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MINIMUM BED PARAMETERS FOR IN SITU
PROCESSING OF OIL SHALE
THIRD QUARTERLY REPORT
APRIL 1 THROUGH JUNE 30, 1980

MASTER

C. E. TYNER

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C. E. Tyner
In Situ Technologies
Division 4734
Sandia National Laboratories
Albuquerque, New Mexico 87185

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ABSTRACT

Oil shale retort runs 028 (16% void) and 029 (7% void), composed of competent shale blocks plus shale rubble, were completed. Retort 028, processed with air at a flux of $0.017 \text{ kg}_{\text{air}}/\text{m}^2_{\text{shale}} \cdot \text{sec}$, had peak temperatures of 700°C , a retorting rate of 1.1 m/day, and a yield of 82% FA. Retort 029, processed with air at a flux of $0.027 \text{ kg}_{\text{air}}/\text{m}^2_{\text{shale}} \cdot \text{sec}$, had peak temperatures of 750°C , a retorting rate of 1.6 m/day, and a yield of 75% FA.

Comparisons of retort model calculations with experimental data from previous retort run 027 (16% void, air flux of $.029 \text{ kg}_{\text{air}}/\text{m}^2_{\text{shale}} \cdot \text{sec}$) were good; observed experimental yield was 95% FA, calculated yield, 92.8%; experimental retorting rates varied from 9.5 to 8.9 cm/hr, calculated rates from 10.3 to 10.0 cm/hr; observed local heating rates ranged from 29 to 14°C/hr , calculated heating rates from 20 to 16°C/hr ; and observed peak temperatures ranged from 815 to 825°C , calculated from 820 to 825°C .

INTRODUCTION AND SUMMARY

This is the third in a series of quarterly reports on the Minimum Bed Parameters for In Situ Processing of Oil Shale Program (FE Control No. 4-79 ET 14165.000). The purpose of the program is to minimize the problems, both economic and environmental, associated with the bed preparation and large scale material removal required by conventional in situ oil shale technologies by determining the minimum conditions (of void, permeability, etc.) actually required for a viable in situ process. This quarter's activities included the successful retorting of 16% and 7% void samples, comparison of previous experimental results with model calculations, and initial use of a computer-based data acquisition system and on-line gas chromatograph.

The retorted samples consisted of 7.6 cm diameter by 28 cm competent cores of oil shale with three slices (0.64 cm each for the 16% void sample--Run 028; 0.32 cm for the 7% void sample--Run 029) of material removed parallel to the axis of the cylinder. Oil shale rubble was used to fill the gaps between shale slices. The samples were sealed in a retort vessel with a very low-thermal-conductivity castable ceramic, ignited with electric heaters, and retorted with air at a flow rate of 3 slm (Run 028) and 5 slm (Run 029). We are not aware of any previous attempts to retort at voids this low in a controlled laboratory environment.

With the 16% void sample, the retorting front moved at a velocity of 4.5 cm/hr (1.1 m/day), while the local heating rate in the retorting zone was about 8°C/min. Peak temperatures were 700°C. Measured yield was 82% FA. With the 7% void sample, the retorting front moved at a velocity of 6.8 cm/hr (1.6 m/day), and the local heating rate was 18°C/min. Peak temperatures were around 750°C, while the measured oil yield was 75% FA.

Much of the analysis of data from a previous 16% void retort,¹ Run 027, has been completed. (The geometry of retort 027 was identical to that of Run 028; the air flow during retorting was higher, 5 slm.) Agreement between experimentally measured parameters and retort model calculations was very good. Peak model temperatures ranged between 820 and 825°C, while observed peak temperatures were between 815 and 825°C.

Calculated retorting rates varied from 10.3 (top of retort) to 10.0 cm/hr (bottom of retort), while measured values were 9.5 to 8.9 cm/hr. Calculated heating rates ranged from 20.5 to 16.2°C/hr, while measured values were between 29 and 14°C/hr. Finally, calculated yield was 92.8% (6.5% loss to oil combustion, 0.7% loss to coking), while observed oil yield was 95% FA.

ACTIVITIES - APRIL 1 to JUNE 30, 1980

A. Retort Runs

Retort runs 028 and 029 were completed this quarter using sliced cylinder samples similar to that used in Run 027 (see second quarterly report¹). Sample voids for the two runs were 16 and 7%, respectively. Figure 1 shows the sample geometry schematically while Figure 2 is a photo of an actual assembled sample (top view).

The retort 028 sample was a 26.6 gpt, 7.6 cm diameter by 26 cm long cylinder with three 0.64 cm slices removed axially. The core was reassembled, instrumented, and the slices (voids) filled with $-.32 \pm .16$ cm, 40.5 gpt rubble. Overall sample void was 16%.

The sample was retorted using air at a flow rate of 3 slm (flux of $0.017 \text{ kg}_{\text{air}}/\text{m}_{\text{sh}}^2 \cdot \text{sec}$), 60% of the flow used in retort 027. Ignition was similar to retort 027, with exit oxygen dropping to about 2% by 0.3 hrs into the run and remaining at approximately that value for the entire run.

