Testing and Performance of the Pacific Northwest Laboratory 6-kg Retort

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ABSTRACT

This report describes and discusses the design, construction, calibration and operations of the Pacific Northwest Laboratory (PNL) 6-kg retort. Use of this retort will help determine the distribution and speciation of Hg, As, Se, and Cd compounds as a function of retorting parameters in shale oil, retort water, and offgas. The first test consisted of heating the oil shale to 500°C with a 100% nitrogen (N₂) sweep gas. Results of this test demonstrated that the system operates as designed; only two minor modifications were necessary to achieve satisfactory operation of the retort.

CONTENTS

INTRODUCTION.....	1
PROJECT OBJECTIVES.....	2
SYSTEMS DESCRIPTION.....	3
DATA ACQUISITION SYSTEM.....	5
RETORT TESTING.....	6
RESULTS AND DISCUSSION OF RETORT RUN PNL-1.....	8
ZEEMAN ATOMIC ABSORPTION SYSTEM.....	10
CONCLUSIONS.....	11
FUTURE OBJECTIVES.....	13
REFERENCES.....	14

INTRODUCTION

Pacific Northwest Laboratory (PNL) is conducting a program on "Partitioning and Chemical Speciation Studies of Volatile Trace Elements" for the Office of Fossil Energy of the Department of Energy (DOE). The program goal is to determine the distribution of mercury (Hg), arsenic (As), selenium (Se), and cadmium (Cd) in the offgas, retort water, and shale oil and to determine the chemical species of these elements in the product streams. These elements were chosen because of their likelihood to be volatilized out of the oil shale rock matrix and redistributed into the product streams of a commercial retort. In this study a fully instrumented 6-kg retort will be used to carefully control retorting parameters capable of changing the distribution and species present in the product streams. This information will be helpful in minimizing environmental concerns while maximizing the quality of the liquid fuel produced in the retorting process.

This report, the first in a series of three, will describe the construction of the PNL 6-kg retort and the testing and performance of the retorting apparatus.

PROJECT OBJECTIVES

The objective of this program is to determine how retorting process parameters affect the partitioning of Hg, As, Se, and Cd from raw oil shale to spent shale, shale oil, retort water, and offgas. Because of their volatile nature, a significant fraction of these elements is released from the raw oil shale matrix during retorting and subsequently migrates to the product shale oil, retort water, or offgas streams. Thus, depending on the form(s) of the chemicals in each product stream, these elements may be mobilized into the environment unless removed from the streams before disposal.

For each of the aforementioned elements, the objectives of this study are to 1) determine the distribution coefficients for each product stream; 2) identify the chemical forms in retort water, offgas, and shale oil with particular emphasis on inorganic or organometallic species known or suspected of being carcinogenic or toxic; 3) investigate the mechanism(s) responsible for mobilizing toxic, or labile chemical forms identified in item 2 into each product stream; and 4) determine the effect of retorting rate, maximum retorting temperature, and retorting atmosphere on items 1 and 3 above.

SYSTEMS DESCRIPTION

A schematic diagram of the retort system can be seen in Figure 1. The main component of the retorting apparatus is a three-zone Thermcraft® furnace and its temperature controller unit. The central controller allows the furnace to be heated at various rates ranging from 0.5°C/minute to 10°C/minute. The furnace is designed to contain a 10-cm-diameter, 304 stainless-steel retort vessel. A thermocouple well is positioned along the centerline of the vessel to monitor the temperature at the top, middle, and bottom of the shale bed.

The sweep gas enters the top of the vessel and flows down through the shale bed. The sweep gas is supplied by compressed gas cylinders and controlled by a pressure regulator and rotometer. The outlet gas temperature is measured by an in-line thermocouple located above the oil/water receiver. The oil/water receiver is maintained at room temperature. From the oil/water receiver, the output gases and condensible vapors are routed to the condensers. Two 0.75-m-long glass condensers are connected in series and cooled to +5°C with a refrigerated bath. The offgas temperature is monitored as it exits the condenser system by an in-line thermocouple. On subsequent retort runs, the Zeeman® atomic absorption (AA) spectrometer will be used to measure Hg in the offgas both before and after it passes through the condensers. During the first experiment, retort run PNL-1, a rotometer was used to simulate the offgas flow (1.0 L/minute) to the Zeeman AA. This gas was subsequently returned to the system so that the total flow rate of the retort system could be accurately determined at a single point.

The retort system is maintained at a positive pressure of 3 psig by a 2.1-m retort water column. The retort offgas flow is monitored by a heat-capacity mass flowmeter that can be recalibrated during retort runs

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Figure 1. Schematic Diagram of PNL 6-kg Retort.

by periodically passing the offgas through a wet-flow test meter. During retorting, the gas composition changes from 100% N_2 to a mixed component system containing various amounts of other gases including light hydrocarbons in addition to N_2 . These additional gases alter the heat capacity of the offgas. This results in a significant error in the readings of the mass flowmeter unless it is recalibrated periodically throughout the run. The thermocouples, mass flowmeter, and wet-test meter are all monitored by the Hewlett-Packard^(a) (HP) 3054 data logger system. This system will be discussed below.

