UCRL- 95140
PREPRINT

LLNL Oil Shale Project Review
METC Second Annual Oil Shale Contractors Meeting

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This paper was prepared for submittal to
METC Second Annual Oil Shale Contractors Meeting
U.S. DOE Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, WV

August 12-13, 1986

Lawrence Livermore National Laboratory

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LAWRENCE LIVERMORE LABORATORY OIL SHALE PROJECT

1. FTPA NUMBER: W-7405-ENG-48

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CONTRACT PERIOD OF PERFORMANCE: FY85, FY86

2. SCHEDULE/MILESTONES:

Milestones for the current contract period cover progress in mathematical modeling of chemistry, process components and systems; laboratory experimental measurement of process physics and chemistry; pilot-scale experimental measurements and interpretation of process components and systems. Emphasis has been on oil generation and degradation during rapid-pyrolysis, char combustion chemistry, and the generation and capture of sulfur and nitrogen species during retorting.

MILESTONES

1.	Quarterly Reports	2/86, 5/86, 8/86, 11/86
2.	Monthly Highlights	10/85 through 9/86
3.	Report - Char combustion kinetics	2/86
4.	Report - Hot solids retorting, model calculations and experimental results	4/86
5.	Report - Sulfur chemistry in hot solid recycle pyrolyzer	8/86
6.	Report - Enthalpy relations for oil shale	10/86
7.	Report - Parameter study (modeling) hot solid retort system with staged FB pyrolyzer and lift pipe combustor	11/86
8.	Report - SO_2 generation and capture in oil shale retorting	9/86

*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

9.	Report - Ammonia release during pyrolysis	9/86
10.	Report - Cracking and coking in hot solid recycle systems	9/86
11.	Report - Parameter study (Modeling) hot solid retort system with gravity mixer and pyrolyzer and cascading bed combustor	9/86

3. **OBJECTIVES**:

The objective of the project is to provide a technical base which will contribute to the advance of oil shale retorting technology including the mitigation of undesirable environmental effects.

4. **BACKGROUND STATEMENT**:

Lawrence Livermore National Laboratory (LLNL) has, over the past decade, conducted research on oil shale retorting via a broad based effort encompassing mathematical modeling, experimental studies of chemical reactions and physical processes, retort systems operations and retort component studies. In recent years, the emphasis has been on surface processes, especially those employing hot-solid as the heat transfer media. Key technical questions in these systems include: 1) the kinetics and stoichiometry of oil generation and degradation (via coking and cracking reactions), 2) char and sulfur combustion chemistry, 3) processing alternatives and scale-up considerations, 4) environmental consequences, especially of sulfur and nitrogen bearing species.

5. **PROJECT DESCRIPTION**:

The LLNL project combines laboratory and pilot-scale experimental measurements with mathematical modeling of fundamental chemistry and physics to provide a technical base for evaluation of oil shale retorting alternatives.

Mathematical modeling of the chemical and physical processes involved in oil shale retorting is a key component of our oil shale project. Our models encompass three levels of complexity: individual chemical reaction modeling, multireaction particle models, and overall retort models. One of the most useful general products of our modeling work is the distillation of data and theories into a compact and usable form.

Our chemical reaction modeling serves to quantify often complex experimental data into usable reaction schemes and kinetic expressions. Our detailed particle models treat multiple species undergoing multiple reactions, and often contain physical effects such as heat and mass transfer. They are used by us and others (e.g., METC) to guide and interpret experiments. Our overall retort models consist of connected models of packed bed, fluidized bed, and/or lift pipe reactors. Each reactor contains detailed chemistry plus particle- and reactor-scale

physical processes. The overall retort models are used to guide and interpret our pilot plant experiments, and to reveal the expected behavior and comparative strengths and weaknesses of different commercial scale retorting processes.

In the laboratory, we have been studying char combustion, sulfur evolution and capture, nitric oxide and ammonia formation and a number of oil loss mechanisms including oil coking and cracking reactions. We are developing new analytic techniques to measure oil yield and determine the forms of sulfur in solid shale samples.

We have operated our 2 ton/day continuous loop solid-recycle retort, using both a 2-stage fluidized bed pyrolyzer and a cascading mixer with gravity bed pyrolyzer, processing both lean and rich Western U.S. oil shale and a typical Eastern U.S. oil shale. The quantity and quality of oil produced under rapid-pyrolysis conditions is of key interest in continuous-loop systems. We have determined oil yield and have characterized the oil as a function of processing conditions and shale type. Residual char on the spent shale is processed via a lift pipe and a delayed-fall cascading bed combustor. The measured char conversion in both units has been successfully compared with laboratory measurements and model predictions using char combustion kinetics. The solid-recycle retorting system provides us with a unique opportunity to study the complex sulfur and nitrogen chemistry in continuous-loop processes, difficult to duplicate in the laboratory. Our retorting experience, coupled with detailed laboratory measurements and new analytic tools for delineating solid sulfur forms, is aiding in our understanding of this chemistry.

6. <u>RESULTS/ACCOMPLISHMENTS</u>:

ACCOMPLISHMENTS

Accomplishments during the current contract period of performance include:

- Laboratory experiments and a modeling analysis were done to obtain the intrinsic kinetics of char combustion. Improved kinetic expressions for carbonate decomposition and for oil cracking were obtained by reanalyses of existing data.

- New relations have been obtained for the heat capacities of shale oil, and the mineral, bound water, and organic fractions of oil shale. New values have been obtained for the heat of pyrolysis and the heat of bound water dehydration. Although developed for Green River shale, they can be modified easily for Eastern shale without any calorimetric data.

- The general pyrolysis kinetics model (PYROL) was modified to include improved kinetics, additional chemical reactions, an arbitrary temperature and pressure history, and improved efficiency for treating activation energy distributions. The model has been applied to a wide range of oil shale retorting conditions and to a more general investigation of alternative methods of analyzing kinetic data.

- A comparison of model predictions and our R-series pilot plant performance (fluidized bed pyrolyzer and cascading bed combustor) showed generally excellent agreement. Preliminary model calculations for the early G-series runs (packed bed pyrolyzer) did not predict as much coking and cracking loss as observed, indicating the need for more information on these loss mechanisms. The model was then used to suggest additional measurements and operating conditions for the subsequent runs so that we would maximize the information gained on cracking and coking.

- One of our overall retort models, STBRSIM, was developed and used to design a base case and do a parameter study for a commercial scale solids recycle retort having a fluidized bed pyrolyzer and lift pipe combustor. Simulation results included the effects of shale grade, recycle ratio, lift pipe pressure, and several other factors, on stream flow rates, temperatures and pressures, bed dimensions, and utility requirements.

- We helped METC install our detailed pyrolysis model, PYROL, and our overall retort models on their computer. This interaction is continuing as they use these models for interpretation of laboratory experiments, and overall assessment of retorting processes.

- A unique microprobe technique that at high magnification assigns a specific color to each mineral observed has been developed and applied to oil shale samples. The method gives evidence for incomplete pyrolysis of pyrite under Fischer assay retorting conditions, and it indicates that iron is concentrated at the surface of ankeritic dolomite grains. An IR-100 Award, given by "Research and Development" magazine for the most significant new instrumental techniques of 1985, was awarded to Don McCoy of LLNL for his work in developing this technique.

- Several methods for cooling shale from a solid-recycle retort are being evaluated. Certain techniques are not well suited to the present application. Cooling in a steam fluidized bed, for example, converts the pyrrhotite to H_2S and hydrogen (about half a pound of sulfur per barrel of oil). Kinetics of this reaction have been determined and are found to be rapid, and thermodynamics favorable, to temperatures as low as 300°C.

- We have measured the amount and rate of ammonia emission from retorting a variety of oil shale samples, including Devonian shale. Measurements were made by means of an ion-specific electrode which cannot be adapted as a continuous on-line method. A new sensitive, real-time method is being devised employing TQMS for the selective analysis of trace quantities of ammonia in the presence of water, methane, and a complex mixture of other gases such as those produced by retorting of oil shale. The ammonium ion is formed in the gas mixture by chemical ionization employing isobutane as the protonating gas; enhanced specificity for ammonium ion is further achieved by removing an interfering mass 18 ion due to water with a nitric oxide charge transfer reaction that is

allowed to occur in the collision cell of the spectrometer. This new analytical method is expected to enable rapid progress in our understanding of nitrogen chemistry in oil shale processing.

- Buddingtonite has been identified as the inorganic source of ammonia produced during combustion of retorted shale. Ammonia stability in the combustor and the kinetics of ammonia decomposition and Buddingtonite decomposition under retorting conditions have been investigated.

- Pyrite decomposition in the pyrolyzer is a major source of H_2S emissions, particularly in the case of Devonian shale. H_2S from organic sources has been differentiated from H_2S from pyrite under high vacuum pyrolysis conditions, and elemental sulfur has been detected as a pyrolysis product. Model compounds have been used to investigate the role of hydrogen and hydrogen donors in promoting pyrite decomposition.

- Results of pilot-scale experiments using the gravity bed pyrolyzer compared to the 2-stage fluidized bed pyrolyzer show that both pyrolyzers produce oil at Fischer assay yield, but with vastly different properties. The fluidized bed with its high recycle gas sweep efficiently collects primarily heavy components. This has a marked impact on oil density and viscosity. The gravity bed, with low to moderate sweep, cracks heavy components to a lighter, better quality product that is collected more effectively.

- Eastern oil shale, containing 4% sulfur and less than .5% mineral carbon, was processed in our gravity bed retort. Fischer assay oil yield was obtained. H_2S concentrations in the pyrolysis gas and SO_2 concentrations in the combustion gas were measured and found to be consistent with our understanding of the chemistry of solid-recycle retorting. Iron oxide, formed from pyrite in the recycle loop, was effective in reducing H_2S concentrations to 1000 ppm. Concentrations of SO_2 in the combustor effluent ranged from 1-2%, compared to trace amounts when processing Western shale. Carbonate minerals are effective scrubbing agents for SO_2, with Western shale containing a mineral carbon to sulfur ratio of 8. This ratio for Eastern shale is less than 0.08.

RESULTS

Our results for the current contract period of performance are detailed in the following topics discussed below:

- Solid-Recycle Retort Experiments
- Progress in Mathematical Modeling
- Laboratory Experiments in Oil Shale Retorting

Results - Solid-Recycle Retort Experiments

We have operated our 2-ton/day continuous-loop solid-recycle system, over the past two years, using both a two-stage fluidized bed pyrolyzer and a cascading mixer with gravity bed pyrolyzer. Combustion of the residual char on the recycled shale is accomplished in an air lift pipe and delayed-fall cascading-bed burner. The quantity and quality of the oil produced under rapid-pyrolysis conditions is of key interest in continuous-loop systems. We have determined oil yield and properties as a function of processing conditions and shale type, using both Western and Eastern U.S. oil shale.

