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EXPLORATORY RESEARCH ON SOLVENT REFINED COAL LIQUEFACTION

Quarterly Technical Progress Report for July 1—September 30, 1979

July 1980

Work Performed Under Contract No. AC01-79ET14800

The Pittsburg & Midway Coal Mining Co.
Shawnee Mission, Kansas

U. S. DEPARTMENT OF ENERGY

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ON
SOLVENT REFINED COAL LIQUEFACTION

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JULY 1, 1979 THROUGH SEPTEMBER 30, 1979

THE PITTSBURG & MIDWAY COAL MINING CO.
P. O. BOX 2970
SHAWNEE MISSION, KANSAS 66201

July 1980

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY
DIVISION OF COAL CONVERSION AND UTILIZATION
UNDER CONTRACT DEAC-0179-ET14800

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ABSTRACT

This report summarizes the progress of the Exploratory Research on Solvent Refined Coal Liquefaction project by The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory for the period July 1, 1979 through September 30, 1979. In a series of experiments with varying feed gas composition, high levels (20-40 mole %) of carbon monoxide resulted in a general degradation of operability and reduced oil yields from Powhatan coal (Pittsburgh Seam). Addition of finely divided pyrite to the reactive Powhatan coal had little effect on oil yields although the molecular weight of the distillation residue was apparently decreased. When finely divided pyrite and magnetite were added to the less reactive Loveridge coal (also Pittsburgh Seam), however, a substantial increase in oil yields and product quality was obtained.

I. SUMMARY

Three series of experiments were conducted with Pittsburgh Seam coals in the SRC II mode with 30% coal in the slurry at one hour residence time, 455°C and 1800 psig. In the first series, the effect of high levels of carbon monoxide (20-40 mole %) in the feed gas on processing of coal from the Powhatan No. 5 Mine was investigated. In the second, addition of finely divided pyrite (FeS_2) to Powhatan coal was studied. In the last series, finely divided pyrite and magnetite (Fe_3O_4) were added to coal from the Loveridge Mine.

High carbon monoxide concentrations were found to contribute to a general degradation of unit operability as evidenced by increased unfiltered coal solution (UFCS) viscosity and plugging of the slurry feed and dissolver systems. Carbon monoxide levels of 20-40 percent resulted in oil yields substantially below those found in earlier work at 5-10 percent concentrations. SRC and insoluble organic matter (IOM) yields were increased and total hydrogen consumption decreased. Carbon monoxide consumption and carbon dioxide production were consistent with the shift reaction at all levels of CO addition.

There was little change in total oil yield from Powhatan coal with added pyrite, apparently due to the already high iron content and reactivity of the coal. Heavy distillate quality was also unchanged, except for decreased desulfurization with pyrite addition. The fusion point of the distillation residue was reduced by 40°C with pyrite in the feed, however, and its solubility in hexane and benzene was increased.

In contrast, total oil yield from the less reactive Loveridge coal was increased 8-11% (absolute) by pyrite addition and to a lesser extent by adding magnetite. A corresponding decrease in SRC and IOM yields was observed. Desulfurization and denitrogenation of the heavy distillate product were also enhanced by the addition of iron containing compounds. Although operability was satisfactory while processing this coal with additives, it became impossible to run when the additives were removed.

Data on solvent extraction of vacuum distillation residues with hexane, benzene, toluene and pyridine are reported this quarter and will be included for the remainder of the contract.

II. INTRODUCTION

This report covers work at The Pittsburg & Midway Coal Mining Co.'s Merriam Laboratory on the Solvent Refined Coal (SRC) process during the period July 1, 1979 through September 30, 1979.

A. Reports of Previous Work

Previous work at this laboratory has been described in interim, final, monthly, quarterly and annual reports to the Office of Coal Research, the Energy Research and Development Administration and the Department of Energy. A summary of these documents appears in the second quarter 1979 report* along with a description of the current contract objectives and a history of the Merriam Laboratory in solvent refining of coal.

B. Currently Reported Work

During the third quarter of 1979 activities at the Merriam Laboratory included:

- SRC II processing of Pittsburgh Seam coal from the Powhatan No. 5 Mine to investigate the effect of high levels (20-40 mole %) of carbon monoxide in the feed gas.
- Addition of finely divided iron compounds to Pittsburgh Seam coals from the Powhatan No. 5 and Loveridge Mines.
- Development of a procedure for solvent extraction of distillation residues with hexane, benzene, toluene and pyridine to characterize non-distillable products.

Conditions and results for all runs reported this quarter are summarized in Table 1.

III. DISCUSSION

A. Investigation of High Levels of Carbon Monoxide in the Feed Gas

Background

These experiments are an extension of work reported previously** on low level (5-10%) carbon monoxide addition. Whereas the earlier work was related to options in hydrogen enrichment, the present study explored the use of synthesis gas with higher levels of carbon monoxide (20-40%) in the SRC II process.

Experimental

The run conditions and results are summarized in Table 1. The feed gas contained about 20 mole % CO in run DOE 331RB and 40 mole % CO in run DOE 332RB with a constant molar flowrate of H_2 plus CO. An equimolar quantity of water was added with the CO to allow the shift reaction to occur in-situ. Total reactor pressure was 2565 psig for both runs. An additional run was attempted at 2065 psig total pressure and 20% CO in the feed, but was unsuccessful.

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* Exploratory Research on Solvent Refined Coal Liquefaction, Quarterly Technical Progress Report for the Period April 1, 1979 through June 30, 1979; July 1980, FE/14800-10.

