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HOT-RECYCLED-SOLID PILOT PLANT
1991 Status Report

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Hot–Recycled–Solid Pilot Plant 1991 Status Report*

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ABSTRACT

At Lawrence Livermore National Laboratory, we are studying aboveground oil shale retorting and have developed the LLNL Hot-Recycled-Solid (HRS) process as a generic, second-generation, rapid pyrolysis retorting system in which recycled shale is the solid heat carrier. In 1984-87, we operated a 1 tonne-per-day HRS pilot plant to study retorting chemistry in an actual recirculation loop[1]. In 1989 we upgraded our laboratory pilot plant to process 4 tonne-per-day of commercially sized shale, allowing us, for the first time, to study pyrolysis and combustion using the full particle size. With the new facility we are able to produce enough oil for detailed characterization studies, can evaluate environmental consequences, and begin answering the many bulk solid handling questions concerning scale-up of the HRS process. In this paper we report on operations of our laboratory (4TU) pilot plant and plans for a field test unit (FTU) at approximately 100 tonne-per-day scale to be sited in the western United States.

INTRODUCTION

Laboratory Pilot Plant Description

Key components of a Hot-Recycled-Solid (HRS) retorting system are being studied in a 4 tonne-per-day laboratory facility at Lawrence Livermore National Laboratory (LLNL), designed to process commercially sized shale (7mm top size). Identified in Figure 1 are five key components comprising the HRS process: 1) a delayed-fall combustor, with a five second solid residence time, 2) a fluidized-bed classifier to control solid discharge and provide a pressure block to separate pyrolysis and combustion atmospheres, 3) a high throughput, short residence time, fluid-bed

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mixer, 4) a moving-packed-bed pyrolyzer with crossflow gas sweep and radial vapor removal, and 5) an air pneumatic lift pipe combustor.