Fluidized Bed Retort

The two-stage fluidized bed retort, shown in Fig. R-1, is a circular cylinder with an inside diameter of 15 cm and a height of 180 cm. A flat

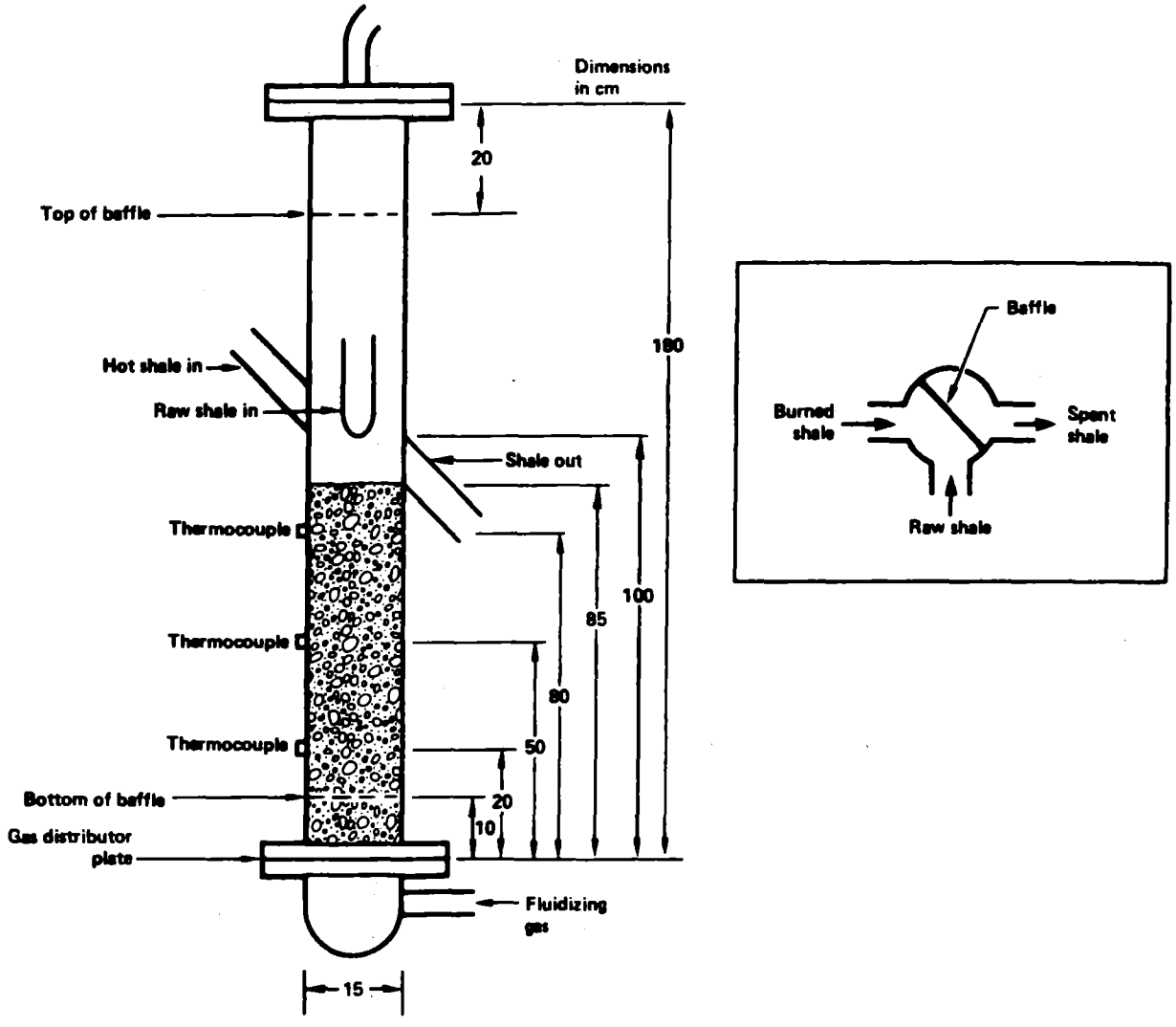


Figure R-1. Two-stage fluidized bed retort.

vertical plate or baffle that extends from near the top of the retort to nearly the bottom separates the two stages. Raw and burned shale enter the retort, mix and travel downward in the first stage. Passing the center baffle plate, the solid travels upward in the second stage and exits at the discharge port. The design provides more uniform residence time for a range of particle sizes.

Gravity Bed Retort

The gravity bed retort, shown in Fig. R-2, consists of three components: a cascading mixer, a solid disperser, and a gravity bed soak tank. In the cascading mixer, the hot and raw shale are combined while tumbling

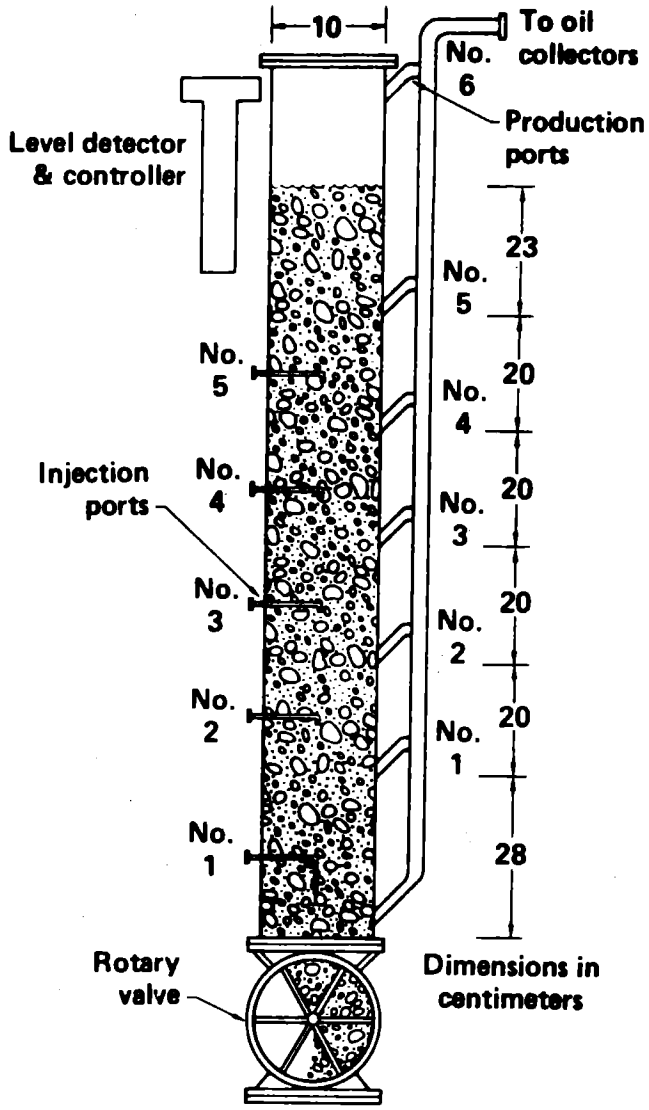


Figure R-2. Soak tank portion of gravity bed retort.

down a series of inclined chutes. The 10-cm square by 50-cm high mixer contains six alternating chutes, which split and recombine the solid, providing thorough mixing in approximately one second transit time. Below the mixer, the solid falls through a disperser, for horizontal spreading, and onto the gravity bed soak tank. In the tank, the solid moves slowly downward in plug flow, allowing the 2-3 minutes needed for pyrolysis to occur. To study product recovery, the soak tank is equipped with five gas injection ports and six product removal ports, as shown.

Solid Recirculation System

The solid-recirculation system consists of three components: a solid surge bin and discharge port, an air lift pipe combustor, and a delayed fall cascading bed combustor. Combustion of char on the spent shale begins in the air lift pipe as the solid is transported to the top of the tower (residence time is approximately one second). Combustion continues in the delayed fall cascading bed burner, which provides 26 seconds of residence time. The burning process is controlled by the amount of air blown horizontally across the unit.

Summary of Run Conditions

Table R-1 summarizes run conditions for the pilot retort experiments. Three Western U.S. shales were studied: an Anvil Points 24 gallon per ton (GPT) shale, an Occidental 15 GPT shale, and a Tract C-a 42 GPT shale. One Eastern U.S. shale was studied: a New Albany 13 GPT shale. Run numbers begin with either R or G. Those beginning with R designate fluidized bed experiments and those beginning with G designate gravity bed experiments.

Oil Yield and Characterization

Oil yield and properties for five fluidized bed experiments and five gravity bed experiments (excluding G-19 and G-22) are compared in Table R-2. Each of the runs processed Anvil Points 24 gallon per ton shale with Fischer assay properties shown. We see from the table that both retorts produced oil at 98% of Fischer assay, but with vastly different properties. The fluidized bed with its high recycle gas sweep and low oil concentration efficiently collects primarily heavy components. This markedly affects oil density and viscosity. The gravity bed with its low gas sweep and high oil concentration cracks the heavy components to a lighter, better quality product which is collected more effectively. Figure R-3 compares the boiling point distribution of the oil collected from typical R- and G-series runs with that from Fischer assay. The R-series oil has a larger, higher boiling point fraction than Fischer assay oil, and the G-series oil has more lower and medium boiling point fractions.

Table R-1. Summary of fluidized and gravity bed retort runs in LLNL pilot-scale solid-recycle oil shale project.