** Solvent Refined Coal (SRC) Process, Quarterly Technical Progress Report for the Period January 1, 1979-March 31, 1979, The Pittsburg & Midway Coal Mining Co.; to be published, FE/496-172.

Carbon monoxide addition contributed to a general degradation of operability. The unfiltered coal solution (UFCS), and hence feed slurry, became increasingly viscous as the CO level was increased. It was, therefore, necessary to raise the temperature of the feed slurry system to maintain circulation. This condition was a contributing factor in subsequent plugging of feed lines from material which had "baked out" on the sides of feed vessels. A plug also developed in the dissolver, shutting down the final experiment (332RB) which had 40 percent CO in the feed.

The large amounts of water added in the feed generally prevented the downstream deposits of ammonium carbonate (bicarbonate) experienced in earlier CO runs, however.

The erratic operation reduced the length of time available for material balances at steady-state conditions and introduced scatter in the data. Although total mass balances were reasonably good, ash could not be accounted for properly and liquid yields should be considered qualitative.

Yields

Carbon monoxide consumption and carbon dioxide production were consistent with the shift reaction as shown in Table 2. Earlier results at 0 and 10 percent CO levels are included for comparison. In all cases, CO_2 appeared at the same rate CO disappeared, on a molar basis, within experimental error. The shift reaction was apparently inhibited in DOE 298R due to lack of water since the percentage of CO feed converted was substantially less than in subsequent runs. An essentially constant proportion of feed CO was consumed during runs DOE 331RB and 332RB which had equimolar amounts of water added to the feed.

A comparison of runs DOE 331RB and 332RB shows a further degradation of performance as CO is increased, particularly in IOM yield. The change in oil yield is not as great, however, as might be expected from the change in hydrogen partial pressure. At these conditions, production of in-situ hydrogen apparently compensates somewhat for lack of feed hydrogen.

Product Quality

The effect of feed gas composition on product quality is shown on Table 4 . There are no clear trends regarding the effect of carbon monoxide addition on heavy distillate or distillation residue analyses.

The viscosities of unfiltered coal solutions (UFCS) are shown in Table 5 and on Figure 1. UFCS viscosity increased as the carbon monoxide in the feed was increased. Viscosity also tended to increase as hydrogen partial pressure (and consumption) decreased.

B. Addition of Iron Compounds

1. Effect of Adding Finely Divided Pyrite to Powhatan Coal

Background

Previous pyrite addition experiments at the Merriam Laboratory demonstrated that addition of coarse pyrite (<150 mesh) did not change oil yields in SRC I processing although product hydrogenation was increased. In the SRC II mode, however, coarse pyrite addition increased oil yields by about 7% absolute (at a 7.5% addition level) while increasing hydrogen and decreasing sulfur and nitrogen in the heavy distillate. Use of finely divided pyrite (~1 micron) in the SRC I process increased recycle solvent by 8% absolute in contrast to results with coarse material.

This section of the report covers the first experiments with finely divided pyrite in the SRC II mode. It is also the first time pyrite was added to Powhatan coal. The results of four SRC II experiments with finely divided pyrite and magnetite addition to a less reactive coal (Loveridge) are detailed in the next section.

Experimental

The run conditions and results are summarized in Table 1. Run DOE 333R was a baseline experiment with Powhatan coal in the SRC II mode without additives. In run DOE 335R, pyrite was added at a level of 5.0% (as pure FeS_2) based on feed coal and the unfiltered coal solution (UFCS)/heavy distillate (HD) ratio was adjusted to keep the total solids in the feed essentially the same as in run DOE 333R. In run DOE 335RB, the same amount of pyrite was added but the UFCS/HD ratio was kept the same as in run DOE 333R, resulting in a higher total solids level in the feed.

The pyrite used in this experiment ("pyrite I") was obtained from the coal cleaning operation of the U. S. Steel Robena Mines, Greene County, Pennsylvania. An analysis is shown in Table 6. The pyrite was finely ground by The Jet Pulverizer Company, Palmyra, New Jersey.

The particle size of the pyrite has been measured by two methods: the Fisher Subsieve Sizer and Coulter Counter. The former method includes particles from 0.2-25 μm in the average, whereas the latter includes only those from 1-25 μm. The average obtained by the Fisher Subsieve Sizer, therefore, is generally lower. The particle size distribution of the pyrite I obtained by the Counter Counter method is shown in Figure 2.

Operation of the unit was satisfactory except for persistent deposits downstream of the dissolver which have characterized processing of Powhatan coal. Post-dissolver water injection was used to prevent plugging of the lines.

Yields

The effect of pyrite addition on the yield structure is summarized below:

Conditions	DOE 333R	DOE 335R	DOE 335RB
Pyrite addition rate,*			
% MF Coal	--	5.0	5.0
Slurry Formulation			
% UFCS	60.0	53.2	58.2
% Heavy Distillate	6.0	11.0	6.0
Total Solids	44.2	43.3	47.0
Yields, Wt % MF Coal			
C_1-C_4	15.5	14.0	14.7
Total Oil	36.6	37.9	39.5
SRC	23.3	25.9	23.2
Insoluble Organic Matter	5.0	5.1	4.9
Hydrogen Consumption	4.6	4.7	4.5

* As pure FeS_2, based on 81% FeS_2 in as received Robena pyrite I.

The variation in yields is close to experimental error although there was a slight increase in total oil when pyrite was added in run DOE 335R and a further increase at the higher total solids level in run DOE 335RB. Since these increases are not completely accounted for by changes in other hydrocarbon yields, it cannot be unequivocally stated that pyrite addition had an effect. Insoluble organic matter (IOM) yield and hydrogen consumption were virtually constant.