The retorting front moved at a velocity of 4.5 cm/hr (1.1 m/day) with a heating rate in the retorting zone of $8^\circ\text{C}/\text{min}$. Peak temperatures were about 700°C , considerably lower (by 100°C) than in retort 027, probably indicating more heat loss (as could be expected at the lower flow rate). Temperature profiles at a number of locations along the bed centerline in the rubble are shown in Figure 3. Figure 4 shows a number of temperature profiles at 6 and 18 cm into the sample. At 6 cm, for example, the plot shows temperatures in the rubble (0) peaking first, followed by the block surface (14), and finally, by the block center (10). Figure 5 shows plots of rubble temperature versus distance down the bed at several points in time. Steady movement of the thermal wave through the bed is evident. Figures 6 and 7 show, respectively, experimental flow rates and exit oxygen concentration and inlet pressure.

Measured yield (based on density determination of shale grade) was 82% FA, somewhat lower than the 95% measured for retort 027. Probable causes for the decreased yield were the lower heating rate (and hence

FIGURE 1. SLICED-CYLINDER GEOMETRY.

FIGURE 2. SAMPLE 027, ASSEMBLED (TOP VIEW).

RUBBLE TEMPERATURES RETORT RUN 028 05/06/80

FIGURE 3.

6,18 CM DEPTH TEMPERATURES RETORT RUN 028 05/06/80

FIGURE 4.

CENTERLINE TEMPERATURE PROFILES **RETORT RUN 028** **05/06/80**

FIGURE 5.

FLOW RATES **RETORT RUN 028** **05/06/80**

FIGURE 6.

increased coking) and higher heat losses. Predicted yield based on the real-time gas analyses was about 70%, using both a material balance calculation² and the LLNL correlation of off-gas alkene/alkane ratios.³ This discrepancy is being investigated.

The retort run 029 sample was similar to that described above, except that rubble regions were only 0.32 cm (1/8") thick and filled with $-.16 \pm .08$ cm ($+1/16 - 1/32$ in) rubble. Overall sample void was approximately 7%.

The sample was retorted using air at a flow rate of 5 slm. Ignition was similar to previous runs. Except for a brief excursion (of unknown cause) of the exit oxygen concentration to 8% late in the experiment, retorting proceeded in a fashion similar to previous runs. (The exit oxygen was brought down to a level of 2.5%--and decreasing--by the end of the experiment by increasing the total flow to 7 slm.) Retort pressure drop (see Figure 8) was not significantly higher than previous experiments, indicating that retorting at 7% void is feasible, at least under the conditions of this experiment.

Temperature profiles (comparable to those shown in Figures 3-5 for run 028) are shown in Figures 9-11 for run 029. One interesting difference (most evident in Figure 10) is the early rubble temperature peak (probably caused by gas phase combustion of oil and product gas), followed by a slight dip and then a broad char combustion peak. The product combustion peak was not evident in the block temperatures (10 or 14). Figure 12 shows inlet and outlet flow rates for run 029.

Material balance calculations made using real time off-gas analysis results were encouraging. The calculations estimated that 2307 g of shale (94% of the total charge of 2642 g) were retorted, while 15% of Fischer Assay oil was combusted, leaving 190 g of oil (84% FA) available for production. Actual yield was 168 g of oil (75% FA). Calculations for the period when the exit oxygen concentration was high indicate the retorting rate had dropped to about half of its previous level and nearly one quarter of the oil generated was being combusted.

Analysis of the data from these two runs is continuing. Results will be reported when completed.

EXIT OXYGEN & INLET PRESSURE
RETORT RUN 028 05/06/80

FIGURE 7.

EXIT OXYGEN & INLET PRESSURE
RETORT RUN 029 06/25/80

FIGURE 8.

RUBBLE TEMPERATURES **RETORT RUN 029** **06/25/80**

FIGURE 9.

6,18 cm DEPTH TEMPERATURES **RETORT RUN 029** **06/25/80**

FIGURE 10.

CENTERLINE TEMPERATURE PROFILES RETORT RUN 029 06/25/80

FIGURE 11.

FLOW RATES RETORT RUN 029 06/25/80

FIGURE 12.

B. Retort Analysis and Model Comparisons

Retort Run 027 (the geometry of which was identical to that of Run 028, while the process air flow was 5 slm [flux of $0.029 \text{ kg}_{\text{air}}/\text{m}_{\text{sh}}^2 \cdot \text{sec}$]) was completed in February 1980, and raw data from that experiment were presented in the second quarterly report.¹ Retort model calculations have since been made using Sandia's block retorting code and actual experimental parameters--flow, block size and grade, etc. A comparison of these results with experimental temperature profiles and the char boundary location (recently determined from post-run core sections) is discussed below.

