

## PYRITE REMOVAL FROM OIL-SHALE CONCENTRATES USING LITHIUM ALUMINUM HYDRIDE

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A new technique has been developed by the Federal Bureau of Mines for removing pyrite from oil-shale concentrates. This was accomplished by treating concentrates with a tetrahydrofuran solution of lithium aluminum hydride at reflux temperature and extracting the resulting soluble sulfide with dilute acid. By this procedure, the pyrite content of a carbonate free oil-shale concentrate was reduced from 5.0 to 0.02 percent, without objectionable alteration of the organic material (kerogen) as indicated by elemental and infrared analyses. Concentrates obtained by this method will be useful in kerogen structural studies.

According to Bradley (1), oil shale of the Green River formation was deposited in shallow, fresh-water lakes during the Eocene period. The kerogen probably formed from microscopic algae and other aquatic organisms; the minerals formed from water-soluble salts and from deposition of stream-carried silt. A typical Green River oil shale contains more than 50 percent mineral, which includes carbonates, quartz, feldspar, illite clay, and pyrite. Pyrite forms in an alkaline and reducing medium and according to Rosenthal (3), may be formed in nature under similar conditions. It is desirable to remove most or all of the minerals from oil shale in order to have a suitable sample for structural study. Ordinary concentration techniques remove other minerals but concentrate pyrite with the kerogen. This presents a special problem.

Pyrite enters into many of the reactions of kerogen, and many physical-property measurements of kerogen cannot be made when pyrite is present. For example, pyrite enters into reduction, oxidation, and hydrolysis reactions; complicates functional group analysis; and causes high background and poor resolution in X-ray diffraction analyses. Organic sulfur analyses necessitate pyritic sulfur corrections.

Previously, quantitative removal of pyrite has not been possible without objectionable alteration to the kerogen. Nitric acid completely oxidizes the pyrite, but oxidizes and nitrates the kerogen. Nascent hydrogen does not entirely remove the pyrite (2). Pyrite can be oxidized by other reagents (5), but if they were used on oil shale, drastic alteration of the kerogen probably would result.

Lithium aluminum hydride treatment quantitatively removes pyrite from oil-shale concentrates. This treatment is rapid and simple, and causes predictable changes to the kerogen.

### EXPERIMENTAL PROCEDURE

Sample Preparation. Two concentrates were used in this study and were prepared from the same raw shale. The first of these, designated as acid concentrate, was prepared in the following manner: A sample of Green River oil shale was ground to pass a 100-mesh screen and treated with one normal hydrochloric acid until free of carbonate minerals. The mixture then was filtered and the

residue washed with boiling water until the filtrate was neutral. The concentrate then was dried under vacuum at 60° C. for 12 hours.

The second concentrate, designated as attrited concentrate, was prepared (4) from the acid concentrate by the following procedure: Cetane was mixed with the sample to make a paste which was ground in a ball mill with an excess of water until a minimum ash was attained for the organic concentrate. The cetane then was extracted from the paste with benzene and the organic concentrate was dried under vacuum at 60° C. for 12 hours. The silicate minerals were removed by this concentration procedure, because they are preferentially wet by water.

A sample of an Illinois bituminous coal was ground to pass a 100-mesh screen and dried under vacuum at 60° C. for 12 hours.

Lithium Aluminum Hydride Treatment. Two-hundred grams of attrited concentrate and 40 grams of lithium aluminum hydride (LAH) were placed in a 3-liter flask, equipped with a reflux condenser to which a Caroxite drying tube was attached. One and one-half liters of tetrahydrofuran was slowly introduced. The reaction mixture was refluxed for one-half hour, cooled to room temperature, and vacuum filtered. The filtration was stopped while the residue was still wet. To destroy the unreacted LAH, the residue was transferred in small portions as rapidly as possible to a 4-liter beaker containing 1 liter of water. This mixture was acidified with 100 milliliters of 1 N hydrochloric acid, heated to boiling, and filtered. This acid treatment was repeated four times to insure complete removal of aluminum ions, as shown by testing the washings with ammonium hydroxide. The residue was washed with boiling water to remove the hydrochloric acid and then dried under vacuum at 60° C. for 12 hours.