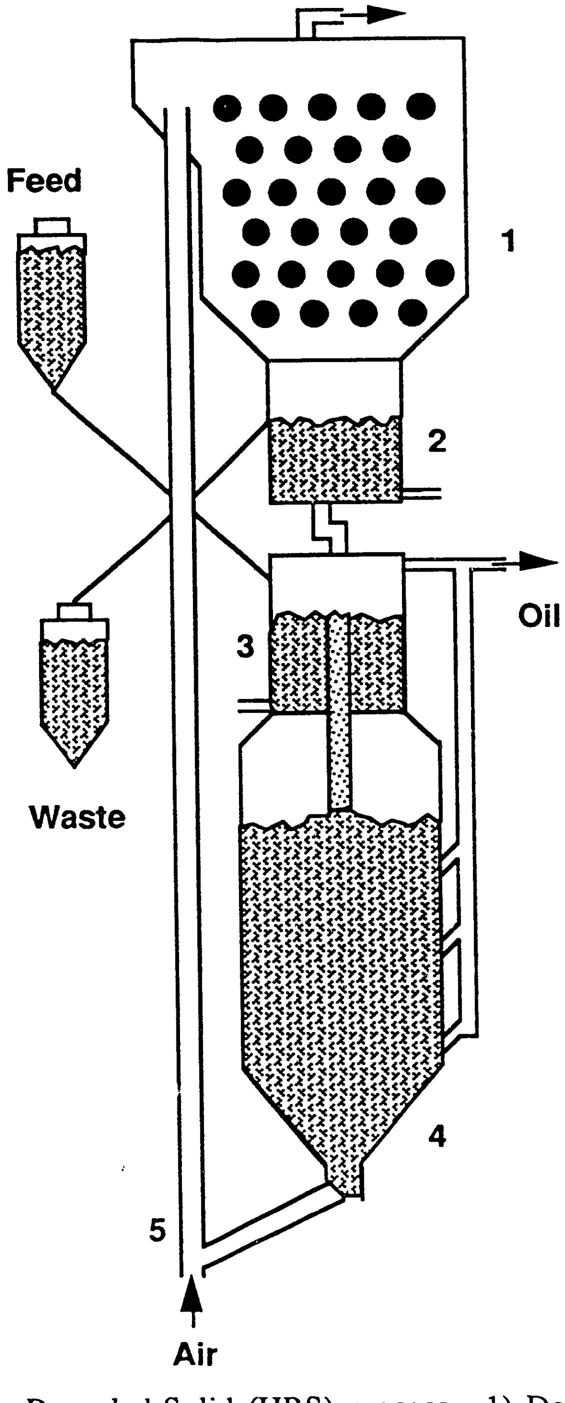

Figure 1. Schematic of Hot-Recycled-Solid (HRS) process. 1) Delayed-fall combustor, 2) Fluid-bed classifier, 3) Fluid-bed mixer, 4) Packed-bed pyrolyzer and 5) Air pneumatic lift pipe

Pyrolysis Components

Fluid-Bed Mixer

Raw and recycled shale must be mixed to begin the pyrolysis process. We use a two-stage, 15-cm diameter, fluid-bed mixer for our tests, with a nominal 30 second solid residence time (Figure 2). The active bed height is 40 cm. By providing a short residence time fluid-bed mixer followed by a moving-packed-bed pyrolyzer, we accomplish the following: 1) rapid mixing in a compact unit, 2) high gas sweep to recover generated oil, 3) reduced gas requirements compared to a fluid-bed mixer and pyrolyzer in one unit, 4) shale residence time variations inherent in fluid-beds mitigated by a downstream packed bed pyrolyzer.