Figure 13 shows typical temperature profiles (of block surface temperatures) versus time at several locations in the retort bed (6, 12 and 18 cm from the top). The results of model calculations at these locations are shown as solid lines for comparison. Figure 14 shows similar results of temperature versus distance down the bed centerline at two different times (1.0 and 2.0 hours into the experiment). Model calculations are again shown as solid lines. Finally, Figure 15 shows an experiment-model comparison of the difference between block wall and block center temperatures (i.e., thermal gradient through the block) at 12 cm into the bed as a function of time.

Agreement between measured and calculated temperatures is surprisingly good, considering such things as the rubble (not considered in model), heat loss in the experiment, etc. Comparison of retorting rate, local heating rate in the retorting zone, yield, and extent of char combustion were also very good. Measured retorting retorts varied from 9.5 cm/hr in the top half of the retort to 8.9 cm in the bottom half. Calculated values were 10.3 and 10.0 cm/hr. Measured heating rate varied from 29.2°C/hr to 14.8°C/hr over the retort, while calculated values ranged from 20.5 to 16.2°C/hr. Measured yield (based on a density determination of Fischer Assay) was 95% of Fischer Assay. The calculated yield for the blocks was 91.3% (7.9% loss to combustion, 0.8% to coking). Assuming a yield for the rubble of nearly 100% (probably a good assumption under the experimental conditions), the overall calculated yield would be 92.8% FA. These results are summarized in Table 1.

Figure 16 shows the calculated and experimental positions of the char boundary, i.e., the boundary between the shrinking core of retorted but unburned shale and the burned shale.

BLOCK SURFACE TEMPERATURES

RETORT RUN 027 02/29/80

FIGURE 13.

CENTERLINE TEMPERATURES

RETORT RUN 027 02/29/80

FIGURE 14.

FIGURE 15. DIFFERENCE BETWEEN SURFACE AND CENTERLINE BLOCK TEMPERATURES.

FIGURE 16. RETORT RUN 027 - CHAR BOUNDARY LOCATION.

Table 1
Comparison of Calculated and Measured Results
from Block Retorting Run 027

		Top of Retort (6-12 cm)	Bottom of Retort (12-18 cm)
Retorting Rate (cm/hr)	Measured	9.5	8.9
	Calculated	10.3	10.0
Heating Rate (°C/hr)	Measured	29.2	14.8
	Calculated	20.5	16.2
		<u>Total</u>	
Yield (% FA)	Measured	95	
	Calculated	92.8	

The experimental char boundary location was determined by axially sectioning the retorted sample perpendicular to the rubble zones and measuring the boundary location in the two inner blocks. Figure 17 is a photograph of the sectioned sample. Agreement is reasonably good, although the calculated boundary is somewhat steeper than that observed.

While the results of this single experiment are insufficient to verify the many aspects of the block retort model, they are encouraging. Block temperature profiles (for relatively small blocks, at least), retorting rates, local heating rates, yield losses, and char boundary location are, for example, being predicted reasonably accurately. Further comparisons to investigate the effects of block size and grade, void fraction, and gas flux and composition will be made as experiments are completed and data analyzed. This will eventually lead to a fully-verified, predictive LVIS retort modeling capability.

C. Other Activities

Other activities completed during the quarter included installation and initial use of a data acquisition computer system and a gas chromatograph, and development of a calculator program to perform oil shale material balance calculations rapidly without use of a computer.

FIGURE 17. SECTIONED VIEW OF RETORT 027.

Installation of the ModComp Modacs III computer system was completed early in the quarter, and software development advanced rapidly enough that the system was used on retort 029. The system currently accepts data (thermal, flow, pressure, etc.) from a datalogger, stores the data on disks, and outputs the data to an HP printer and plotter for display. Software for direct plotting and printing is being developed as manpower allows.

A Hewlett-Packard gas chromatograph for retort off-gas analysis was also brought on-line during the quarter. Sample turn-around time for a complete gas analysis through C₄'s is 30 minutes. For shorter retort runs, bomb samples are also taken at the 15 minute points between real time samples for post-run analysis.

One reason for requiring real-time off-gas data is to allow use of that data in analyzing progress of the retort--in real time. The material balance scheme developed by Hommert² can, for example, use the data to determine rates of retorting, oil combustion, carbonate decomposition, etc. One criticism of the material balance calculation has been that it requires a computer. While the general availability of computers at most oil shale retorting experiments somewhat invalidates this criticism, the need for a quick, convenient, non-computer scheme for solving the material balance equations (which involves a 9 x 9 matrix inversion) does exist. A program capable of running on an HP41C hand-held calculator has been developed for this purpose. Fully prompted data input (gas compositions, total flow, shale grade, etc.) requires about one minute, while execution of the program to yield the amounts of shale retorted and oil produced, the percentages of oil burned and carbonates decomposed, etc., requires an additional four minutes. The calculator routine has been used to analyze gas data from retorts 027, 028, and 029. Results agree exactly with those obtained from computer runs.

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