The acid concentrate and the bituminous coal were treated using a similar procedure, except that 20-gram samples with 4 grams of LAH were used.

Nitric Acid Treatment. Pyrite was removed from the attrited concentrate by boiling the sample for one-half hour in 2 N nitric acid and filtering and leaching with boiling water until the filtrate was neutral. The product was dried under vacuum at 60° C. for 12 hours.

Sample Analyses. Pyrite content was determined by the modified Mott method (6). Qualitative evidence for the presence of pyrite was obtained from X-ray diffraction spectra using its 33° 2 theta peak. Ash content was determined at 1000° C. Elemental analyses were determined using the following methods: Carbon and hydrogen by combustion, nitrogen by Kjeldahl, total sulfur by Eschka, organic sulfur by subtraction of pyritic from total sulfur, oxygen by difference, and chlorine by Schoninger. Organic elemental composition was calculated on a mineral and chlorine free basis.

Infrared spectra were obtained using the potassium bromide pellet technique.

## RESULTS AND DISCUSSION

Pyrite Removal. Pyrite is quantitatively removed from the oil-shale concentrates. Lithium aluminum hydride treatment lowers the pyrite content of the

attrited concentrate from 5.3 percent to 0.02 percent and the pyrite in the acid concentrate from 3.1 to 0.02 percent as shown in Table 1. Further evidence of

Table 1. - Decrease of pyrite and ash content due to LAH treatment

	Attrited Concentrate		Acid Concentrate		Bituminous Coal	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
Pyrite, wt. %	5.3	0.02	3.1	0.02	1.8	0.2
Ash, wt. %	8.8	5.5	44.5	43.0	9.4	6.7
Pyrite, X-ray Peak Heights	16	0	4	0	6	0

pyrite removal is shown by disappearance of the X-ray diffraction pyrite peak in the LAH treated concentrates. Pyrite removal is also reflected by decrease of the ash in the attrited concentrate from 8.8 to 5.5 percent and in the acid concentrate from 44.5 to 43.0 percent. This ash reduction approximates the amount expected due to pyrite removal.

This method, which was developed for oil shale, reduced the pyrite content of the bituminous coal sample from 1.8 to 0.2 percent.

Effect on Kerogen. Examination of available data shows little change in the kerogen structure by LAH treatment. Organic elemental analyses (Table 2) reveal

Table 2. - Organic composition of various samples

	Attrited Concentrate		HNO <sub>3</sub> Concentrate	Acid Concentrate		Bituminous Coal	
	Untreated	Treated		Untreated	Treated	Untreated	Treated
WT. % <sup>1/</sup>							
H	10.2	10.9	9.0	10.2	10.8	5.7	5.7
C	77.5	79.9	70.1	77.5	78.6	77.6	78.0
N	2.6	2.7	4.3	2.5	2.6	1.4	1.4
S	1.4	1.5	1.0	1.3	1.5	2.7	3.2
O <sup>2/</sup>	8.3	5.0	15.6	8.5	6.5	12.6	11.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
ATOMIC RATIOS							
H/C	1.58	1.63	1.54	1.58	1.65	0.88	0.88
N/C	0.03	0.03	0.05	0.03	0.03	0.02	0.02
S/C	0.005	0.006	0.005	0.006	0.007	0.01	0.02
O/C	0.08	0.05	0.17	0.08	0.06	0.12	0.11

<sup>1/</sup> Based on mineral and chlorine-free sample

<sup>2/</sup> By difference

no significant differences, except for oxygen, between treated and untreated samples. The elemental analyses indicate a loss of 3.3 percent oxygen for the attrited concentrate and 2.0 percent for the acid treated concentrate. The atomic ratios of hydrogen to carbon, nitrogen to carbon, and sulfur to carbon for the LAH treated sample are approximately the same as the untreated concentrates. However, the oxygen to carbon ratios of the treated concentrates are lowered from 0.08 to approximately 0.05.