Run No.	Date	Steady State Time (min)	Raw Feed Rate (gm/min)	Hot/Raw Ratio	Residence Time (s)	Sweep Gas Type	Sweep Gas Rate (mMol/s)	Injection Ports Open	Flows (mMol/s) 1st Lift	2nd Lift	Combustor	Temperatures (Deg Celcius) Raw Shale	Recycle Shale	Retort	Oil Yield (% FA yield)
Anvil Points 24 GPT Shale															
R-1	1Mar84	120	960	4.1	210	N2	260	-	150	-	172	19	645	498	84
R-3	4Apr84	40	991	4.0	209	Recycle	313	-	112	-	77	19	627	498	100
R-4	3May84	60	953	4.1	208	Recycle	322	-	103	-	87	21	625	495	97
R-6	24May84	240	625	4.1	309	Recycle	301	-	109	-	62	23	623	496	100
R-7	18Jul84	105	1409	4.1	137	Recycle	317	-	105	-	93	131	616	510	100
G-9	6Mar85	35	567	5.4	269	N2	26	1-5	112	107	189	68	654	498	91
G-10	6Mar85	30	640	4.7	269	N2	16	6	112	109	151	87	659	509	93
G-12	3May85	25	762	4.2	245	N2	27	1-5	113	107	217	90	660	507	104
G-13	3May85	25	777	4.2	242	N2	24	5	113	106	218	101	666	507	103
G-15	21Jun85	25	701	4.9	237	H2	50	5-6	104	102	143	67	661	507	99
G-19	27Mar86	30	756	3.9	232	N2	4	6	106	101	143	81	684	499	87
G-22	17Apr86	31	844	3.6	224	H_2O	8	6	110	113	128	90	682	492	90
Occidental 15 GPT Shale															
G-3	17Jan85	23	1070	3.6	200	N2	14	6	112	100	150	40	635	493	80
G-4	17Jan85	25	790	3.7	262	N2	14	6	112	99	149	75	636	496	78
G-5	17Jan85	25	807	4.7	213	N2	14	6	111	99	151	100	636	527	76
G-6	14Feb85	20	783	5.1	210	Recycle	38	1-5	114	103	151	64	626	503	83
G-7	14Feb85	25	785	5.2	205	N2	29	1-5	114	99	153	81	629	508	72
G-8	14Feb85	20	1071	3.8	194	N2	18	6	97	108	153	96	634	493	84
Tract C-a 42 GPT Shale															
G-14	6Jun85	16	671	5.0	224	D2	29	5-6	100	96	73	78	691	484	102
Eastern New Albany 13 GPT Shale															
G-26	6June86	38	591	4.9	282	N2	20	1-5	115	116	162	19	684	522	105

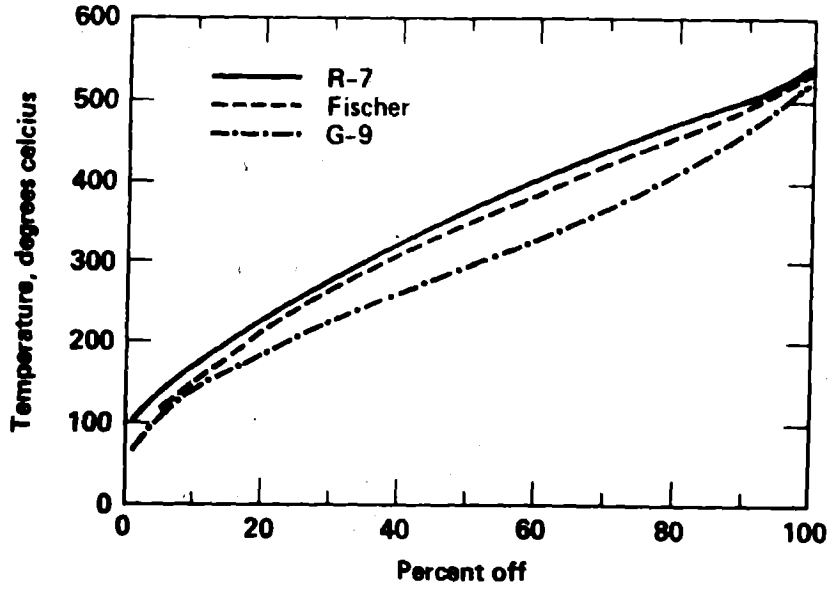


Figure R-3. Simulated distillation of three Anvil Points shales.

Table R-2. Oil yield and properties for Anvil Points 24 GPT shale.

	Fischer Assay	5 Fluidized Bed Runs	5 Gravity Bed Runs
Yield (% of FA)	100.	98.	98.
Density (gm/cc)	0.908	0.938	9.884
Viscosity (cp)	24.	400.	8.5
Nitrogen (%)	2.1	2.1	1.6
H/C Molar Ratio	1.68	1.59	1.59

Oil Coking and Cracking

Gravity bed runs G-19 and G-22 were performed to investigate the extent of oil loss under autogeneous conditions where oil and vapor removal is not assisted by any sweep gas except for the product generated. For these two runs oil yield was measured at 87 and 90% of Fischer assay, without a corresponding increase in gaseous products. Analysis of the solid showed an increase in carbon content compared to previous runs. This indicates that the principal mechanism for oil loss is via oil degradation reactions which primarily produce coke.

The chemistry of oil cracking in the presence of hot-recycled-solid is presently poorly understood. Cracking kinetics may be related to the gaseous environment and perhaps to the nature of the solid phase as well. Improved cracking kinetics under conditions where less than 5% oil loss results would be particularly beneficial to our modeling effort. Research in this area is presently of the highest priority. Our long term goals include: a) work on gas phase and surface cracking; b) an understanding of the similarities and differences with regard to surface cracking, coking, and oxidized solid reactions; c) a clarification of the rolls of contact time and solid temperature on oil loss processes; d) an investigation of the beneficial effect of recycle gas when retorting in the presence of burnt shale.

Laboratory Coking and Cracking Studies

Oil cracking is being studied in laboratory experiments in which oil vapor is passed through a packed bed of sand or oxidized shale at various temperatures. In the study, liquid oil is volatilized and mixed with a carrier gas and then injected into the packed bed. By varying the amount of carrier gas, residence times from 3 to 20 seconds were studied. Results for Australian Condor shale oil indicate a maximum of 40% oil loss with sand packing, with the primary product being light gases. This is consistent with our understanding of volumetric gas phase cracking reactions. When shale ash is used as the packing, the same oil shows as much as 70% loss, with coke being the primary product. This result indicates that the Condor shale ash contains active surfaces which promote additional oil cracking and alter the primary products formed. We intend to perform similar experiments on Green River shale soon.

In another set of experiments oil generated under Fischer assay conditions is passed into a cylindrical reactor held at 550°C . A sand-packed reactor caused an 8% oil yield loss while an empty reactor exhibited an 11% loss. Organic carbon analysis of the retorted shale, reactor packing, oil, and gas showed all the oil yield loss was due to gas generation with no apparent coking (solid formation). The cracked oils had a higher nitrogen content and higher carbon/hydrogen atomic ratio than Fischer assay oil. Gas chromatographic analysis of the oils showed a higher proportion of aromatic hydrocarbons and higher alkene/alkane ratios for the cracked oils. Mass spectroscopic analysis of the gases revealed an increase of H_2 and light hydrocarbons (C_1-C_3) and a decrease in H_2S with cracking. These results are typical of gas phase cracking, consistent with the sand packed experiments on Condor shale, but inconsistent with the shale ash experiments in which coke was the primary product.

In a third set of experiments we tested the effect of ferrous sulfate addition ($FeSO_4 \cdot 7H_2O$) on batch assay oil yield and composition by mixing iron sulfate with raw shale prior to retorting. Yield losses as high as 21% were observed with the addition of moderate amounts (18 wt.%) of ferrous sulfate. Organic carbon analysis of retorted shale, oil, and gas showed that both coking (solids formation) and cracking (gas formation) are responsible for the oil-yield loss. Furthermore, it appears as though coking is the predominant process when low levels of

iron sulfate are added; cracking does not become important until more than 10% ferrous sulfate is added. Elemental analysis of the oils showed a slight decrease in nitrogen content with the iron additive but no effect on the carbon/hydrogen atomic ratio was observed. Gas chromatographic analysis of the oils revealed a higher aromatic hydrocarbon content (relative to straight-chain hydrocarbons) when iron sulfate was added. A small increase in alkene/alkane ratios was observed for the light hydrocarbons (C_1-C_6) as more ferrous sulfate was added; heavier hydrocarbons also show higher alkene/alkane ratios although the ratios tend to be independent of the amount of iron sulfate added. Mass spectroscopic analysis of the gas was perhaps most informative. Addition of small amounts of iron sulfate (less than 8%) led a to large reduction in H_2. A decrease in H_2S and methane and a small increase in CO_2 was also observed at this level of iron sulfate. At higher levels of iron sulfate however (~18% $FeSO_4 \cdot 7H_2O$) the CO_2 evolution is greatly stimulated while the H_2 level decreases only slightly compared to the low iron experiments; H_2S decreases fairly linearly as more sulfate is added.

In summary, addition of ferrous sulfate is found to cause oil yield losses, due to both coking and cracking. A decreased yield of H_2 seems to be associated with the coking while the cracking results in an increase in CO_2. Although any mechanisms are purely speculative at this point, hydrogen may be depleted as follows:

$$6FeSO_4 + 4H_2 \rightarrow 2Fe_2O_4 + 4H_2O + 6SO_2$$

This reaction is known to occur in the thermogravimetric analysis of ferrous sulfate in a hydrogen atmosphere.

Sulfur Chemistry

Operation of the continuous-loop solid-recycle retort provides a unique opportunity to study the complex chemistry of sulfur-containing compounds at various stages throughout the recycle loop. A triple quadrupole mass spectrometer (TQMS) was used to detect sulfur-containing species in the pyrolysis gas. Table R-3 summarizes the species and quantities observed for typical R-and G-series runs, processing Anvil Points 24-GPT shale, and one Eastern shale run.

One of the most striking differences between hot-solid retorting and conventional hot gas retorting is the fraction of sulfur in the pyrolysis gas. In both types of retorting the principal sulfur-bearing gas is H_2S. However, as much as 20% of the sulfur in raw shale is released as H_2S under Fischer assay conditions, whereas, less than 0.1% of the sulfur is emitted as H_2S in the case of solid-recycle retorting. The kinetics of sulfur removal by constituents in oxidized shale have been studied in the laboratory. These results, shown in Fig. R-4, indicate that oxidized shale is an effective scrubber of H_2S, with a rate constant roughly equal to that from iron oxide and dolomite combined. Iron oxide is formed from pyrite as it travels around the recycle loop. In the pyrolyzer, pyrite (FeS_2) is converted to pyrrhotite (FeS). Pyrrohitite is burned to iron oxide (Fe_2O_3) in the combustor, and recycled to the retort.

Table R-3. Sulfur Bearing Species in Pyrolysis Gas (ppm).