The relative yields of heavy distillate and middle distillate were consistent with changes in the feed slurry formulation (see Table 1). For example, more heavy distillate was recycled in run DOE 335R to keep the total solids level the same as in run DOE 333R, so less was available as product.

Product Quality

The effect of pyrite addition on product quality is shown below:

	DOE 333R	DOE 335R	DOE 335RB
Pyrite addition rate*			
% MF Coal	--	5.0	5.0
Heavy Distillate Analyses			
% H	7.70	7.71	7.96
% S	0.28	0.36	0.34
% N	1.05	1.04	1.05

	DOE 333R	DOE 335R	DOE 335RB
Distillation Residue Fusion Point, °C	152	114	107

* As pure FeS_2, based on 81% FeS_2 in as received Rcbena pyrite I.

The heavy distillate nitrogen level was unchanged and the variation in hydrogen content was small. The desulfurization was decreased with pyrite addition in contrast to previous SRC II work with coarse pyrite where desulfurization was increased.

The fusion point of the distillation residue was significantly reduced by pyrite addition, dropping from 152 to 107-114°C. In addition, the solubility of the distillation residue in hexane and benzene was significantly increased (see section III-C).

Unfiltered coal solution (UFCS) viscosities are shown on Table 7 and Figure 3. The variation in UFCS viscosities resulted primarily from changes in the formulation with a correlation apparent between the amount of residue (IOM + SRC) in the feed and UFCS viscosity.

Comparison of replicate viscosity measurements with two different products during steady state operation of runs DOE 333R and 335R shows an average variation of about 10%. This includes any difference between products as well as variation in the viscosity measurements.

The feed slurry viscosities are shown on Table 8 and Figure 4. A minimum with temperature typical of coal feed slurries was obtained. Since the UFCS, which is used to make up the feed slurry, had a viscosity in run DOE 335R3 which was lower than in run DOE 333R, the higher feed slurry viscosity in run DOE 335RB may be attributable to the 3% higher solids level.

Replicate measurements at 270°F and a shear rate of $0.415\ s^{-1}$ on the same sample from run DOE 335RB showed about 5% variation between trials.

2. Effect of Adding Finely Divided Pyrite and Magnetite to Loveridge Coal

Background

The results of previous pyrite addition experiments at the Merriam Laboratory were summarized in section III-B-1. It was also found that magnetite addition generally increased total oil yields although the effect was not as great as with pyrite. Magnetite also removes H_2S quantitatively from the gas stream, resulting in lower sulfur levels in the products, and tends to lower gas production.

This section describes addition of finely divided pyrite and magnetite to the less reactive Loveridge coal in the SRC II mode.

Experimental

The run conditions and results are summarized in Table I. In runs DOE 336R and 337R two different lots of pyrite were used as additives, with high and low purity, respectively. In run DOE 338R, magnetite was added at a level sufficient to remove all traces of H_2S from the dissolver effluent. Run DOE 339R was a baseline experiment without added catalyst.

Run DOE 336R was completed with only about 4 percent recycle solvent in the formulation. The slurry became unmanageable after a switch from pyrite I to pyrite II, however, so the recycle solvent level was increased to 10 percent in run DOE 337R. This formulation was continued through the magnetite and control runs.

All additives were from the coal cleaning operation of the U. S. Steel Robena Mines, Greene County, Pennsylvania. Analyses are shown on Table 6. The two samples of pyrite, I and II, were obtained at different times and differed significantly in purity and apparent particle size. The additives were finely ground by The Jet Pulverizer Company, Palmyra, New Jersey.

The particle size of the additives has been measured by two methods: the Fisher Subsieve Sizer and Coulter Counter. The average obtained by the Fisher Subsieve Sizer is generally lower, as discussed in section III-B-1. The particle size distributions of the additives obtained by the Coulter Counter method are shown in Figures 2, 5 and 6.

Pyrite I and pyrite II were added at levels corresponding to 5.0% pure FeS_2 based on coal as was done in the Powhatan runs reported above. Magnetite was added initially at the same iron level as the pyrite additives and then increased gradually until all traces of H_2S were removed from the reactor effluent.

Further addition of magnetite would not be expected to have any effect since there would be no sulfur available for conversion of Fe_3O_4 to a catalytically active $Fe_{1-x}S$ compound.

Operation was satisfactory during runs DOE 336R, 337R and 338R with pyrite or magnetite added to the feed. When run DOE 339R was attempted without an additive, however, operability quickly deteriorated. Continued operation became impossible just as lined-out conditions were achieved. This corresponded to the point where essentially all magnetite from run DOE 338R had left the system. This confirmed earlier results indicating that it is not possible to run Loveridge coal at these conditions in our equipment without an additive.

Yields

The effect of adding pyrite and magnetite on yields and product quality is shown in Table 9. Total oil yield is increased significantly (8-11% absolute) by pyrite addition and to a lesser extent by magnetite addition. Most of the increase is in the heavy distillate fraction. There is a corresponding decrease in SRC and IOM yields. There is also a small increase in gas yields due to the additives.

A comparison of pyrite I and pyrite II is confounded by the difference in formulations. It appears, however, that pyrite I was more active than pyrite II due to the 5.2% difference in SRC yields which is more than would be expected from the change in formulation. This is in spite of the smaller particle size of pyrite II, although the difference obtained by Coulter Counter may be due to non-pyritic fines included in the material.