DATA ACQUISITION SYSTEM

An HP Model 3054 data logger is the key component of the retort data acquisition system. This system consists of an HP 3497A data acquisition and control unit and an HP 85A computer. The HP 3497A includes two 20-channel analog input cards and a reciprocal frequency counter card. The analog input cards can be connected to thermocouples to record temperatures or can be used simply as voltage recorders for the mass flowmeter or the Zeeman AA output signal. The reciprocal frequency counter is used to monitor interrupts from the wet-test meter for recalibration of the mass flowmeter.

The original version of the data logger software was developed at Lawrence Berkeley Laboratory (LBL), Berkeley, California, and was extensively modified for our application. In its current form, the program can record data for up to 25 channels on a magnetic tape cartridge as well as listing it on the thermal printer concurrently. Five data points are displayed on the screen at selected intervals with the others available to the operator on demand through the use of soft-keys. The program also provides a flow calibration based on wet-test meter data

(a) Hewlett Packard, Inc., Avondale, Pennsylvania.

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when the meter is switched into the system. The calibration is displayed on the screen each time a wet-test meter interrupt is received. The mass flowmeter can then be recalibrated to provide an accurate and continuous permanent record on the tape. Final display and reduction of the data will be done on a VAX 11/780 computer system using existing data reduction routines such as the BBN Research Systems RS/10 program currently available on the VAX. The data logger program has been modified so that the data written on the tape are in a format that can be transmitted from the retort laboratory to the VAX via telephone lines. A 1200-baud modem, RS-232C interface, and terminal emulator software have been added to the system and fully tested.

RETORT TESTING

The two main components of the retorting system that required testing and calibration were the sweep gas system (rotometers and mass flow controllers) and the furnace. Standard reference methods were used to calibrate the wet-test meter, which in turn was used to calibrate the mass flow controllers. The main objectives when calibrating the furnace were 1) to eliminate any temperature differentials between the center zone and the two end zones of the furnace, and 2) to prevent the furnace from overshooting the temperature set point during the heatup phase of the retort run. To satisfy these requirements, the furnace was first tested with an empty retort vessel in place. Three thermocouples were located on the exterior surface of the retort vessel (one near the top and bottom, and one in the center). Next, heating rate tests were conducted with the retort vessel loaded with pea gravel (to simulate a thermal load). The furnace was programmed to heat at 1°C/minute to a maximum temperature of 500°C. This test run was made with the system monitored by the data acquisition system. A number of minor design modifications were found to be necessary. After these modifications were completed, the retort was prepared for the first actual test run with Anvil Point shale.

The object of retort run PNL-1 was to determine how the retort system would behave under heating rate and gas flow conditions similar to those used in inert gas retort runs at LBL. There, Hg has been monitored on-line in the offgas and measured in the shale oil and retort waters (Hodgson et al. 1981). For this run the retort vessel was filled with 6 kg of raw shale (from 0.25 in. to 30 (600 μ m) mesh) and suspended in the furnace. An N₂ input gas flow rate of 2.0 l/minute and a nominal heating rate of 1.0°C/minute (8.2 hours to reach 500°C) were selected for retort run PNL-1. The furnace was programmed to level off at 500°C and maintain that temperature for 1 hour to bring the retort vessel to 500°C. When the retort vessel reached 500°C, the furnace power was turned off and the system allowed to cool to room temperature for 24 hours with N₂ flowing through the vessel.

The data logger monitored the retort temperatures and flow rates at 2-minute intervals. The calibration of the mass flowmeter was checked every 30 minutes during the early part of the run and every 15 minutes during shale oil production (350°C to 450°C). At approximately 110°C, physically adsorbed water on the raw shale was volatilized and condensed from the offgas into the oil/water receiver vessel and the first condenser. Beginning at about 350°C, shale oil began to appear in the first condenser. No significant amount of material was collected in the oil/water receiver until near the end of shale oil production. The material that accumulated in the oil/water receiver appeared to be the heavy distillate fraction of the shale oil, which began condensing and congealing immediately after exiting the heated zone of the furnace.