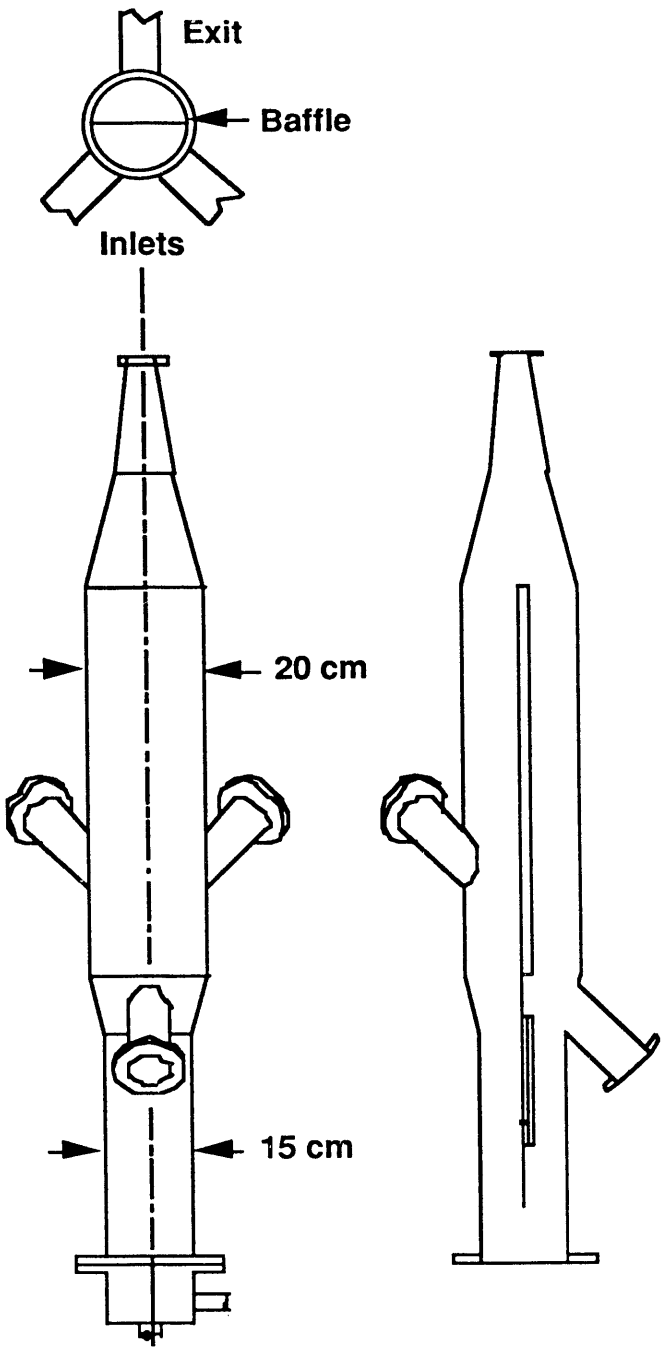

Figure 2. Schematic of 2 Stage Fluid-Bed Mixer, Front, Side at Top Views

Packed-Bed Pyrolyzer

The kinetics of oil shale pyrolysis have been accurately measured in the laboratory [2]. Based on these results, a solid residence time of under 2 minutes is required at 500°C to complete pyrolysis. Concurrently, oil is lost during pyrolysis due to coking and cracking, which is a function of gas-solid contact time. In the pilot plant, shale leaving the mixer enters a 20 cm diameter by 125 cm high packed-bed pyrolyzer with circumferential gas removal (Figure 3). Since we employ radial vapor removal, conditions of solid residence time and gas-solid contact time are accomplished in our 4 tonne-per-day pyrolyzer which directly apply to any scale*. A residence time of 3 minutes is provided in our design at a recycled to raw shale ratio of three to one. Shorter residence times are achieved by simply maintaining a lower bed level. Features include: 1) uniform residence time of solid, 2) short path length for oil vapor removal, with direct applicability to larger scale, 3) smaller reactor volume (less voidage) and less gas sweep compared to fluid-beds, and 4) process flexibility to alter residence time (by changing bed height) and 5) excess, surge volume to accommodate process upsets.

* It can be shown that gas-solid contact time in these systems is independent of vessel diameter

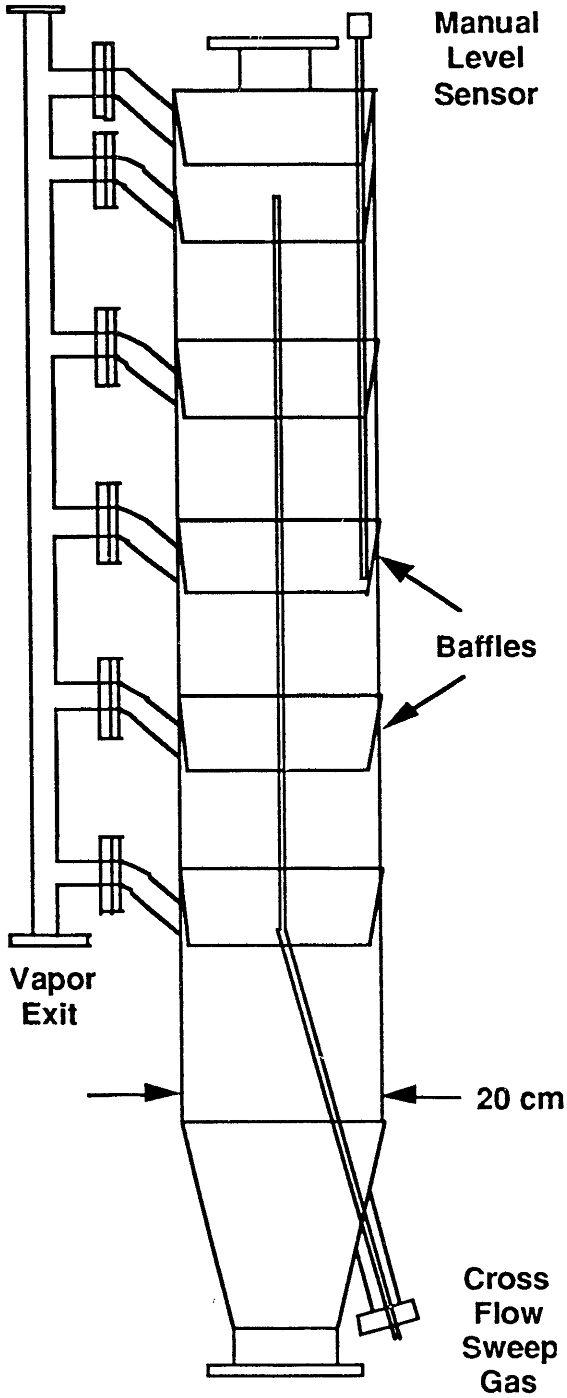

Figure 3. Schematic of Packed-Bed Pyrolyzer Showing Baffles, Vapor Exits, Sweep Gas Injection and Manual Level Sensor