	AP 24 GPT R-7	AP 24 GPT G-9	Eastern 13 GPT G-26
Hydrogen sulfide	175.0	520.0	280.0
Methyl mercaptan	9.0	20.0	58.0
Ethyl mercaptan	13.0	6.0	27.0
Propyl mercaptan	3.0	1.0	8.0
Dimethyl disulfide	0.5	5.0	9.0
Carbonly sulfide	7.0	3.0	36.0
Carbon disulfide	0.3	0.8	6.0
Thiophene	30.0	15.0	50.0
Methyl thiophene	40.0	19.0	105.0
Total Gas Flow (mMol/s)	20.0	40.0	36.0

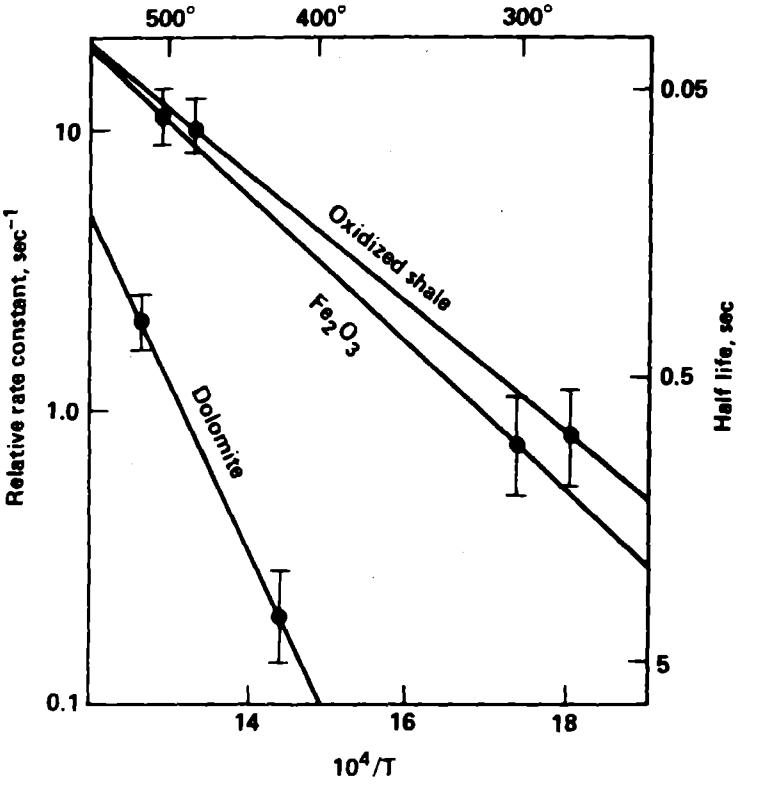


Figure R-4. Kinetics of H_2S removal.

Low concentrations of H_2S were measured for both Western and Eastern shales, even though Eastern shale contains approximately seven times more sulfur. The results indicate that the form of sulfur rather than amount is important in solid-recycle systems. Sulfur that enters the system as pyrite, is self-scrubbed since the iron oxide to sulfur ratio is independent of concentration. Sulfur leaving the pyrolyzer as FeS enters the combustor system and is burned to Fe_2O_3 and SO_2. We have measured SO_2 concentrations in the combustor effluent for the R- and G-series runs as well as for Eastern shale run G-26. The concentration of SO_2 in the combustor effluent for Western shale was below detectable limits (less than 10 ppm). For Eastern shale, the concentration ranged from 1 to 2%. We have measured the rate of SO_2 capture with dolomite in the laboratory and have found it to be rapid at first, but the rate slows long before all the dolomite is reacted. This suggests that the capacity for scrubbing is limited, at least at temperatures below approximately 625°C. This explains the high SO_2 concentrations from combustion of Eastern shale, which has a mineral carbon to sulfur ratio of 0.08 (compared with 8 for Anvil Points shale). This represents a 100-fold decrease in dolomite scrubbing capacity. In one experiment, Eastern shale was spiked with 25%, by weight, dolomite. This increased to 0.8 the mineral carbon to sulfur ratio, but was found to have no observable effect on the SO_2 concentration, showing that the scrubbing capacity of carbonate, at one tenth that of Western shale, is insufficient to control SO_2 emissions, at least under these conditions.

Results - Progress in Mathematical Modeling

Combustion Kinetics for Char

The intrinsic kinetics of the reaction of oxygen with carbonaceous residue in rapidly pyrolyzed Colorado oil shale were determined by a series of isothermal fluidized-bed experiments in the temperature range of 384 to 474°C. The char was produced from 100 L/Mg (24 gal/ton) oil shale by rapid heating to 530°C and isothermal pyrolysis for 5 min. The oxidation rate, determined by mass spectrometer measurements of evolved CO and CO_2, was found to have second-order dependence on the unreacted char, as given by the following rate law.

$$-\frac{d\left(\frac{\text{char}}{\text{initial char}}\right)}{dt} = 1.33\ s^{-1}Pa^{-1}\exp\left(\frac{-9763\ K}{T}\right)P_{O2}\left(\frac{\text{char}}{\text{initial char}}\right)^2$$

The study of combustion kinetics at oxidation temperatures higher than 475°C is precluded by the presence of CO_2 evolved from carbonate capture of SO_2. Oxidation of char produced from acid-leached raw shale results in an appreciably lower reaction rate, confirming the suggested catalytic activity of mineral carbonates. Further experimentation indicates that a lower heating rate during the pyrolysis (i.e., a lower effective pyrolysis temperature) significantly decreases the subsequent reactivity of the char to oxidation.

Other Reaction Kinetics

Data for the thermal cracking of fast heating rate oil produced in a laboratory fluidized bed (110% FA) have been available and show faster cracking than Fischer assay oil at temperatures below 550°C (Bissell et al., 1983, UCRL-89976). We analyzed the data between 450 and 600°C and obtained a good fit with the following first order equation.

$$-\frac{1}{C_{oil}}\frac{d\,C_{oil}}{d\,t} = 435\ \exp(-7837/T(K))\ (s^{-1})$$

A revised kinetic model for dolomite and calcite decomposition was obtained. This uses the general reaction scheme and calcite self-decomposition kinetics found by Campbell (1975, UCRL-52089-II). The kinetics for the dolomite decomposition and calcium carbonate--quartz reaction were found as a function of temperature and CO_2 pressure by analyzing the isothermal data of Jukkola et al. (I&EC, 45, 2711, (1953)).

Enthalpy Relations for Oil Shale

New relations have been obtained for the heat capacities of the mineral, bound water, and organic fractions of oil shale. New values have been found for the heat of pyrolysis and recommended for the heat of bound water dehydration. The predictive capability of these relations is illustrated in Fig. M-1. The new relations should be more accurate than those used previously, at temperatures and shale compositions outside the limited ranges of the available calorimetric oil shale data. This includes easy adaptation to Eastern shale without requiring any calorimetric data.

Pyrolysis Model Improvements and Results

The general pyrolysis kinetics model (PYROL) was modified to include improved kinetics and additional chemical reactions. The model now includes 32 gas/vapor species, 41 condensed species, and 117 reactions. The new reactions include hydrogenation of semicoke to cokable oil, hydrogenation of cokable oil to uncokable oil, and hydrogenation of char to methane. The new semicoke species is the initial product of the oil coking reaction along with methane and hydrogen. It pyrolyzes further to char and hydrogen. Accurate kinetics are not yet available for all of these reactions, but parameter studies have shown that hydrogenation of char is probably the most important reaction that must be included in order to get good agreement between calculated and measured pyrolysis gas compositions.

Significant changes were also made in kerogen pyrolysis stoichiometry. A maximum oil yield of 120% of Fischer assay is allowed for Type I kerogen, although the maximum yield could be approached only by pyrolysis at high temperature (rapid heating) and with high sweep. In addition, the amounts of certain pyrolysis products (e.g., cokable oil, uncokable oil, H_2, H_2O and NH_3) were made dependent on the hydrogen partial pressure. The hydrogen-dependent kerogen stoichiometry produces slightly improved agreement for high-pressure hydrogen pyrolysis at the expense of poorer

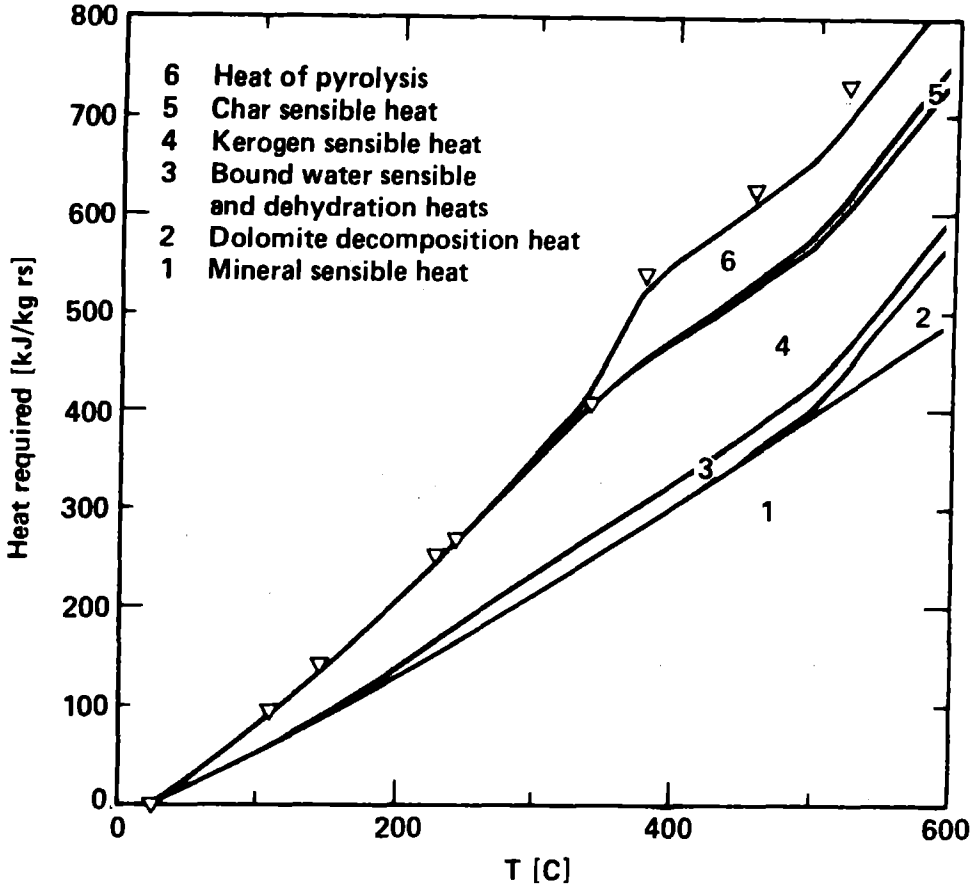


Figure M-1. Predicted heat requirements for heating 34.3 gpt shale compared to the data of Wise et al. (1971, USBM-RI7482). Pyrolysis occurred between 340 and 370°C for these experiments.

agreement elsewhere. More testing of the model must be done to clarify this point.

With the model's new capabilities of simulating arbitrary temperature and pressure histories, PYROL has been applied to a wider range of pyrolysis conditions. One particularly important application has been to the sealed-bomb experiments of Evans and Felbeck. The model is able to quite accurately track the generation and eventual disappearance of oil (due to coking and cracking) as the pyrolysis products remain exposed to a high temperature environment.

PYROL has been extremely useful in providing simulated reaction rate "data" for a comprehensive investigation of alternative methods of analyzing kinetic data for reactions requiring a distribution of activation energies. Correlations have been developed for those complex reactions in terms of a set of simple "effective" kinetics (reaction order, activation energy, and frequency factor) for reaction rates obtained from either isothermal or nonisothermal methods. In addition, algorithms have been developed from the PYROL results that enable the use

of a microcomputer to rapidly determine kinetic parameters, including the activation energy distribution, from reaction rate profiles measured at two or more heating rates.