The overall infrared spectra (Figure 1) are much the same for the treated and untreated samples. Infrared spectra, however, show elimination of the 5.9 micron band which is attributed to carbonyl groups. The change noted in the 9 to 10 micron region presumably is due to better resolution of the silicate mineral bands. The carbonyl elimination and oxygen decrease may be explained by the reduction of a carboxyl group or an ester linkage to form alcohols.

Nitric acid treatment of the attrited concentrate for pyrite removal increases the nitrogen content from 2.6 to 4.3 percent and oxygen from 8.3 to 15.6 percent.

### CONCLUSIONS

Pyrite has been quantitatively removed from concentrates by using lithium aluminum hydride.

The concentrate produced by LAH treatment is well suited for kerogen structural studies because the LAH reacts only with specific functional groups. Of the functional groups present in kerogen, LAH reduces carbonyl oxygen but does not attack other groups such as ethers, alkenes and amines. Since such changes can be evaluated, they do not interfere with structural studies. Hence, the lithium aluminum hydride method for the removal of pyrite is preferable to the use of strong oxidizing agents, such as nitric acid, which cause non-specific changes in the kerogen.

Since LAH treatment eliminates the pyrite from kerogen concentrates, further treatment with dilute hydrofluoric acid should produce a near mineral-free sample, which would be valuable for future studies on kerogen structure.

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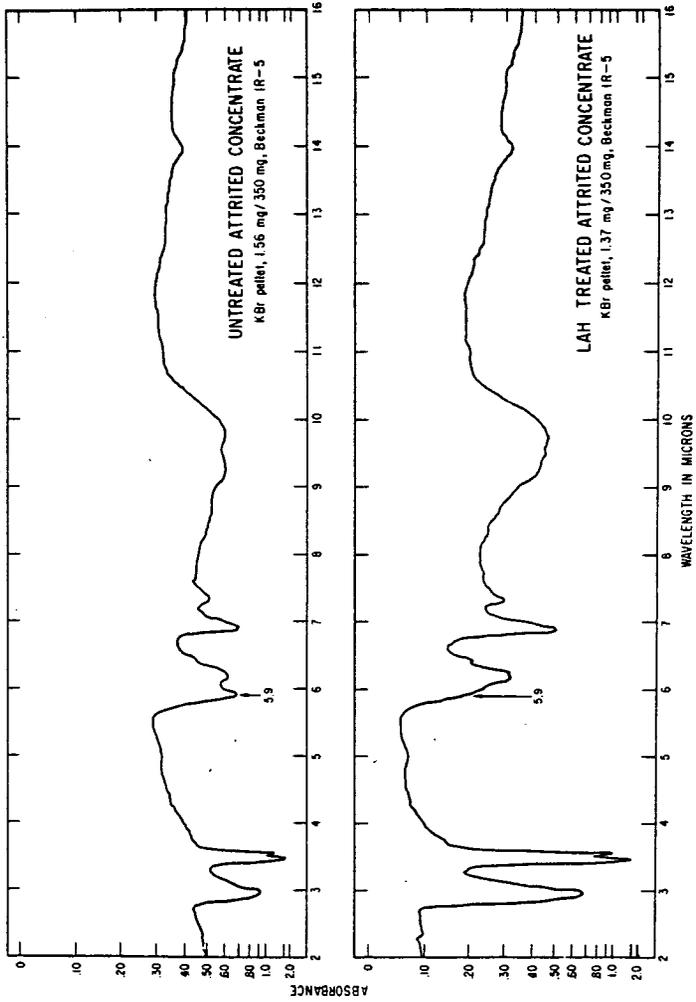


FIGURE 1 - INFRARED SPECTRA OF CONCENTRATES.

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