Combustion Components

Combustion kinetics in solid-recycle systems are poorly understood due to the complexity of the process. Shale combustion is sensitive to processing conditions and residual carbon, hydrogen and sulfur content and kinetics. Nitrogen compound formation and destruction mechanisms in the presence of oxidized shale at low temperatures (500-600°C) are poorly understood. Also, during pneumatic transport, particle attrition, solid velocities and other particle dynamics for mixed particle systems are not well understood. Low temperature combustion may result in significant CO and unburned hydrocarbon emissions while possibly limiting nitrogen oxide and SO_2 emissions.

Air Lift-Pipe

We study combustion during pneumatic transport using a 5.4-cm diameter lift-pipe system. The lift is designed to combust a major portion of the char on the spent shale, with a slight excess of oxygen in the flue gas. Complete combustion of the largest particles will not occur in one pass through our combustion system. However, in our design fines are preferentially discharged and larger particles are recycled, providing multiple passes through the system to complete combustion.

Delayed-Fall Combustor

Following the lift, the solid tumbles through a delayed-fall combustor consisting of a series of rods to inhibit free fall. Air is blown either co- or counter-current to the solid. The delayed-fall combustor (Figure 4) was designed with a 5 second solid residence time and enough air to bring the solid to the desired recycle temperature. Based on mathematical modeling, co-current air injection appears more efficient, due to a longer retention time for fine shale. We will critically evaluate both processing options through operation of our pilot plant.

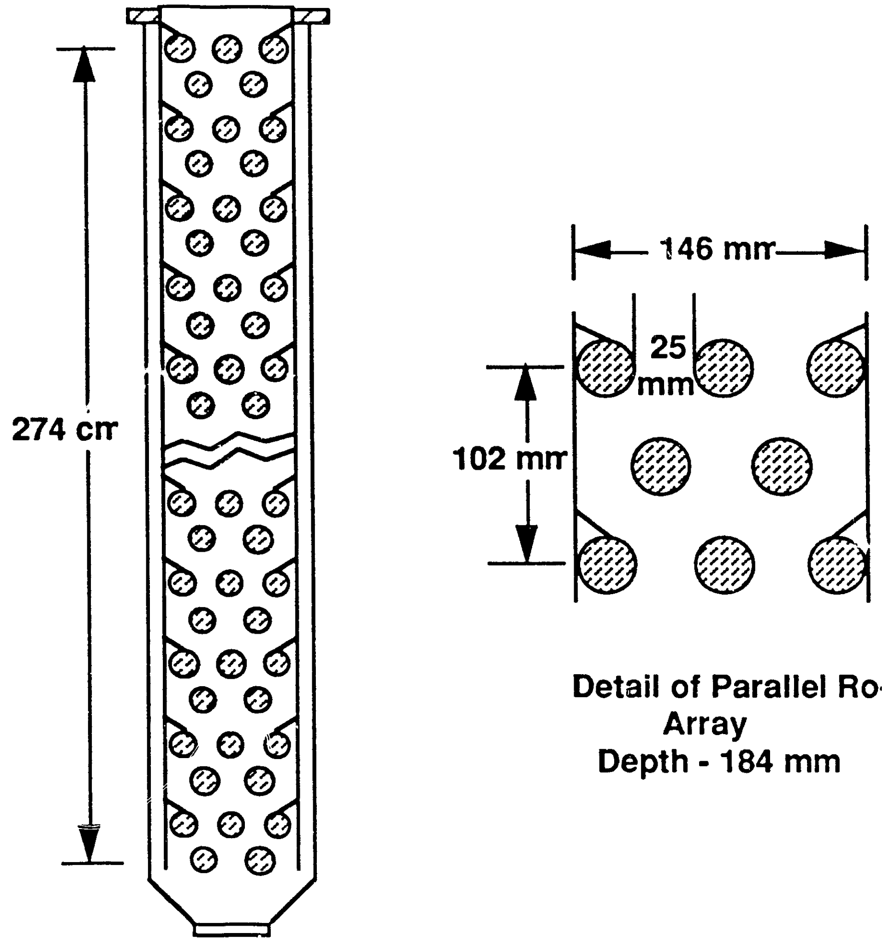

Figure 4. Schematic of Delayed-Fall Combustor

Fluid-Bed Classifier

After the delayed-fall combustor, the solid falls into a fluid-bed classifier (Figure 5) which performs three main functions:

1) It provides a solids discharge from the circulating loop in such a way that the rejected material includes the smallest circulating particles.