Development of a Multireaction Combustion Model

The goal is to develop a comprehensive combustion model that will include all of the important chemical reactions, as well as both inter- and intra-particle heat and mass transfer, for an arbitrarily-specified temperature and pressure history. Hopefully, the model will predict the rate and amount of heat release, the dependence of SO_2 and NO_x release on temperature and particle size, ignition behavior, and other important phenomena of the combustion of retorted oil shale.

A preliminary model (HEAT) for combustion reactions of char, nitrogen, and sulfur has been outlined. The reactant and product compositions are described in terms of eleven gas-phase species and fourteen condensed-phase species. The broad classifications of reactions considered are: thermal decomposition of residual organic material and various minerals, oxidation of gas-phase and condensed-phase species, reactions involving reduction of NO_x, and reactions involving capture of SO_2. A total of 30 such reactions are planned for the initial version of HEAT. Work is now underway in the laboratory to obtain the reaction kinetics needed by the model.

Model Simulation of Pilot Plant Experiments

We have used our RETORT overall process model to simulate the performance of our pilot plant in both of its configurations (fluidized-bed pyrolyzer = R series, packed-bed pyrolyzer = G series).

A full comparison between model predictions and pilot plant data was done for experiments R-3,4,6, and 7. The necessary actual operating conditions were supplied to the model which then calculated expected retort behavior. For each experiment, predictions and measurements agreed to within 1% FA for oil yield, 6% relative difference for waste shale organic carbon, 12°C for the pyrolyzer heat balance, 4°C for the surge bin temperature change, and 7°C for the lift pipe temperature rise. For most cases, these differences were smaller. The largest discrepancy was that the predicted amount of air needed to achieve the specified combustor outlet temperature was 1.4 times that measured. This might be due to an underestimation of combustion kinetics or oxygen diffusivity.

A very productive interaction takes place between model, pilot plant, and laboratory when we use the model to simulate our pilot plant runs. Initial attempts to simulate the early G-series runs were not particularly successful. The calculations did, however, suggest run conditions and additional measurements for the later G-series runs which would help sort out the discrepancies. The discrepancies also suggested areas in which the model could be improved. These included the heat capacity relations and cracking kinetics mentioned earlier. The new char combustion kinetics experiments and analysis described above were largely motivated by the R-series combustor air discrepancy.

Thermal Cracking in a Cross-Swept Packed-Bed Pyrolyzer System

In simulating the G-series experiments, a detailed analysis was made of oil vapor residence times in various parts of the pyrolysis section, since this directly affects the extent of thermal cracking expected. Some of the conclusions, most of which would also apply to a commercial scale retort, were the following.

A large fraction of the cracking can occur outside of the packed bed itself, including the cascading mixer headspace, product stream piping to the condenser, and post-pyrolyzer surge bin (standpipe). Cracking can be minimized by a downward sweep of the cascading mixer headspace, prompt cooling of product oil, and surge bin sweep. The packed bed level should be maintained at just below a gas exit port. A modest amount of cross flow sweep (say 1.5 moles/kg raw shale) in the packed-bed pyrolyzer will minimize cracking there if distributed correctly. The optimum distribution for a given rate of sweep gas can be calculated using our RETORT model.

Simulation of Commercial-Scale Retorts

Updated base-case calculations for a 50,000 barrel/day plant were made for a hot-solids process having a staged fluidized-bed pyrolyzer and lift-pipe combustor (HSFB process). Our STBRSIM computer code with its detailed reactor models of the above reactors was used for these calculations.

Figure M-2 shows the base-case operating conditions and calculated design and performance conditions. These included 30 gal/ton raw shale preheated to 100°C, 6.7 mm maximum raw shale particle size, 3.3:1 mass recycle ratio, and 3.2 minutes pyrolysis residence time at a mean pyrolysis temperature of 513°C. The oil yield was nearly 99% of Fischer assay (out of a 105% maximum). Principal losses in oil yield were from cracking of oil vapor (2.5% FA) and from incomplete pyrolysis of kerogen (3.2% FA). Four percent of the raw shale was assumed to pyrolyze only partially before being elutriated from the fluidized bed.

Simulation results for the HSFB system include the effects of changes in raw shale grade, recycle shale ratio, duration of oil cracking, lift-pipe operating pressure, surge bin residence time, unretorted kerogen in elutriated fines, and oxygen-enriched air. The implications for flow rates, temperatures and pressures, bed dimensions, and utility requirements were evaluated. The results of these calculations help identify the relative importance of the various operating and design parameters. Figure M-3 shows two examples from the parameter study.

Base case calculations were made for a 50,000 barrel/day solids-recycle retort having a packed-bed pyrolyzer and cascading-bed combustor (HSCB process). For this we used our RETORT model which uses our general packed-bed reactor model to simulate the pyrolyzer and the combustor, and our lift pipe model for that component. The operating conditions were made as similar as possible to the HSFB system discussed above.

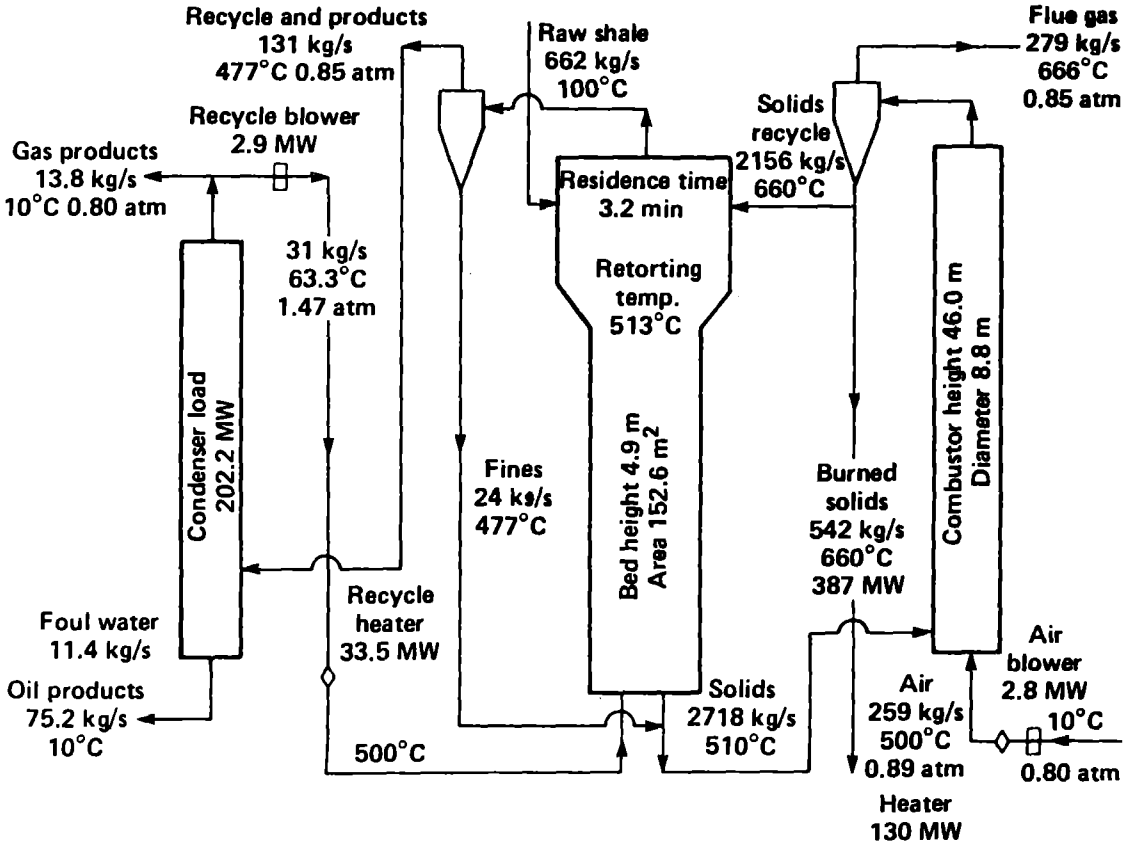
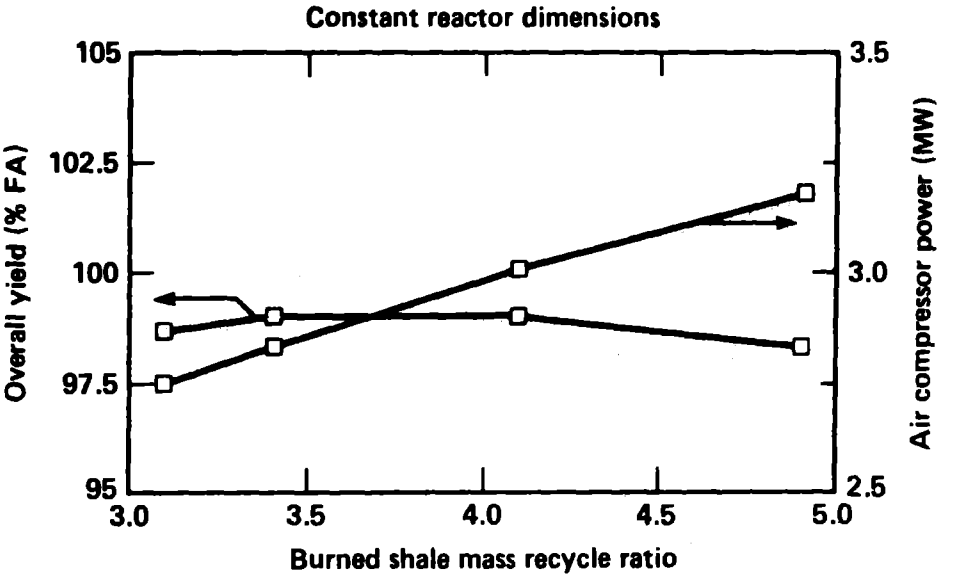


Figure M-2. Base case flowsheet for 50,000 barrel/day fluidized bed retort system.



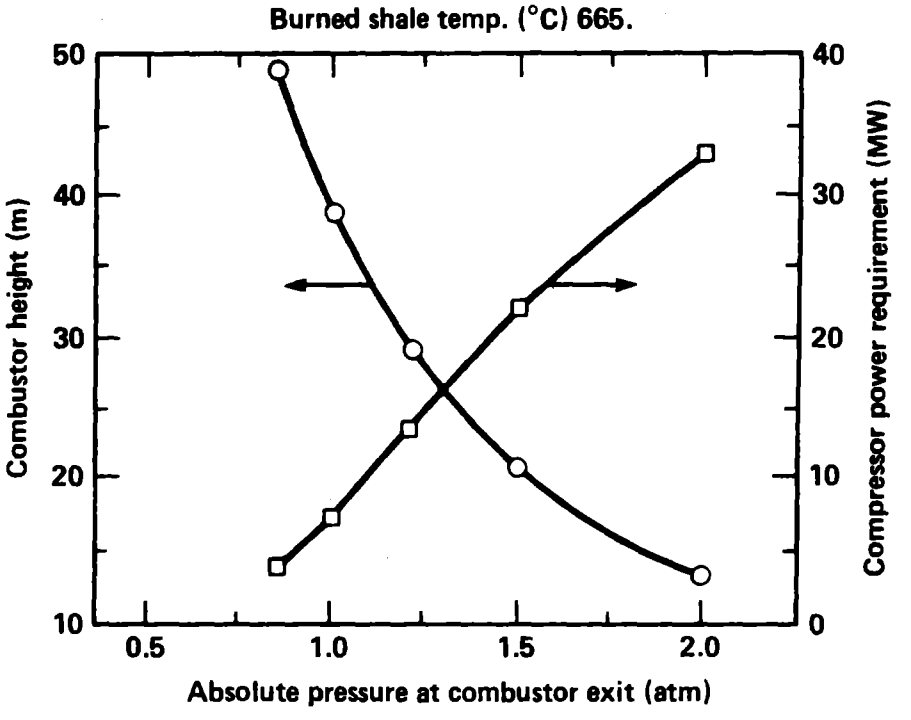


Figure M-3. Typical parameter study results from our simulation of a commercial scale HSFB system.

