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LLNL OIL SHALE PROJECT MONTHLY HIGHLIGHTS FOR OCTOBER, 1982

November 30, 1982  
UOPKK 82-18

M E M O R A N D U M

TO: Douglas Uthus/Arthur Hartstein/Jerry Ramsey, DOE Germantown  
FROM: A. E. Lewis, Project Manager  
SUBJECT: LLNL Oil Shale Project Monthly Highlights for October, 1982

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Oil Cracking Kinetics and Diagnostics

Modifications to the cracking apparatus have been completed extending the range of residence times over which we can make measurements to 0.2 to 15 sec. The shorter residence times now available have allowed us to extend the temperature range to 650°C, and measurements of cracking over silica sand have been completed. The data is currently being analyzed, and the apparatus has been readied for measurements over burnt shale. We have also obtained gas-chromatography analyses on all the oil samples and are in the process of looking for correlations between composition and cracking conditions and extent.

Pyrite Oxidation

Approximately 70 percent of the sulfur in raw oil shale is in the form of the mineral pyrite ( $\text{FeS}_2$ ). Retorting of shales of average oil yield produces a retorted shale retaining between 50 and 80% of the original sulfur as pyrite and pyrrhotite ( $\text{FeS}$ ). The use of retorted shale as a fuel results in the combustion of these iron sulfides and the production of  $\text{SO}_2$  most of which is captured by the carbonate minerals in oil shale. We are investigating the rate of sulfide oxidation, and the distance  $\text{SO}_2$  moves within oil shale before it is captured.

We have found that both pyrite and pyrrhotite have at least two stages of oxidation in air at temperatures around 500°C. The first stage is very rapid, producing a mixture of iron sulfate and iron oxide. This stage is faster than char oxidation. The second stage of oxidation is slower than char oxidation and the resulting minerals depend upon the conditions of combustion, particularly the partial pressure of  $\text{SO}_2$ , temperature, and whether carbonate minerals are present.

Microprobe examination of the interiors of oil shale samples oxidized at 575°C in air reveals the complete conversion of iron sulfides to iron oxide ( $\text{Fe}_2\text{O}_3$ ) and a nearly uniform distribution of sulfur throughout the carbonate minerals--the sulfur was not concentrated near the edges of the iron oxide. This suggests a high mobility of sulfur, probably as  $\text{SO}_2$  gas.

Presently we are measuring the role of oxygen pressure on the effectiveness of burnt oil shale to scrub  $\text{SO}_2$  from the gas phase in a situation similar to a dilute-phase fluidized-bed combustor.

### Stickiness of Retorting Shale

In the July Highlights (UOPKK 82-16) we reported our first test of stickiness of oil shale on a stainless-steel pan heated from room temperature to 520°C. After making equipment changes and preparing feed materials, we ran five more tests on raw shales and mixed raw-and-burnt shales in three narrow grade ranges. These shales were fractionated from a mix of Anvil Points and C-a material in the size range from 3.4 to 6.4 mm by flotation in solutions of thallous formate having progressively lower densities. The grade ranges were 0 to 27 L/Mg, 83 to 104 and 187 to 208.

We were surprised to find that the angle at which 50% or more of the sample slid down the incline, as well as the range of slide angles for the entire sample, was only slightly influenced by grade and, contrary to expectation, decreased with increasing grade. Median slide angles were 27.7°, 21.7° and 20.4° (averages) for the lean, medium and rich raw shales at retorting temperatures. Mixtures of one part raw shale to 3.5 parts burnt shale had slide angles about 2.2° greater. Very few particles stuck, none permanently, and all slid down at angles below 40°. It appears that, on stainless steel surfaces in thin layers, hot retorting shale will present no sticking problems.

A UCRL report is being prepared.

### Visitors to LLNL Oil Shale Project

- 10/13/82 Joseph Domagalski, University of Denver Research Institute, to select oil-shale samples for experiments.
- 10/14/82 Bernard Chapman, Physical Technology Unit of CSIRO (Australia), to discuss aspects of the release of trace metals, arising from the prospective oil-shale mining at Rundle in Queensland, and their transport in surface waters. Also, computer model for simulating metal transport in rivers.
- 10/20/82 Hiroshi Miyai and Akihiko Mako, Chiyoda Dames & Moore Co., Ltd., to discuss environmental and waste management aspects of oil-shale development.
- 10/27/82 Art Hartstein, DOE Germantown, and David Sheesley, DOE Laramie, to discuss FY83 budget.
- 10/27/82 Peter G. Alfredson and Professor Malcolm J. Messinger, CSIRO (Australia) to discuss retorting of oil shales, fluid-bed pyrolysis, combustion of spent shale, and gasification of coals and chars.
- 10/28/82 Dr. M. King Hubbert, formerly with U.S. Geological Survey, to discuss LLNL Oil Shale Project and origin of petroleum.
- 10/28/82 Alan Leff, Standard Oil of Ohio to discuss decomposition kinetics, residence-time studies and oil-pyrolyzer facility.

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