RESULTS AND DISCUSSION OF RETORT RUN PNL-1

Figure 2 contains temperature and flow rate profiles for the 9-hour data acquisition period of retort run PNL-1. The slope of the temperature profile (solid line) was determined using a regression method. The slope, $0.93^{\circ}\text{C}/\text{minute}$, closely matches the $1.0^{\circ}\text{C}/\text{minute}$ heating rate set into the temperature programmer. The maximum temperature variation across the furnace during the run was 6°C and occurred at the very end of the heating program. Maximum shale oil production occurred at approximately 400°C , which correlated well with the maximum offgas outlet temperature (dashed line) and offgas flow rate (dotted/dashed line). Shale oil production decreased to zero as the temperature approached 450°C . Examination of the spent shale revealed clusters of spent shale bound by a reticulated carbon material, which appeared to originate from the residual heavy distillates unable to flow out the retorting zone. The mass balance data for retort run PNL-1 are summarized in Table 1. The weight ratio of spent-to-raw shale was 0.75. The amount of oil and water recovered was equivalent to 20.4 and 2.16 gal/ton, respectively. These values were 80% and 65% of the Fisher Assay results (Table 1), respectively. The values were comparable to those obtained from a series of similar retort runs at LBL (Hodgson et al. 1981). One notable difference from the LBL retort results was the mass imbalance of -11%. This appears to have resulted because the mass flowmeter was not recalibrated often enough during the retort run, and possibly because the molecular weight of the offgas was estimated because no gas composition data were taken. These problems will be remedied in future PNL retort runs.

After two weeks at 4°C , the shale oil/retort water mixture was separated into shale oil and retort water fractions. On subsequent retort runs, the shale oil/retort water mixture will be separated immediately after the run. These samples will be analyzed to determine the elemental distribution and speciation for Hg, As, Se, and Cd in retort product streams.

Figure 2. Plot of Retort Temperature, Gas Outlet Temperature and Gas Outlet Flow Rate from Retort Run PNL-1.

TABLE 1

Product Distribution for Laboratory Retort Experiment PNL-1

	<u>Material Distribution</u>		<u>PNL-1 Retort Run, gal/ton</u>	<u>Fisher Assay gal/ton</u>
	<u>Mass, g</u>	<u>Distribution, %</u>		
Raw Shale	5775.0			
Spent Shale	4308.8	74.6		
Oil	447.5	7.7	20.4	25.6
Water	53.9	0.9	2.2	3.4
Gas	291.2	5.0		
Imbalance	-629.9	-11.8		

ZEEMAN ATOMIC ABSORPTION SYSTEM

A Zeeman AA system was obtained from HAD^(a) Instruments that was similar to that described by Girvin and Fox (1980). It was delivered in early December 1983 and initial testing performed off-line at that time. It will be used during the second retort run and subsequent Hg retort runs to monitor the total mercury concentration in the offgas. The HP data logger will be used to collect data from the Zeeman system during the run. Data collected will include both the total uncorrected absorption signal and the net background corrected signal, which are directly proportional to the Hg concentration present in the offgas.

(a) Hadishi Instruments, Berkeley, California.

CONCLUSIONS

The retort operated as expected with two minor exceptions. One difficulty was the distribution of the shale oil and retort water through the plumbing system. This problem was caused because the retort gas was not being cycled through the oil/water receiver. The original design relied on gravity to direct the flow of condensed retort water and shale oil into the collection vessel. A redesign of the oil/water receiver that allows the oil- and water-laden gas stream to impinge on the walls of the container should eliminate this problem. The second problem concerned the efficiency of the condensers, which allowed some minor breakthrough of light distillate. This problem can be easily corrected by the use of an ethylene glycol/water-based coolant. Using this mixture as the heat exchange medium in the refrigeration system will enable the condensers to be cooled to -5°C . This procedure will be tested during the next retort run. This should prevent any significant amount of the light hydrocarbons from accumulating in gas lines or water columns.

The gas handling system, the flow monitor, the data acquisition system and associated software, and the data transmission system from the data logger to the VAX mainframe computer all functioned as designed during retort run PNL-1.

These results have demonstrated that the retorting and data acquisition systems are now fully operational (see Figure 3).

Figure 3. The 6-kg Retort at Pacific Northwest Laboratory.

FUTURE OBJECTIVES

The primary administrative objective is to integrate the retorting and analytical method development programs, previously funded as separate programs. The immediate technical objectives are to conduct retort runs using a gas chromatograph to monitor the offgas composition and the Zeeman AA to measure on-line the total mercury in the offgas. These runs will be followed by subsequent analysis of the shale oil and retort water for total and speciated Hg, As, Se, and Cd. This phase of the program relates to the distribution of material at a maximum temperature of 500°C. Subsequent retort runs will be run at maximum retorting temperatures of 750°C and 1000°C. Sweep gases that will be used include 100% N₂ and a mix of 75% N₂ and 25% steam. Special emphasis will be placed on simulating the heating rates and sweep gas composition currently used in prominent surface retorting technologies. The product streams from these retort runs will be analyzed and the results compared to determine the relationship between retorting parameters and the distribution of the various chemical forms of Hg, As, Se, and Cd.

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