Several significant design and performance differences between the HSFB and HSCB systems were predicted. Principal reactor volumes for the HSCB system were smaller than the HSFB system by factors of 0.26 on the combustor side and 0.62 on the pyrolyzer side for an average factor of 0.36. The HSCB process required 2% less shale to be processed because of the smaller rate of fines elutriation. Utility and auxiliary requirements for the HSCB system were lower by factors of 0.23 for air and gas blower power, 0.79 for quantity of waste gas, and 0.79 for water utilization.

Modeling Assistance to METC

We helped METC install our detailed pyrolysis model, PYROL, and our overall retort models, STBRSIM and RETORT, on their computer. This interaction has continued as they use PYROL for interpretation of laboratory experiments and development of their ASPEN model.

Results - Laboratory Experiments in Oil Shale Retorting

Nitrogen and Sulfur Chemistry

An improved understanding of nitrogen and sulfur in the oil shale pyrolyzer and combustor is one important part of the LLNL chemistry research effort. However, it is only a part of a chemistry program that supports our pilot retort experiments and contributes to the development of a detailed mathematical model applicable to a wide variety of oil shales and retorting processes. The chemistries of char combustion, of oil loss mechanisms (coking, cracking, oxidation), and of the interaction of hot burned shale with retort products are some of the other active research areas.

Progress in the area of nitrogen and sulfur chemistry was presented at the LLNL Oil Shale Briefing less than a year ago. A good deal has been accomplished since that time. This review will outline these accomplishments which include significant contributions by staff members using various approaches. Our eventual goal is to include nitrogen and sulfur chemistry in the retort model so we can estimate the effect of a change in retorting conditions on emissions.

Sulfur Chemistry Program

Principal questions of interest include the following:

a. Pyrite chemistry in the retort.
b. H_2S scavenging; iron chemistry; carbonate minerals.
c. Organic sulfur.
d. SO_2 release from the combustor.
e. The Eastern oil shale case.
f. Sulfur chemistry during cooling.

There is progress to report in a number of these areas. The triple quadrupole mass spectrometer has been used to monitor trace organic sulfur gases from the pilot retort. Improved accuracy and sensitivity have been achieved; fully automated tuning using artificial intelligence techniques is being developed. We have been particularly pleased with our ability to

predict sulfur chemistry for solid-recycle retort experiments using Devonian shale.

Details concerning two areas, pyrite chemistry and sulfur emissions during cooling, will be presented.

Pyrite Chemistry in the Retort

Figure L-1 shows the hydrogen sulfide evolved during batch retorting of a Mississippian-age Eastern oil shale. This oil shale sample has primarily pyritic sulfur (both pyrite and marcasite) in high concentration (nearly 5% by weight), and it has a negligible carbonate mineral content. Pyrite decomposition occurs in two distinct phases and only a portion of the expected H_2S is released. Also shown in Fig. L-1 is the result of a similar batch retorting experiment swept with 10% H_2S in argon. Even in the absence of carbonate minerals, retorted Devonian shale is an excellent scavenger of hydrogen sulfide. We are investigating explanations involving iron chemistry. The shale contains approximately twice as much iron (on a mole basis) as is needed to form pyrite from the inorganic sulfur. The retorted shale has been used to eliminate hydrogen sulfide produced during pyrolysis of a high sulfur coal. We have discussed this result with scientists at the Illinois Survey who are interested in exploring applications of retorted Eastern shale as a sulfur scavenger for coal processing.

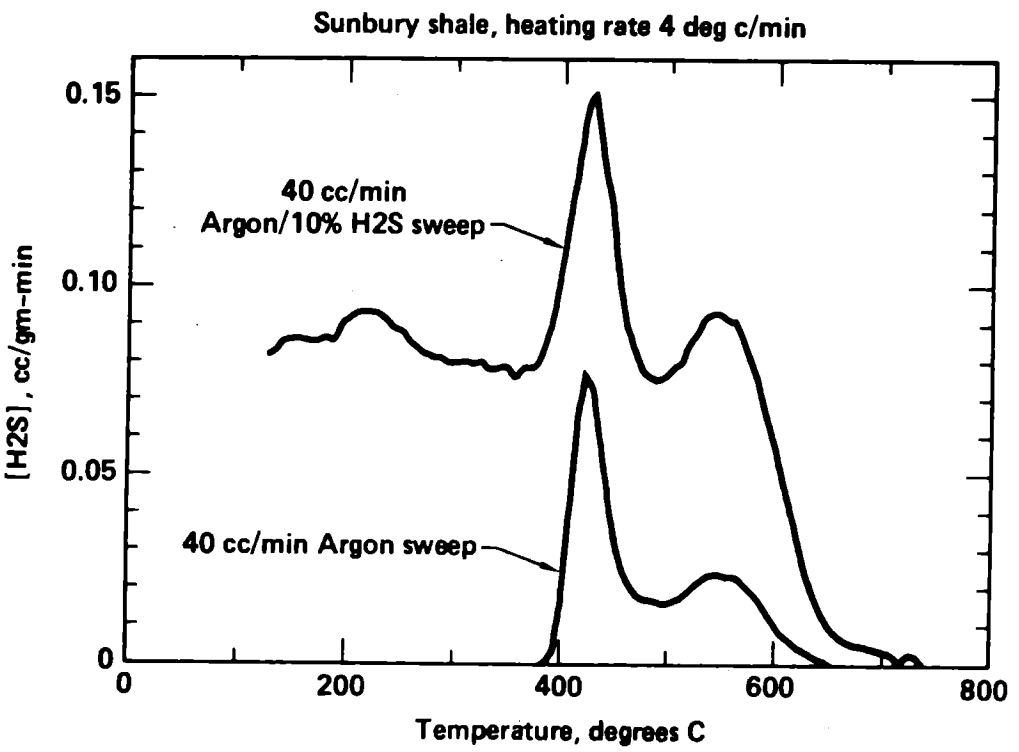


Figure L-1. H_2S Evolution from Kentucky oil shale.

Pyrolysis of Colorado oil shale under batch retorting conditions results in only a single--the initial--H_2S evolution peak. However, we have recently obtained evidence that pyrite decomposition is incomplete when a sample is heated to 500°C (Fischer assay). The failure to observe the higher temperature H_2S evolution peak must be due to the greater scavenging potential of Colorado shale minerals, particularly siderite and ankeritic dolomite (the carbonate mineral crystals have iron-rich surfaces). A unique computer method for color coding specific minerals under high magnification to show detailed chemical composition of such geological samples won an IR-100 award for D. D. McCoy of LLNL, its developer.

We have initiated model compound studies to sort out the role of hydrogen and hydrogen donors in the FeS_2 decomposition process and to determine whether pyrite reacts directly as a solid or first releases S_2. Figure L-2 shows TGA traces of pyrite decomposition with nitrogen sweep and with a sweep of nitrogen containing 5% hydrogen. Clearly, hydrogen has an important effect. The TGA experiments can be run under conditions that allow H_2 reactions to be distinguished by their diffusion limitations.

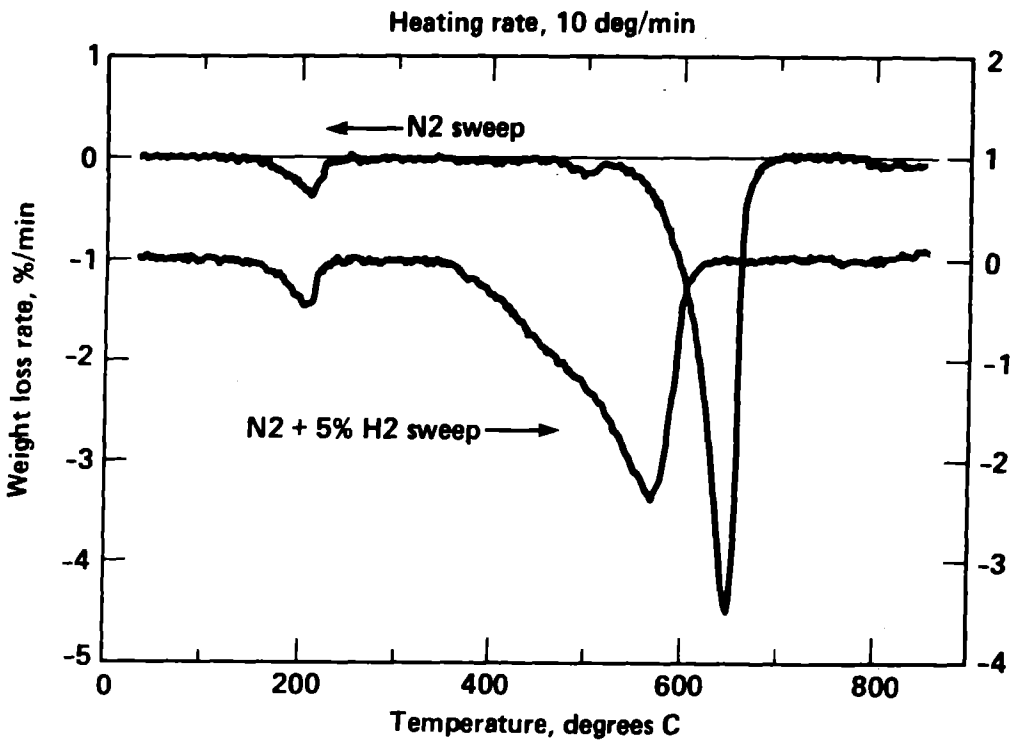


Figure L-2. Thermogravimetric measurements on pyrite.