Product Quality

Desulfurization and denitrogenation of the heavy distillate product were increased by the additives in the order:

pyrite I > magnetite > pyrite II > no additive

The vacuum distillation residue fusion point was lowered from 149°C to 113-119°C by iron containing additives. The solubility of the residue was also increased (see section III-C).

The viscosities of unfiltered coal solutions (UFCS) are shown on Table 10 and Figure 7. The UFCS viscosity was reduced considerably by pyrite and magnetite addition. The relative viscosities of UFCS from runs DOE 336R, 337R and 338R appear to be correlated with the amount of solids (ash + IOM) in the corresponding feeds.

The viscosity of run DOE 337R feed slurry is shown on Table 11 and Figure 8. The viscosity decreased significantly as shear rate was increased. It was also observed that the minimum in viscosity with temperature typical of coal feed slurries was less pronounced at higher shear rates.

C. Solvent Extraction of Distillation Residues

The solubilities of the vacuum distillation residues in various solvents are reported for the current runs and will be presented for experiments conducted during the rest of the contract period. A complete description of the experimental procedure, equipment, sample selection and precision is given in Appendix A.

These studies were undertaken to characterize the non-distillable products from coal liquefaction. These fractions represent the major fuel product from the SRC I process and it is desirable to be able to measure the effect of process variables directly on these materials. In the SRC II process, the residue is to be used for the production of hydrogen. Characterization of the distillation residue, however, is expected to yield useful information about the chemistry of the process.

The objectives of these studies were, therefore, to:

1. Determine the effect of operating conditions on the solubility of the distillation residues in various solvents.
2. Study the extracts by elemental analysis and determine the amount of volatile matter in the residue.
3. Compare the solubility of the distillation residues in benzene and toluene.

It was found that solvent extraction of distillation residues can be done with reasonable precision. An occasional sample may give a peculiar result so that duplicate extractions are recommended. Evaluation of a sample should include a series of extractions with different solvents since the relative solubilities will change with operating conditions.

Hexane, benzene, toluene and pyridine were chosen as solvents initially and gave a reasonable spread in solubility. As expected, the solubility in toluene has been close to that in benzene, but some variability was observed. Solubility in benzene was usually slightly less and occasionally the spread was appreciable. When the spread between benzene and toluene was large, the hexane solubility was generally large as well.

The solubilities of the vacuum distillation residues in various solvents are shown in Table 12.

The absolute solubilities are confounded by the amount of ash in the sample but the amount of organic matter soluble in pyridine is fairly constant. The ratios of solubilities in other solvents to that in pyridine are, therefore, included to allow comparison of materials derived from different types of runs (with different ash contents) on a common basis.

A comparison of the experiments with 20 and 40% carbon monoxide in the feed gas, runs DOE 331RB and DOE 332RB, respectively, indicates a significant decrease in hexane solubility and smaller decreases in benzene, toluene and pyridine solubility as the carbon monoxide concentration was increased.

When pyrite was added to Powhatan coal in run DOE 335RB, the yields were essentially the same as in the control run, DOE 333R. There was a significant increase in the hexane solubility of the distillation residue with added pyrite, however, along with smaller increases in benzene and toluene solubility. The apparent reduction in molecular weight of the non-distillable fraction brought about by the catalyst was also evidenced by a lower residue fusion point and lower UFCS viscosity.

When iron containing compounds were added to Loveridge coal, the ratios of hexane, benzene and toluene solubilities to pyridine solubility were generally increased by the additives in the order:

pyrite I > pyrite II > magnetite

The result is similar to the effect of the additives on total oil yield and indicates that molecular weight reduction is enhanced by iron compounds in the non-distillable as well as volatile product fractions.

D. Maintenance and Modifications

1. Maintenance

a. During the first run of the carbon monoxide series, a vertical length of 9/16" O.D. pipe connecting the intermediate temperature, high pressure separator to a condenser failed. When the failure was analyzed, it was found that it was probably the result of chloride stress corrosion cracking. It was recommended that the 316 stainless steel be used only in the solution annealed condition. If the problem continues, Incoloy 800H may have to be substituted. The details of the analysis are included in Appendix B.

b. The intermediate temperature, high pressure (ITHP) separator developed restrictions throughout runs DOE 331RB-335RB. Plugging and corrosion problems have occurred whenever Powhatan coal has been used. A sample of plug material from one of these runs was analyzed and the following materials were detected:

Fe	28.22%
S	22.22%
Ni	5.03%
C	1.89%
H	0.89%

Ni and Fe are present in this residue in about the same ratio as in 316 stainless steel, the construction material for the ITHP separator. Although the quantitative analysis accounts for only 68.22% of the residue, it is apparent that the 316 SS corroded at an accelerated rate when Powhatan coal was used.

c. During run DOE 335RB, several of the Love temperature controllers arced shut. After consultation with the manufacturer, it was determined that the relays would have to be replaced more frequently (once a quarter) than originally scheduled.