2) It functions as a surge tank to smooth irregularities in solids loop flow.

3) It provides a pressure block to separate combustion and pyrolysis atmospheres.

The classifier can be fluidized with inert gas or air. If air is used, combustion of residual char will occur. We designed the classifier with a shale residence time of 40 to 120 seconds, depending on the height of the solid discharge.

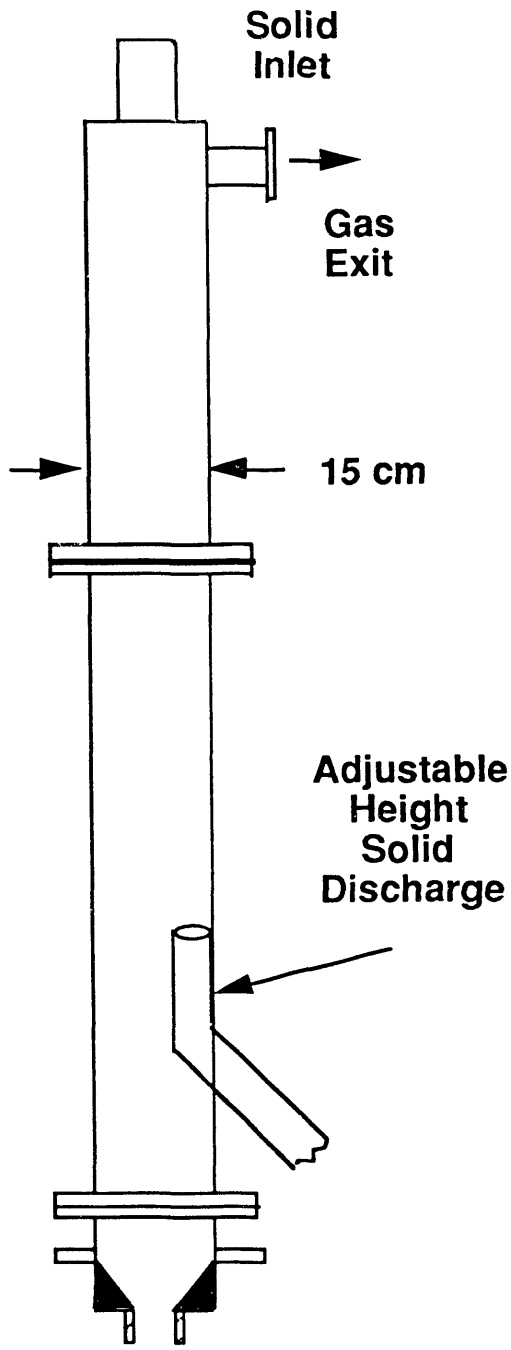

Figure 5. Schematic of Fluid-Bed Classifier

4-TPD RETORT OPERATIONS AND TEST RESULTS

In our 4 tonne-per-day pilot plant we internally circulate 7.5 kg/min of shale around the process at a recycle/raw ratio of 3:1. Two L-valves are used for solids flow control, one below the packed-bed pyrolyzer and the second below the fluid-bed classifier. Each valve contains a skid to interrupt the solid flow. The skid is equipped with a continuous and pulsed gas supply. The continuous flow of gas keeps jets located horizontally along the skid clear. The pulsed gas is controlled via a solenoid valve which is opened approximately once per second. When the solenoid opens, the combined gas flow forces a quantity of solids off the skid and through the valve. Approximately 250-300 gms of solids are moved for each 100 ms gas pulse. Thus to obtain the design solid flow rate of 7.5 - 10 kg/min (7.5 kg/min of recycled shale and 2.5 kg/min of raw shale) the L-valve is operated at 30-40 cycles per minute.