After screening a number of materials, polyphenylene was used as a sulfur-free model compound for the char forming step in kerogen pyrolysis. Polyphenylene charring promoted pyrite decomposition, and the decomposition temperature decreased as the ratio of polyphenylene to pyrite was increased. The use of a nitrogen plus 5% hydrogen sweep had no effect on the decomposition temperature of polyphenylene/pyrite mixtures. Other polymers that fail to promote pyrite decomposition also shield pyrite from reaction with H_2. We plan to use the mass spectrometer to determine if hydrogen evolution trails hydrogen sulfide evolution when polyphenylene/pyrite mixtures are heated in a batch retort. This is the expected result if the hydrogen donor reduces pyrite prior to releasing H_2.

The equilibrium involving S_2 and pyrite (reaction (1)) is highly unfavorable at temperatures where H_2S is released from oil shale (Log (K_{eq}) = -5 at 500°C).

$$2FeS_2 \rightleftarrows 2FeS + S_2 \qquad (1)$$

The high reactivity of S_2 requires that it be acknowledged as a possible reactant. We have detected S_2 by mass spectrometry at retort temperature under high vacuum. However, initially hydrogen donor formation will be investigated as the rate limiting step for pyrite decomposition under retorting conditions. We intend to extend our studies to a less highly crystalline pyrite (framboids) more typical of pyrite in oil shale.

Sulfur Effluents Produced During Cooling

Cooling of the hot discharged shale is an important and somewhat neglected area. Capital equipment requirements are significant. The Colony Project would have used three rotary drums 100 ft. long. Cooling may have an impact on disposal, and very little is known about changes in the spent shale that result from differences in the cooling technique. We have just begun an investigation in this area (principal investigator: R. G. Mallon) and can report our initial progress.

A retort that uses hot recycle shale for solid-solid heat transfer has two options for discharge of spent shale: a) burnt shale from the exit of the combustor, or b) the mixture of retorted shale and burnt shale from the pyrolyzer exit. The potential for cooling spent shale from the pyrolyzer (AP-24 shale) in a steam fluidized bed was first investigated. A substantial amount of hydrogen sulfide (equivalent to about half-pound per barrel of oil) and hydrogen resulted from reaction (2).

$$3FeS + 4H_2O \rightleftarrows Fe_3O_4 + 3H_2S + H_2 \qquad (2)$$

Thermodynamics allows the reaction (Log(K_{eq}) = -3.4 at 500°C), and the kinetics are rapid even at 300°C (see Fig. L-3).

Our aim is to define optimum conditions for cooling shale from the solid-recycle retort and investigate environmental implications. Work in this area has begun.

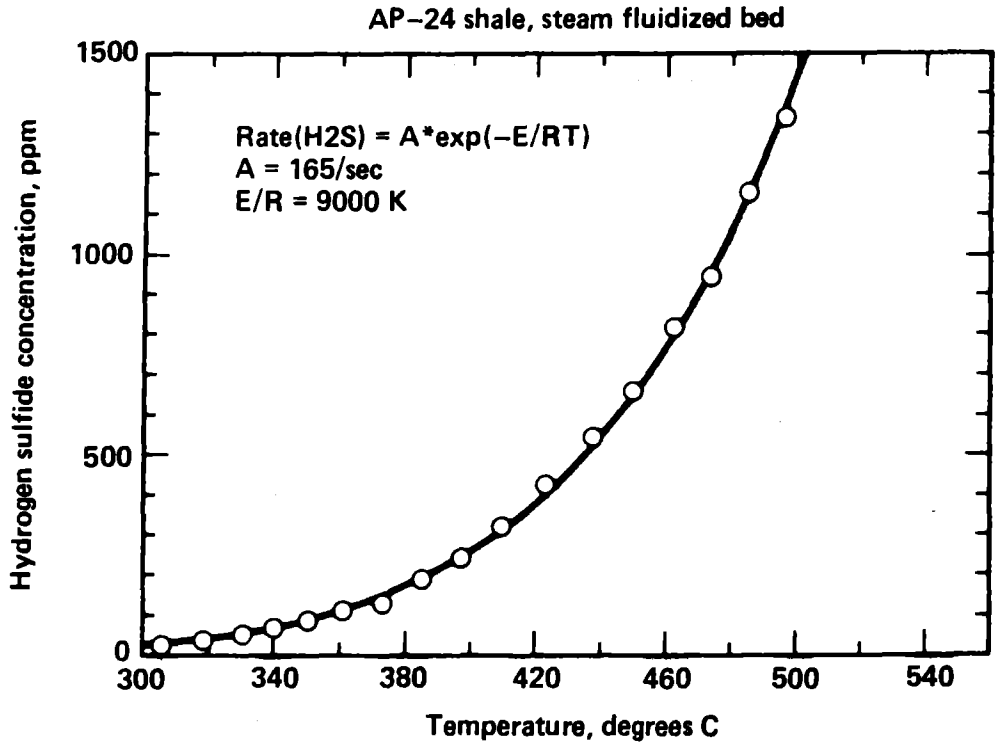


Figure L-3. H_2S evolved from spent shale in steam.

Nitrogen Chemistry

At present NO_x emissions are measured routinely during pilot retort runs. Details of the chemistry of nitric oxide formation during shale combustion have been published (see R. W. Taylor, C. J. Morris, and A. K. Burnham, "Nitric Oxide (NO) Emissions from Combustion of Retorted Oil Shale," 18th Oil Shale Symposium Proceedings, 1985, pp. 278-90). In addition, we have analyzed for NO_x produced from retorting and burning Devonian oil shale in the solid-recycle retort. In this experiment, excess char was available for combustion; the retorted shale was burned in an oxygen-lean environment in order to control temperature rise. Under such circumstances, nitric oxide emissions should be minimal. This was the case; emissions were below our limit of detection (1 ppm in the flue gas, so less than 2 milligrams NO_x per ton of shale processed).

Ammonia Evolution During Pyrolysis

Ammonia generation in the retort has been the focus of considerable effort (principal investigator: M. S. Oh) in our study of nitrogen chemistry. There are important reasons to understand ammonia formation in some detail. These include the following: a) ammonia has some market value to a commercial project; b) there are stringent emission standards for ammonia; c) ammonia may be of value for on-site NO_x emissions control by means of chemistry such as shown by reaction (3).

$$6NO_2 + 8NH_3 \xrightarrow[\text{heat}]{\text{catalyst}} 7N_2 + 12H_2O \qquad (3)$$

Complications in understanding ammonia evolution include the thermal instability of ammonia and multiple sources of oil shale ammonia. The two primary ammonia sources are the organic nitrogen of the kerogen and the inorganic nitrogen of the mineral Buddingtonite. The distribution of nitrogen between these two sources is about 1:1 for Colorado oil shale. Devonian oil shale has only organic nitrogen in significant quantity. A number or Colorado oil shale samples have been pyrolyzed using a batch assay method, and NH_3 liberated is as shown in Fig. L-4. Ammonia generated from kerogen pyrolysis is observed in the 400-500°C temperature range; that produced during charring and that from Buddingtonite is noted at temperatures to 700°C.

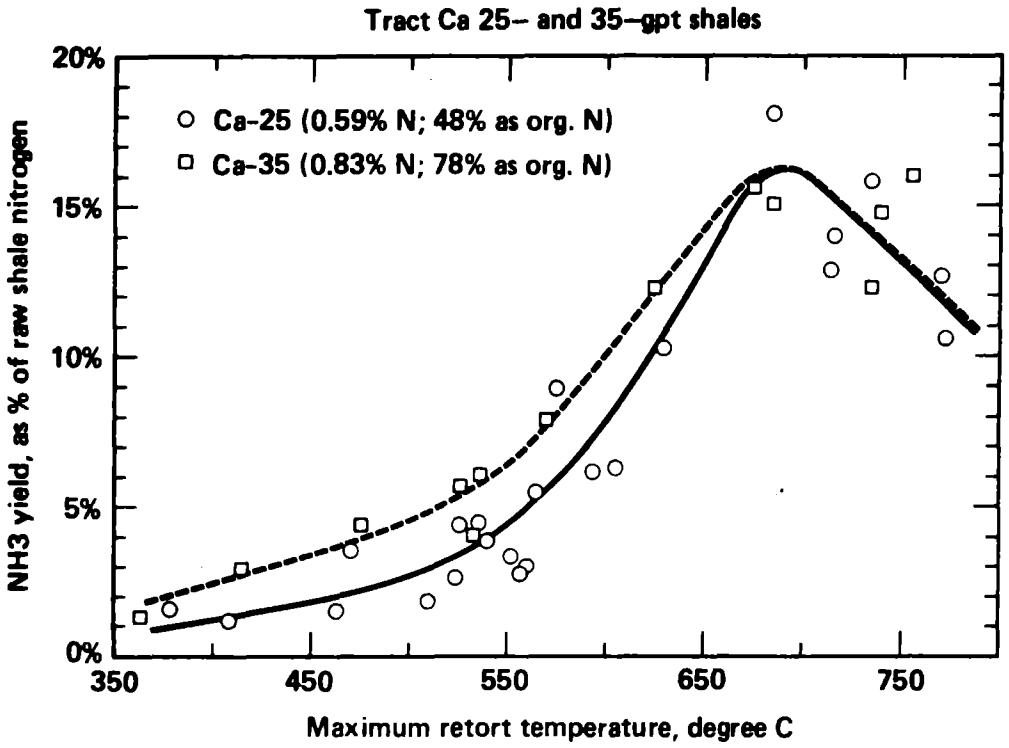


Figure L-4. Cumulative ammonia evolution.

We have been developing an improved real-time analysis technique for ammonia in the complex mixture that is pyrolysis gas. Methods presently in use in our lab, Drager tubes and ion specific electrode (see Fig L-4.) have deficiencies that limit their use for obtaining data suitable for kinetic modeling. In fact, no convenient instrumental technique for instantaneous detection of ammonia at the ppm level in the presence of water, hydrogen sulfide, and hydrocarbon gases is available. As a result, the triple quadrupole mass spectrometer (TQMS) in our laboratory is being uniquely modified by R. W. Crawford for this specific application.