2. Modifications

a. Slurry Feed System

The slurry feed system has been modified as shown on Figure 9*. The unfiltered coal solution (UFCS) is forced to the feed system by 30-40 psi pressure in the atmospheric flash and is collected on one of two weigh scales. One part of the UFCS is collected in a boiling flask and taken off as product (UFCS product return). The other part of the UFCS is directed to a collection pot to be reformulated (UFCS weigh pot). When the desired quantity of UFCS is present in the weigh pot, it is transferred by gravity to the slurry mix pot. With this configuration, the weigh scale is not subject to the vibration and torque required to mix the slurry. (The solids in the slurry mix are kept in suspension by recirculation and stirring.) When the slurry in the feed pot drops to a certain level, the recirculation stream from the slurry mix pot is directed to the feed pot. The recirculation loop on the feed pot, in turn, feeds the Hills-McCanna high pressure metering pump.

b. Distillation Column

The distillation column was taken apart to replace the stainless steel packing with glass packing because of suspected corrosion of the packing. It was found, however, that while the packing was in good condition, the support blocks at the ends of the column were badly corroded. These were found to be constructed from 400 series (magnetic) stainless steel and were replaced with 316 stainless steel.

c. Temperature Control of the Slurry Mix and Feed Pots

The temperature of the slurry mix and feed pots was raised during the carbon monoxide runs due to thickening of the slurry. Since the heaters on the sides and bottom of the pots were regulated by the same controller, the sides tended to overheat as the levels in the pots were reduced. This was corrected by placing the side heaters on variacs, independent of the controllers, so heat input to the sides could be reduced as the level in the pots dropped.

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* The slurry feed system has been described previously; Solvent Refined Coal (SRC) Process, Quarterly Technical Progress Report for the Period April 1, 1978 through June 30, 1978, The Pittsburg & Midway Coal Mining Co.; May 1978, FE/496-157.

d. Dissolver

It was necessary to send the DOE 1 dissolver off site to a machine shop after it was coked solid in run DOE 332RB. To avoid a delay in starting the next run, a "modified GU5" dissolver was fabricated from 11/16 inch (17.5 mm) I.D. tubing as shown on Figure 10.

TABLE 1

Summary of Process Conditions, Yields and Product Analyses

Conditions	DOE 331RB	DOE 332RB
Coal	Pittsburgh Seam[a]	
Dissolver	DOE 1	
Nominal Slurry Residence Time, hr	1.00	1.02
Coal Feed Rate, lb/hr/ft^3	21.6	21.2
Average Dissolver Temperature, °C	452	453
°F	846	847
Dissolver Pressure, psig	2565	2565
Feed Gas Composition		
Mole % H_2	80.3	60.3
Mole % CO	19.7	39.7
Hydrogen Feed		
Wt % based on slurry	3.47	2.64
MSCF/ton of coal	44.03	33.4
Slurry Formulation, wt %		
Coal	30.0	30.0
Recycle Coal Solution	59.3	58.0
Recycle Solvent	10.7	12.0
Slurry Blend Composition		
Coal	30.0	30.0
Middle Distillate (193-288°C, 380-550°F)	3.2	3.0
Heavy Distillate (>288°C, >550°F)	28.5	27.0
SRC	23.4	24.2
Ash (from recycle coal solution)	10.4	9.8
Insoluble Organic Matter (from recycle coal solution)	4.5	6.0
Total Solids	44.9	45.8
Yields		
H_2O	0.2	(11.[illegible])[b]
CO	--	--
CO_2	18.3	35.6
H_2S	2.6	4.7
NH_3	0.5	0.4
C_1	5.1	5.2
C_2	3.4	3.2
C_3	2.8	2.3
C_4	1.4	1.1
Total C_1-C_4	12.7	11.3
Naphtha, C_5-193°C	8.2	6.7
Middle Distillate, 193-288°C	16.9	17.0
Heavy Distillate, >288°C	8.5	8.2
Total Oil	33.6	31.9
SRC	29.4	31.8
Insoluble Organic Matter	5.7	7.9
Ash	13.1	12.9
Total	116.1	125.9
H_2 Reacted, gas balance	3.9	2.4
CO Reacted, gas balance	12.2	23.5
Lineout Index	1.14	1.12
Product Analyses		
Heavy Distillate Analyses		
% C	88.74	88.89
% H	7.57	7.38
% S	0.45	0.61
% N	1.15	1.14
% O (by Difference)	2.09	1.98
Specific Gravity	1.0817	1.0870
Distillation Residue Analyses		
% C	64.53	66.99
% H	3.90	3.82
% S	3.57	3.20
% N	1.27	1.30
% Ash	27.21	24.56

a) Powhatan Mine No. 5.
b) Loss; water produced from dry coal less water consumed in shift reactor.

TABLE 1 (Continued)

Conditions	DOE 333R	DOE 335R	DOE 335RB
Coal	← Pittsburgh Seam[a] →		
Reactor	← Modified GU5[b] →		
Nominal Slurry Residence Time, hr	1.04	1.02	1.01
Coal Feed Rate, lb/hr/ft^3	20.8	21.2	21.2
Average Dissolver Temperature, °C	455	455	455
°F	851	851	851
Dissolver Pressure, psig	1800	1800	1800
Hydrogen Feed			
Wt % based on slurry	4.15	4.08	4.07
MSCF/ton of coal	52.6	51.6	51.6
Additive	--	Pyrite I	Pyrite I
Additive level, wt % based on MF coal[c]	--	5.0	5.0
Slurry Formulation, wt %			
Coal	30.0	30.0	30.0
Recycle Coal Solution	60.0	53.2	58.2
Recycle Solvent	10.0	15.0	10.0
Pyrite I	--	1.8	1.8
Slurry Blend Composition, wt %			
Coal	30.0	30.0	30.0
Middle Distillate (193-288°C, 380-550°F)	3.6	3.8	4.5
Heavy Distillate (>288°C, >550°F)	31.7	37.9	30.7
SRC	20.5	15.0	17.8
Ash (from recycle coal solution)	9.8	8.6	11.4
Insoluble Organic Matter (from recycle coal solution)	4.4	2.9	3.8
Pyrite I	--	1.8	1.8
Total Solids	44.2	43.3	47.0
Yields			
H_2O	9.1	8.0	8.4
CO	0.3	0.3	0.3
CO_2	0.9	0.8	0.9
H_2S	2.5	3.4	3.3
NH_3	0.5	0.6	0.6
C_1	6.1	5.4	5.7
C_2	4.1	3.8	3.9
C_3	3.3	3.1	3.3
C_4	1.9	1.7	1.8
Total C_1-C_4	15.4	14.0	14.7
Naphtha, C_5-193°C	10.4	11.2	9.5
Middle Distillate, 193-288°C	18.1	20.2	17.1
Heavy Distillate, >288°C	8.1	6.5	12.9
Total Oil	36.6	37.9	39.5
SRC	23.2	25.9	23.2
Insoluble Organic Matter	5.0	5.1	4.9
Ash	11.1	11.1	11.1
Total	104.6	107.1	106.9
H_2 Reacted, gas balance	4.6	4.7	4.5
Additive Conversion Byproducts[d]	--	2.4	2.4
Product Analyses			
Heavy Distillate Analyses			
% C	89.19	89.24	89.15
% H	7.70	7.71	7.96
% S	0.28	0.36	0.34
% N	1.05	1.04	1.05
% O (by difference)	1.78	1.65	1.50
Specific Gravity	1.0645	1.0640	1.0553
Distillation Residue			
% C	64.49	58.80	55.72
% H	3.76	3.68	3.47
% S	2.89	5.60	6.22
% N	1.29	1.12	1.06
% Ash	27.21	32.83	35.91
Fusion Point, °C	152	114	107