During recirculation, as solid enters the lift-pipe from the pyrolyzer L-valve, a surge in the local pressure occurs proportional to the solids loading in the lift. Figure 6 shows a typical pressure response. We use this information to determine solid recirculation rate, discussed below.

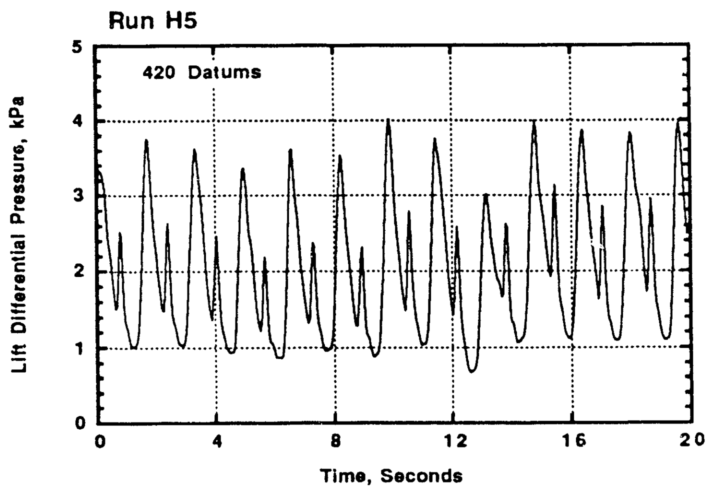

Figure 6. Lift Pipe Pressure Response to Pulsed Solid Loading

Solid Flow Measurement

Controlling the solid flow rate is very important to proper operation of the retort system. At the same time its measurement is difficult. In the pilot retort system provisions have been made for measuring the solid flow at three points. Two of these, the raw shale feed and spent shale discharge rates are easily measured via changes in vessel weight.

A more difficult measurement is the total solids flow circulating within the system. To measure the solid recirculation rate, we installed a star-valve within the loop between the delayed-fall-combustor and the fluid-bed-classifier. The flow rate is measured by controlling the rate of rotation of the valve so as to maintain a small constant head of material above the valve. Although operational, this star valve adds some complications to the overall system, since it is the only moving part in the hot hostile environment, making it subject to failure. Also, it presents a possible upset to the overall system if levels are not properly maintained. For these reasons it would advantageous to use some other means of monitoring total solids flow.

As it turns out, one of the basic process units, the lift-pipe, has the potential of allowing for measurement of solids based on the change in pressure from bottom to top of lift-pipe, ΔP. This pressure drop is clearly related to the solids loading in the lift which in turn is related to the solids flow rate. Using a simple algorithm, the total solid flow rate in the lift, S, is given by

$$S = \rho_s U A \qquad (1)$$

where ρ_s is the effective density of solid material in the lift, U is the average solid velocity, and A is the cross-sectional area of the pipe. If it is assumed that slip velocity of the solid does not depend on loading and that loading, ρ_s, is directly proportional to the increase in ΔP with solids flow then S can be given by

$$S = K\,(\Delta P - \Delta P_0) \qquad (2)$$

where K is a constant representing all constant parameters and ΔP_0 is the pressure drop with no solids flow. Based on measurements presented elsewhere[3] the values of K varied from about 3 to 4. This variation of K should not be a surprise since the average solid velocity, U, is certainly some function of gas flow rate and operating temperature and pressure. Below, we compare solid flow using the rotary star valve with estimates using the lift ΔP over the course of run H7.

