* has excellent API gravity, low wax and 1050°F+ vacuum residuum content, and somewhat reduced arsenic and nitrogen as compared with other

shale oils. This oil (*E*) was prepared by selectively coking heavy ends during the retorting process (see Table 3). There was a penalty in terms of coking loss, but most lost product would have been consigned to the residuum fraction anyway.

Shale oil *D* was prepared as a standard oil for judging the quality of *E*. It consisted only of main and light fractions from the HRS retort. Heavy oil that condensed in the hot condenser was rejected. Wasting this fraction lowered the effective yield. Yet, oil *E* is superior even to *D* by most measures (see Table 9, and also compare Tables 7 and 8). By selectively coking the heavy cut, the metal content of the shale oil is reduced substantially (the oil *E* case). Attempted condensation to remove chelating agents present in the heavy fraction is less effective due to hot condenser inefficiencies (mist formation results in some dust and heavy oil blow-by; the oil *D* case).

Whence Metals in Shale Oil?

With specific markers for oil (Fe), water (Mg), and dust (Ca), it should be possible to draw conclusions concerning sources of metal ions in shale oil. For instance, since retort water becomes saturated with carbonate salts as it stands in contact with dust, those oils high in Mg content contain water (saturated with MgCO₃). Furthermore, a high Ca:Mg ratio usually indicates a relatively dry oil containing dust. When an oil's calcium analysis is quite high, there is a lot of dust present. Finally, with oil-soluble iron as a tag for inorganic oil impurities, experiments can be now devised to answer the significant questions concerning the origin of oil-soluble metals posed earlier.

If dust were entirely prevented from entering the condenser system during retorting, the importance of spent shale dust as a source of metal ions would be defined. Shale oil *F* was produced in the HRS pilot retort with the exclusion of down-stream dust. Only completely vaporized pyrolysis products, free of solids (<0.02%) and oil mist, were allowed to pass from the retort into the condensation train. Table 10 shows the metal content of this oil. Ca and Mg content are very low as a result of the near absence of dust. This retort water was not the usual saturated solution of carbonate minerals. However, the transition metals (Fe, Co, Ni, V, and Zn) were in the oil at a level typical of those HRS shale oils condensed with dust present (compare Table 10 with Tables 4 and 7). Thus, the large quantity of oil-soluble metal ions in this particular oil must have either distilled from the retort as organic complexes or formed after the vaporized oil entered the condensers.

Vacuum distillation of shale oil *F* by the ASTM D-1160 procedure, showed that less than 3% of the iron was in compounds sufficiently volatile to distill at 550°C (see Table 10). Consequently, neither dust nor volatile metal complexes contributed much iron to the oil, and condenser corrosion is implied. This is consistent with a very low Fe

content (<1.5 ppm) for shale oil generated in an aluminum/glass system (i.e., under Fischer Assay conditions).¹⁰ While others have not reported corrosion of this type, prior work has been done using other methods. These focused on other parts of the retort, or stressed oxidation, embrittlement, and acid attack.^{11,12}

Table 10. A Lower Mg and Ca Content, But No Less Fe, for Shale oil *F*, Condensed Dust-Free.

Element	Shale Oil <i>F</i>	650-1050, 1050°F ⁺ VGO Cut	Vac Resid	Residuum's contribution
Ni	15.3	<0.6	51.0	11.9
V	2.0	<1	7.9	1.8
Fe	329	15	1330	310
Ca	1.25	0.23	6.4	1.49
Mg	0.25	0.01	1.1	0.24
Cu	20.5	<1	84.1	19.6
Zn	4.1	1.0	15.5	3.6
Co	6.5	<1	25.9	6.0
Na	2.15	0.95	7.9	1.9
Al	0.7	0.36	3.0	0.7

units: ppm

The low Fe content of shale oil *E* (with heavy ends recycled to extinction) would suggest that corrosion responsible for iron in HRS shale oils occurs predominantly in the hot condenser where the heavy fraction begins to condense. If corrosion is estimated from the Fe content of the oil, about one-third pound of iron per day was lost from the pilot retort's condenser. The 304 stainless steel of the hot condenser may have been the source of some nickel as well as iron in the oil. Unless corrected for nickel contributed by steel, Ni:V ratios of shale oils could be misleading. A need exists to better assess shale oil's corrosive properties toward all metals present in 304 stainless steel. Solubility of various metals in shale oil at condensation temperatures would be valuable information. Chromium, while a significant component of 304 stainless steel, is barely detected in HRS shale oils (see Table 2).

One cannot totally rule out the possibility that metal ions distill as unstable compounds, short-lived complexes, or transient intermediates. Certain transition metal elements present at the few-ppm level probably come over during retorting. The oil-soluble organometallics (Co, Zn, and V) are in this group. They are unlikely corrosion products since they are unimportant components of 304 stainless steel. Yet, caution must be exercised in defining the source of any ppm-level metal. As noted earlier, gasket corrosion contributes some copper to the oil and retort water. A variety of metals are present as trace impurities in steel, and a small

retort always has gaskets, welds, and connectors of various compositions susceptible to corrosion.

Cold shale oil in contact with metals, dust, and salts has some capacity for leaching surface elements. Additional ions from oil shale dust are taken up by an oil when the work-up includes heating to distill away water. In one instance, a sample prepared according to the procedure for shale oil *A* contained 580-ppm Fe. Refluxing several days with dust present apparently increased the amount of oil soluble metal. Since the surface-to-volume ratio decreases as retort size increases, corrosive action of the oil might be somewhat less at larger scale. Attention to making surfaces in contact with the hottest shale oil inert will be the practical solution to obtaining a product of low metal content. Modern inert materials are available for lining or coating surfaces of a hot condenser. Heat conducting, corrosion resistant materials used in the chemical process industry—including glasses and ceramics—should be well suited for this application. Monitoring tags for oil, water, and dust will prove valuable as new materials are evaluated and as processing methods to improve oil quality are tested.

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