a) Powhatan Mine No. 5.
b) Two upflow dissolver sections made from 11/16" I.D. tubing connected by a 5/16" I.D. transfer line.
c) Addition level based on pure FeS_2.
d) Additive fed-ash from additive.

TABLE 1 (Continued)

	DOE 336R	DOE 337R	DOE 338R	DOE 339R
Conditions				
Coal	← Pittsburgh Seam[a] →			
Dissolver	← Modified GU5[b] →			
Nominal Slurry Residence Time, hr	1.00	1.00	1.02	1.03
Coal Feed Rate, lb/hr/ft^3	21.5	21.5	21.1	20.9
Average Dissolver Temperature, °C	455	457	455	456
°F	851	855	851	853
Dissolver Pressure, psig	1800	1800	1800	1800
Hydrogen Feed				
Wt %, based on slurry	4.03	3.92	3.99	4.02
MSCF/ton of coal	50.9	49.5	50.4	50.8
Additive	Pyrite I	Pyrite II	Magnetite	--
Additive level (% based on MF coal)[c]	5.0	5.0	5.7	--
Slurry Formulation, wt %				
Coal	30.0	30.0	30.0	30.0
Recycle Coal Solution	64.2	57.7	58.0	60.0
Recycle Solvent	4.0	10.0	10.0	10.0
Additive	1.8	2.3	2.0	--
Slurry Blend Composition, wt %				
Coal	30.0	30.0	30.0	30.0
Middle Distillate (193-288°C, 380-550°F)	3.9	5.1	3.7	3.8
Heavy Distillate (>288°C, >550°F)	22.7	29.7	26.7	28.7
SRC	24.9	20.3	23.9	27.0
Ash (from recycle coal solution)	11.4	9.0	9.5	5.5
Insoluble Organic Matter (from recycle coal solution)	5.3	3.6	4.2	5.0
Additive	1.8	2.3	2.0	--
Total Solids	48.5	44.9	45.7	40.5
Yields				
H_2O	4.8	3.8	5.4	4.0
CO	0.5	0.5	0.3	0.3
CO_2	0.7	0.7	1.1	1.0
H_2S	2.9	2.8	--	1.4
NH_3	0.5	0.4	0.4	0.3
C_1	6.2	6.0	5.6	5.7
C_2	4.2	4.0	3.6	3.5
C_3	3.4	3.1	2.7	2.5
C_4	1.9	1.8	1.5	1.4
Total C_1-C_4	15.7	14.9	13.4	13.1
Naphtha, C_5-193°C	8.4	9.7	9.1	7.5
Middle Distillate, 193-288°C	13.0	14.8	12.8	11.7
Heavy Distillate, >238°C	20.9	14.4	10.3	11.6
Total Oil	42.3	38.9	32.2	30.8
SRC	26.0	31.2	36.6	37.4
Insoluble Organic Matter	5.5	5.6	6.5	6.9
Ash	8.1	7.9	7.7	7.6
Total	107.0	106.7	103.6	102.8
H_2 Reacted, gas balance	4.6	4.8	3.7	2.8
Additive conversion byproducts[d]	2.4	1.9	(0.1)[e]	--
Lineout Index	1.04	1.04	0.96	1.08
Product Analyses				
Heavy Distillate Analyses				
% C	89.01	89.04	88.68	89.10
% H	8.10	7.61	8.10	8.04
% S	0.32	0.45	0.34	0.53
% N	1.15	1.28	1.25	1.33
% O (by difference)	1.42	1.62	1.63	1.00
Specific Gravity	1.0585	1.0679	1.0532	1.0810
Vacuum Bottoms Analyses				
% C	63.57	64.61	67.45	75.95
% H	3.72	3.72	4.06	4.31
% S	4.85	4.72	4.36	2.09
% N	1.25	1.32	1.48	1.60
% Ash	28.33	28.48	24.68	5.81
Fusion Point, °C	118	113	119	149

a) Loveridge Mine
b) Two upflow dissolver sections made from 11/16" I.D. tubing connected by a 5/16" I.D. transfer line.
c) As pure FeS_2 or Fe_3O_4.
d) Additive fed-ash from additive.
e) Negative.