Pilot Plant Run Results

Seven engineering tests (H1-H7) have been completed to date in which 24 gallon-per-ton Green River oil shale was processed. Results for run H7 are presented in the following. For this run, lift gas was separated from the solid above the delayed-fall combustor and the fluid bed classifier was operated with air. As shown in Figure 7, we operated at two feed rates, 2 and 2.5 kg/min with a recycle ratio of 2.5-3 to 1. Comparison of the solid recirculation rate using the star valve (DFC Solid) versus lift ΔP (Lift Solid) was very good, using K of 4.1. Gas flows to the fluid beds, lift and product are shown in Figure 8. The system operated stably with constant pressure maintained in the head space above the pyrolyzer and fluid-bed classifier (Figure 9). By minor adjustments in back pressure and L-valve pulse rates, reasonably constant recirculation rates were obtained with variation in bed level (Figure 10) well within limits to complete pyrolysis. Finally, temperatures around the recirculation loop are shown in Figure 11, at the top of the pneumatic lift pipe (T-CLS), in the fluid-bed classifier (T-FBC), at the exit of the fluid-bed mixer (T-FBM-EX) and midway through the packed-bed pyrolyzer (T-PYR-88). Oxidized shale at 685°C was recirculated and mixed with the 105°C raw shale feed to produce a 515°C equilibrium temperature in the mixer and pyrolyzer. During the period shown in the figures 400 kg of raw shale were processed. Results from this and future runs will form the basis for determining overall operating characteristics and scale-up potential of the HRS process.

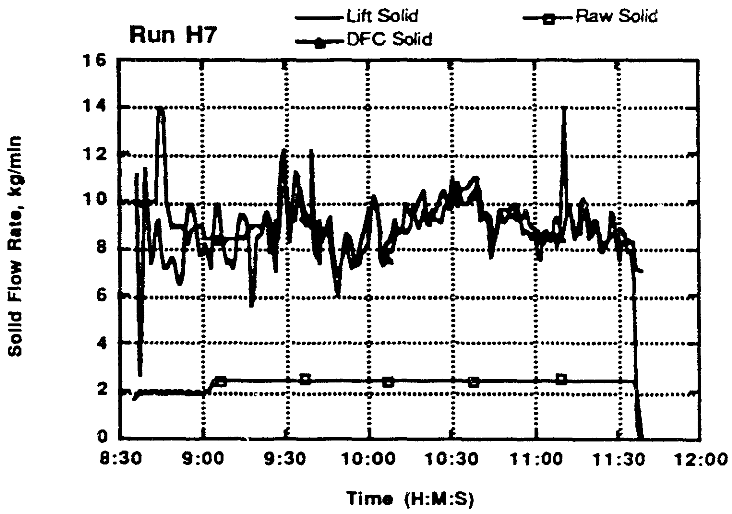

Figure 7. Solid Flow of Raw Feed and Recirculated Solid for Run H7.

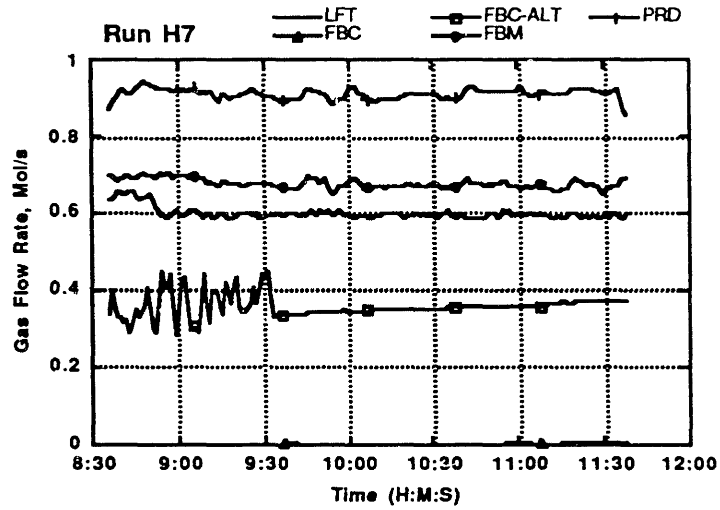

Figure 8. Gas Flows in the Fluid Beds, Pneumatic Lift and Product Collection System for Run H7.