Figure L-5 shows a diagram of the TQMS. Ammonia is not an ideal candidate for the conventional ms/ms experiment. It does not have unique and characteristic fragments. With normal electron impact ionization, water and carbon-13 methane yield m/e=17 ions that obscure ammonia. However, with chemical ionization using isobutane, the ammonium ion (m/e=18) forms selectively, and only the electron impact ion formed inefficiently from water interferes (see Table L-1). This interfering ion is removed selectively by charge exchange with nitric oxide in the center quadrupole (the collision chamber) of the spectrometer. Nitric oxide does not react with the ammonium ion

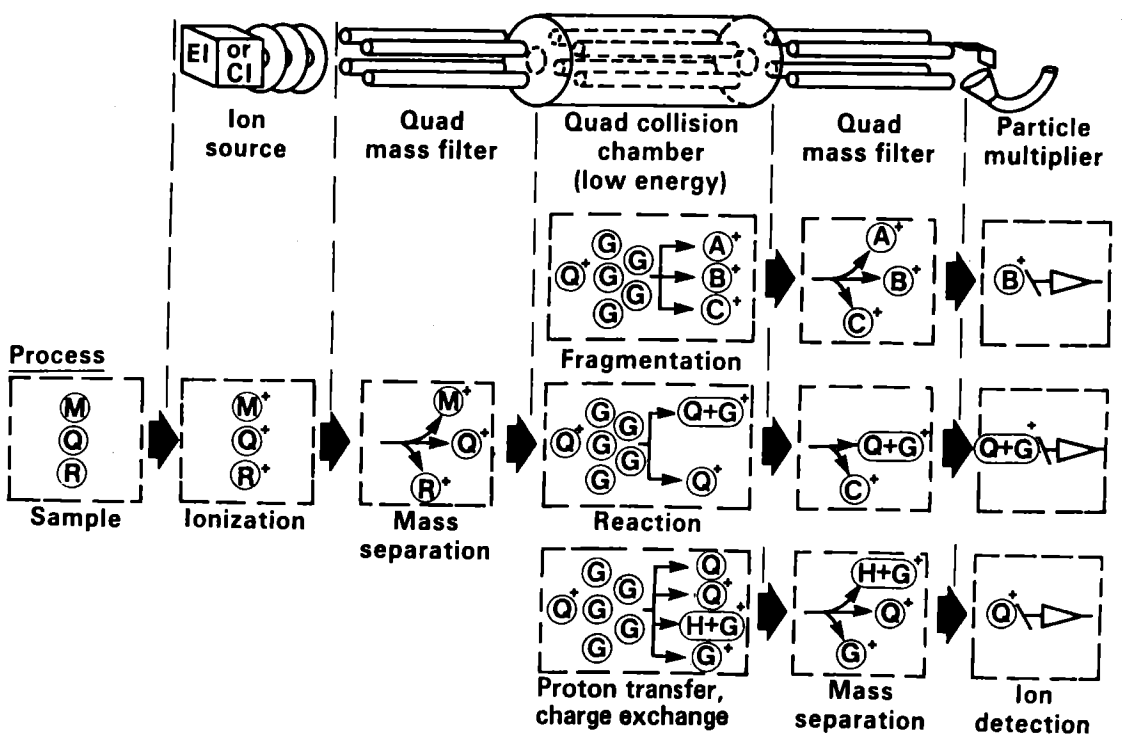


Figure L-5. Triple quadrupole mass spectrometer.

Table L-1. Reactions in the Mass Spectrometer

I. Electron Impact; m/e=17

a. $NH_3 \rightarrow NH_3^+$

b. $H_2O \rightarrow HO^+$

c. $^{13}CH_4 \rightarrow {}^{13}CH_4^+$

II. Chemical Ionization; m/e=18

a. $NH_3 \rightarrow NH_4^+$

b. $H_2O \rightarrow H_2O^+$

III. Scavenging in the Collision Chamber

a. $H_2O^+ + NO \rightarrow NO^+ + H_2O$

b. $NH_4^+ + NO \rightarrow$ No Rxn

The technique has excellent sensitivity and selectivity. We can detect a few ppm ammonia in pure water vapor. The method has been tested by studying the decomposition of ammonia on sand. Figure L-6 shows typical results (heating rate, 4°C/min; flow, 26 cc/min of 1% ammonia in argon). Global kinetic parameters can be determined from the data. We also will apply the kinetic expression derived by Temkin and Pyzhev from an analysis of the decomposition mechanism to our results. This complex expression which defines the true kinetic behavior should provide additional insight in the fate of ammonia in the pyrolyzer and combustor.

$$\frac{d[NH_3]}{dt} = \frac{(K_{\pm})(P_{N_2})^{(1-\beta)}\left[1-\frac{1}{K_{eq}}\cdot\frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}\right]}{\left[\frac{\phi}{P_{H_2}}+\frac{1}{K_{eq}}\cdot\frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}\right]^{\beta}\cdot\left[\frac{\phi}{P_{H_2}}+1\right]^{(1-\beta)}}$$

Buddingtonite decomposition has also been investigated. Figure L-7 shows results of pyrolysis of a natural specimen. It was not possible to obtain such data using TGA or DSC methods, because the loss of water from both the Buddingtonite and associated minerals masks the loss of ammonia and because ammonia release is nearly athermic. The TQMS experiment has

provided information concerning the thermal behavior of the mineral Buddingtonite that was not previously available.

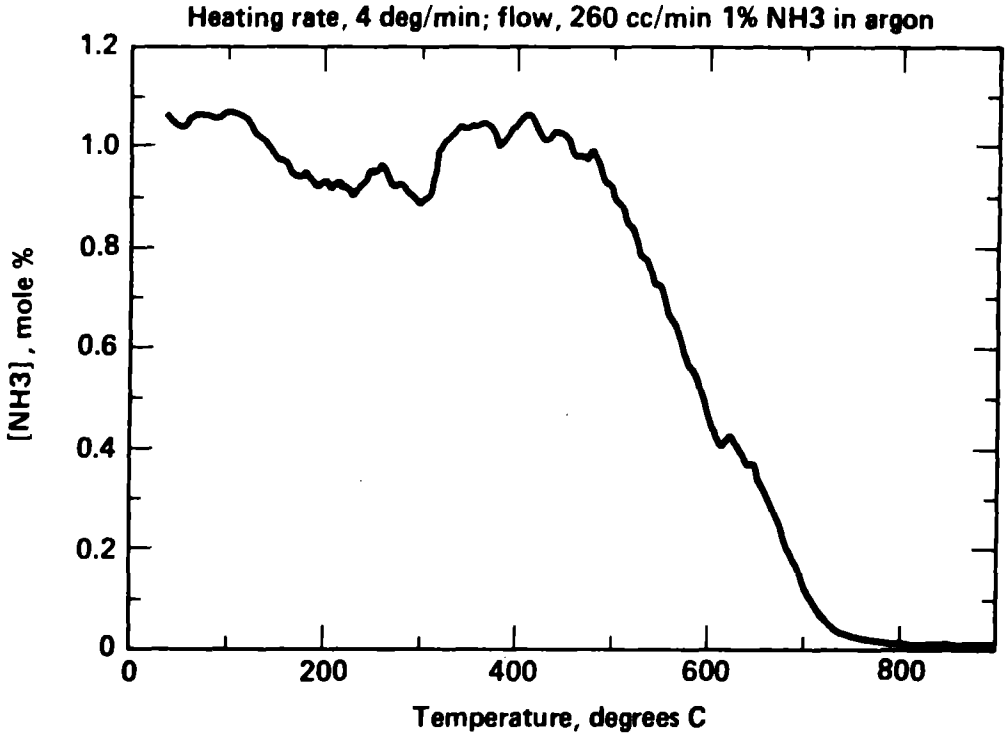


Figure L-6. Ammonia decomposition over sand.

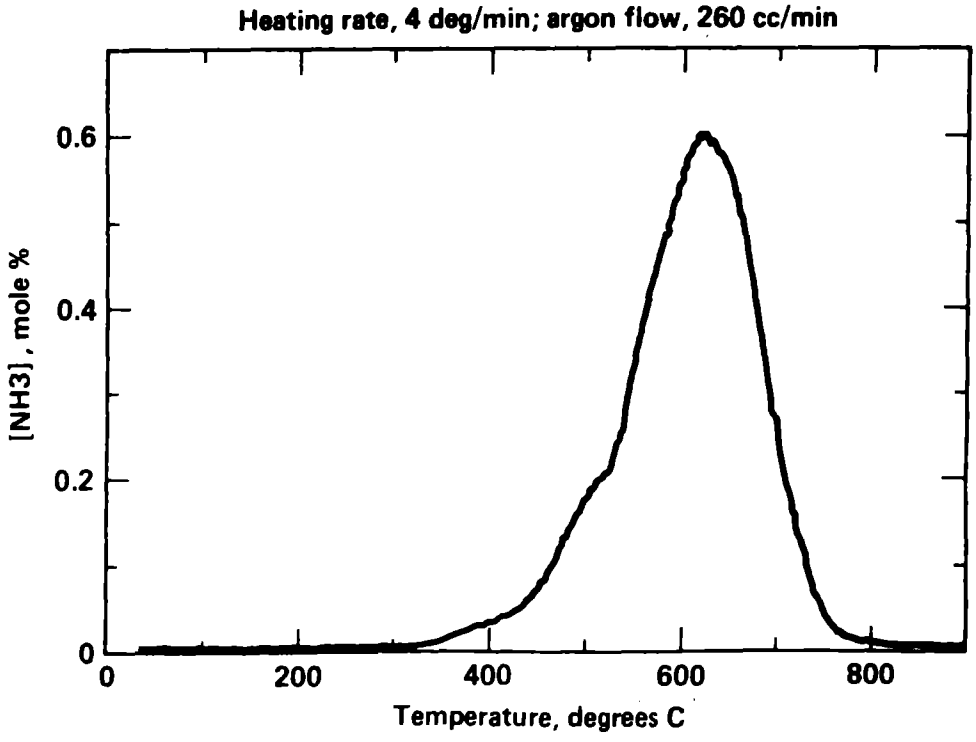


Figure L-7. Ammonia from Buddingtonite decomposition.

Key experiments involving ammonia evolution from Colorado and Devonian oil shale are underway. The effluent from the batch retort must be maintained above 100°C prior to introduction to the mass spectrometer since ammonia can be removed as water condenses by the formation of aqueous ammonium carbonate. Improvements in retorting techniques as well as analysis methods should result from this work.

7. EVALUATION OF POTENTIAL FUTURE PLANS:

- Perform model comparisons of G-series pilot plant runs after incorporating our latest rate equations and physical properties into the model. Update the R-series simulations with the revised model and reconcile R- and G- series differences.

- Continue evaluation and parameter study of the commercial scale retorts using the revised model.

- Improve our sulfur chemistry models for both pyrolysis and combustion environments by distilling and fitting the available data, incorporating these results into multireaction sub-models, and then including the most important aspects in our reactor models.

- Further develop the general combustion model by determining and incorporating more complete reaction kinetics for char, sulfur, and nitrogen. Develope a model of a fluidized bed combustor.

- Continue research and publish ammonia evolution data obtained via the ion specific electrode method; report the effect of temperature, heating rate, and shale source on the yield of NH_3.

- Continue research and publish results of the real-time TQMS method for ammonia analysis. Develope model of H_2S and NH_3 generation and decomposition under retorting conditions; define the contribution of pyrite and Buddingtonite, as well as kerogen and char.

- Study the chemical reactions and physical processes necessary for cooling discharged shale.

- Obtain improved cracking kinetics and assess the importance of mineral components as cracking catalysts; study the effect of mineral additives on cracking losses; investigate the importance of homogeneous gas phase cracking, cracking on solid surfaces and coking.

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