TABLE 2

Summary of CO Addition and Consumption

DOE	296R[a]	298R[a]	331RB	332RB
Feed Gas Composition[b]				
H_2	100.0	90.0	80.3	60.3
CO	0	10.0	19.7	39.7
Total Pressure, psig	1800	2065	2565	2565
CO Added				
moles/hr	--	2.56	5.11	10.23
g/hr	--	71.7	143.1	286.3
wt %, based on coal	--	21.0	40.0	81.5
MSCF/ton of coal	--	5.7	10.83	22.06
CO Consumed (or produced)				
moles/hr	(0.04)	0.53	1.56	2.95
g/hr	(1.2)	14.7	43.7	82.6
wt %, based on coal	(0.3)	4.3	12.22	23.5
MSCF/ton of coal	(0.09)	1.18	3.31	6.36
CO_2 Produced				
moles/hr	0.04	0.40	1.49	2.85
g/hr	1.9	17.4	65.4	125.3
wt %, based on coal	0.7	5.1	18.28	35.65
MSCF/ton of coal	0.09	0.89	3.16	6.15
% Feed CO Consumed	--	21	31	29

a) From the Quarterly Technical Progress Report for the period January 1 through March 31, 1979; FE/496-172.

b) Water-free basis, mole %.

TABLE 3

Effect of CO Addition on Yields

DOE	296R[a]	298R[a]	331RB	332RB
Run Conditions				
Average Dissolver Temp, °C	455	455	452	453
Nominal Slurry Residence Time, hr	1.01	1.05	1.00	1.02
Feed Gas Composition[b]				
Mole % H_2	100	90.0	80.3	60.3
Mole % CO	0	10.0	19.7	39.7
Total Pressure, psig	1800	2065	2565	2565
Partial pressure H_2[c], psia	-	1809	1617	1047
Partial pressure CO[c], psia	-	200	395	686
Yields[d]				
Total C_1-C_4	13.5	14.4	12.7	11.8
Total Oil	39.8	40.6	33.6	31.9
SRC	25.0	25.6	29.4	31.8
IOM	5.0	5.1	5.7	7.9
Hydrogen Consumption[d]				
Feed H_2	5.4	5.0	3.9	2.4
From CO	--	0.3	0.9	1.7
Total	5.4	5.3	4.8	4.1

a) From the Quarterly Technical Progress Report for the period January 1 through March 31, 1979; FE/496-172.
b) Water free.
c) At dissolver inlet, includes vaporization of liquid feed.
d) Weight % of MF coal.

TABLE 4

Effect of Feed Gas Composition on Product Quality

	DOE 296R*	DOE 298R*	DOE 331RB	DOE 332RB
Feed Gas Composition				
Mole % H_2	100	90.0	80.3	60.3
Mole % CO	0	10.0	19.7	39.7
Total Pressure, psig	1800	2065	2565	2565
Partial pressure H_2, psia	--	1809	1617	1047
Partial pressure CO, psia	--	200	395	686
Heavy Distillate Analyses				
% C	88.19	89.18	88.74	88.89
% H	7.36	7.19	7.57	7.38
% S	0.49	0.52	0.45	0.61
% N	1.25	1.24	1.15	1.14
% O (by difference)	1.71	1.87	2.09	1.98
Distillation Residue Analyses				
% C	64.68	63.39	64.53	66.99
% H	3.72	3.68	3.90	3.82
% S	2.91	2.96	3.57	3.20
% N	1.29	1.31	1.27	1.30
% Ash	27.2	27.8	27.2	24.6
Fusion Point, °C	136	131	120	160

* From the Quarterly Technical Progress Report for the period January 1 through March 31, 1979; FE/496-172.

TABLE 5

Unfiltered Coal Solution Viscosities[a]
Runs DOE 331RB and DOE 332RB

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, 10^3 cP
331RB P-40	210	3.32	1.10
	210	8.30	1.00
	230	3.32	0.539
	230	8.30	0.481
	230	16.61	0.459
	270	3.32	0.301
	270	8.30	0.220
	270	16.61	0.195
332RB P-30	210	0.166	18.7
	210	0.415	18.1
	230	0.166	7.45
	230	0.415	6.69
	230	0.830	6.01
	230	1.66	5.59
	270	0.830	1.55
	270	1.66	1.45
	270	3.32	1.27
	270	8.30	1.07

a) Brookfield Model LV viscometer
Spindle No. 28
Procedure: 45 minute initial warmup and equilibration;
20-30 minute equilibration after temperature change;
10 minute equilibration after shear rate change.

TABLE 6

Additives Analyses

	Pyrite I	Pyrite II	Magnetite
Weight[a]			
%			
Fe	37.95	30.20	61.70
S	42.38	34.38	0.20
C	3.97	5.81	0.20
H	0.53	0.69	0.17
Moisture[b], wt %	1.15	1.40	0.35
Ash[c], wt %	61.11	75.70	102.09
Mole Ratio S/Fe	1.95	1.99	--
Purity	80.33% FeS_x	64.58% FeS_x	85.29% Fe_3O_4
Average Particle Size, μm			
by Fisher Subsieve Sizer	0.6	--	1.3
by Coulter Counter[d]	3.1	1.7	4.3

a) dry basis
b) as volatiles at 110°C under He atmosphere
c) as received
d) particle size distributions shown on Figures A-1, 2, 3

TABLE 7

Unfiltered Coal Solution Viscosities[a]
Runs DOE 333R, 335R and 335RB

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, cP
333R P-40	210	8.30	196
	210	16.61	168
	230	8.30	136
	230	16.61	115
	270	16.61	71
333R P-45	210	8.30	218
	210	16.61	190
	230	8.30	146
	230	16.61	123
	270	16.61	74
335R P-29	210	8.30	80
	210	16.61	63
	230	16.61	51
	270	16.61	37
335R P-32	210	8.30	96
	210	16.61	72
	230	16.61	52
	270	16.61	39
335RB P-57	210	3.32	242
	210	8.30	170
	210	16.61	139
	230	8.30	141
	230	16.61	105
	270	16.61	74

a) Brookfield Model LV viscometer.
All spindle #34 except 335RB which was spindle 28.
Procedure: 45 min. initial warmup and equilibration;
20-30 min. equilibration after temperature change;
10 min. equilibration after shear rate change.