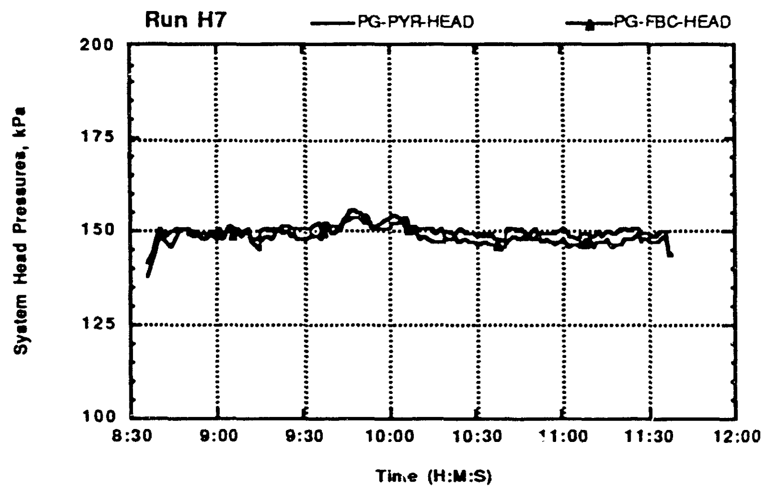

Figure 9. Head Space Pressures for Run H7

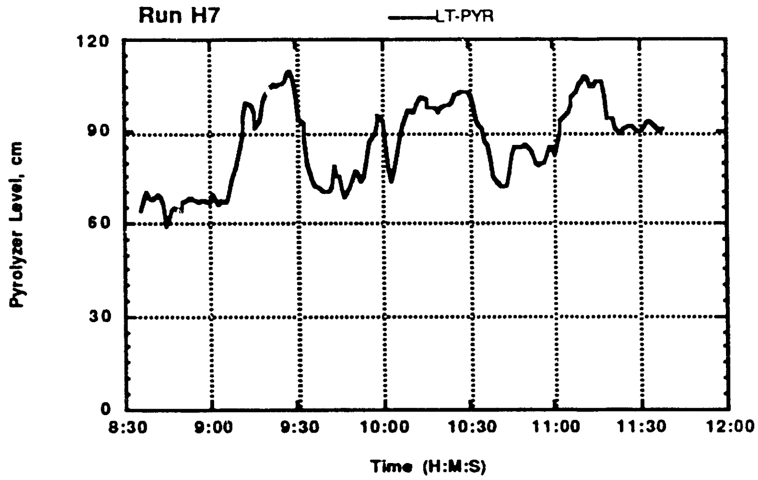

Figure 10. Pyrolyzer Level Maintained During Run H7

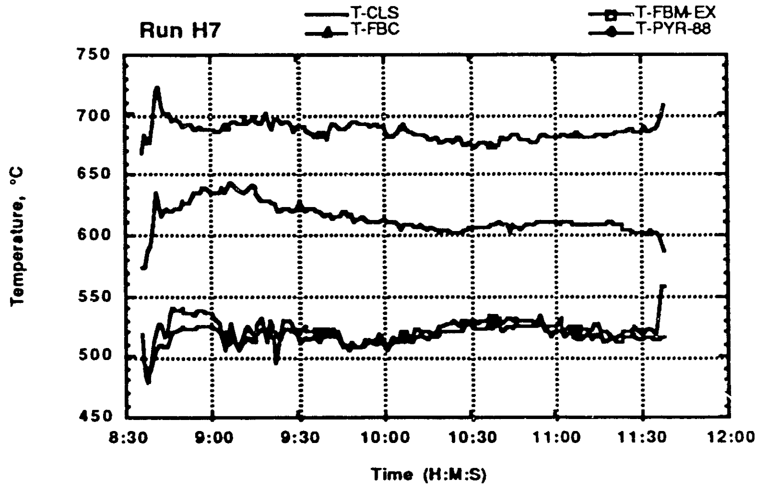

Figure 11. Temperatures Measured Around Recirculation Loop for Run H7.

Conclusions

Successful pilot plant operations have been achieved to date, with initial data reduction underway. We hope to complete a run series and quantify our results in the months to come. Based on these results we will be able to begin detailed design of a larger field test of the HRS process at approximately 100 tonne-per-day scale, which we hope will eventually lead to commercialization of the process early in the next century. We are seeking Government and private industry support to begin construction of a field test unit (FTU) in 1993 or soon after.

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