TABLE 8

Feed Slurry Viscosities[a] Runs DOE 333R and 335RB

Run No. DOE-	Temperature °F	Shear Rate, Sec^{-1}	Viscosity, cP
333R P-36	210	0.415	4631
	210	0.830	3077
	210	1.66	2236
	210	3.32	1669
	210	8.30	1088
	230	0.830	2934
	230	1.66	1943
	230	3.32	1360
	230	8.30	901
	270	1.66	2260
	270	3.32	1320
	270	8.30	709
	270	16.61	496
335RB P-64	210	0.166	14036
	210	0.415	9199
	210	0.830	5345
	210	1.66	3751
	210	3.32	2549
	230	0.166	10864
	230	0.415	6281
	230	0.830	4298
	230	1.66	3196
	230	3.32	2312
	270	0.415	14908
	270	0.830	7756
	270	1.66	6653
	270	0.415	15606

a) Brookfield Model LV viscometer
Spindle 28.
Procedure: 45 minutes initial warmup and equilibration;
20-30 minutes equilibration after temperature change;
10 minutes equilibration after shear rate change.

TABLE 9

Effect of Additives on Yields and Heavy Distillate Quality

	DOE 336R	DOE 337R	DOE 338R	DOE 339R
Conditions				
Additive	Pyrite I	Pyrite II	Magnetite	--
Addition Rate[a]				
as received material	6.2	7.8	6.7	--
as pure FeS_2 or Fe_3O_4	5.0	5.0	5.7	--
Slurry Blend Composition[a]				
Coal	30.0	30.0	30.0	30.0
Naphtha & Middle Distillate	3.9	5.1	3.7	3.8
Heavy Distillate	22.7	29.7	26.7	28.7
SRC	24.9	20.3	23.9	27.0
Ash (from UFCS)	11.4	9.0	9.5	5.5
IOM (from UFCS)	5.3	3.6	4.2	5.0
Additive	1.8	2.3	2.0	--
Total Solids	48.5	44.9	45.7	40.5
Results				
Yields[a]				
C_1-C_4	15.7	14.9	13.5	13.1
Naphtha, C_5-193°C	8.4	9.7	9.1	7.5
Middle Distillate, 193-288°C	13.0	14.8	12.8	11.7
Heavy Distillate, >288°C	20.9	14.4	10.3	11.6
Total Oil	42.3	38.9	32.2	30.8
SRC	26.0	31.2	36.6	37.3
IOM	5.5	5.6	6.5	6.9
Hydrogen Consumption[a]	4.6	4.8	3.7	2.8
Heavy Distillate Analyses				
% C	89.01	89.04	88.68	89.10
% H	8.10	7.61	8.10	8.04
% S	0.32	0.45	0.34	0.53
% N	1.15	1.28	1.25	1.33
% O (by difference)	1.42	1.62	1.63	1.00
Vacuum Bottoms Fusion Point, °C	118	113	119	149

a) Weight %, based on dry coal

TABLE 10

Unfiltered Coal Solution Viscosities[a]
Runs DOE 336R, 337R, 338R and 339R

Run No. DOE-	Temperature, °F	Shear Rate, Sec^{-1}	Viscosity, cP
336R P-38	210	1.66	1253
	210	3.32	956
	210	8.30	734
	210	16.61	636
	230	3.32	630
	230	8.30	446
	230	16.61	374
	270	3.32	412
	270	8.30	257
	270	16.61	194
337R P-65	210	3.32	401
	210	8.30	282
	210	16.61	224
	230	3.32	301
	230	8.30	209
	230	16.61	155
	270	8.30	140
	270	16.61	98
338R P-48	210	1.66	912
	210	3.32	753
	210	8.30	644
	210	16.61	610
	230	3.32	448
	230	8.30	355
	230	16.61	322
	270	3.32	234
	270	8.30	163
	270	16.61	137
339R P-38	210	0.415	6756
	210	0.830	6741
	210	1.66	6606
	230	0.415	2855
	230	0.830	2585
	230	1.66	2474
	230	3.32	2304
	270	0.830	856
	270	1.66	706
	270	3.32	583
	270	8.30	511
	270	16.61	474

a) Brookfield Model LV viscometer
Spindle #28
Procedure: 45 minutes initial warmup and equilibration;
20-30 minutes equilibration after temperature change;
10 minutes equilibration after shear rate change.

TABLE 11

Feed Slurry Viscosity[a]

Run DOE 337R

Temperature °F	Shear Rate, Sec^{-1}	Viscosity, 10^3 cP
210	0.083	78.5
210	0.166	37.8
210	0.415	21.2
230	0.083	44.2
230	0.166	26.2
230	0.415	17.3
230	0.830	10.9
270	0.166	39.3
270	0.415	16.8
270	0.830	7.61
270	1.66	5.51

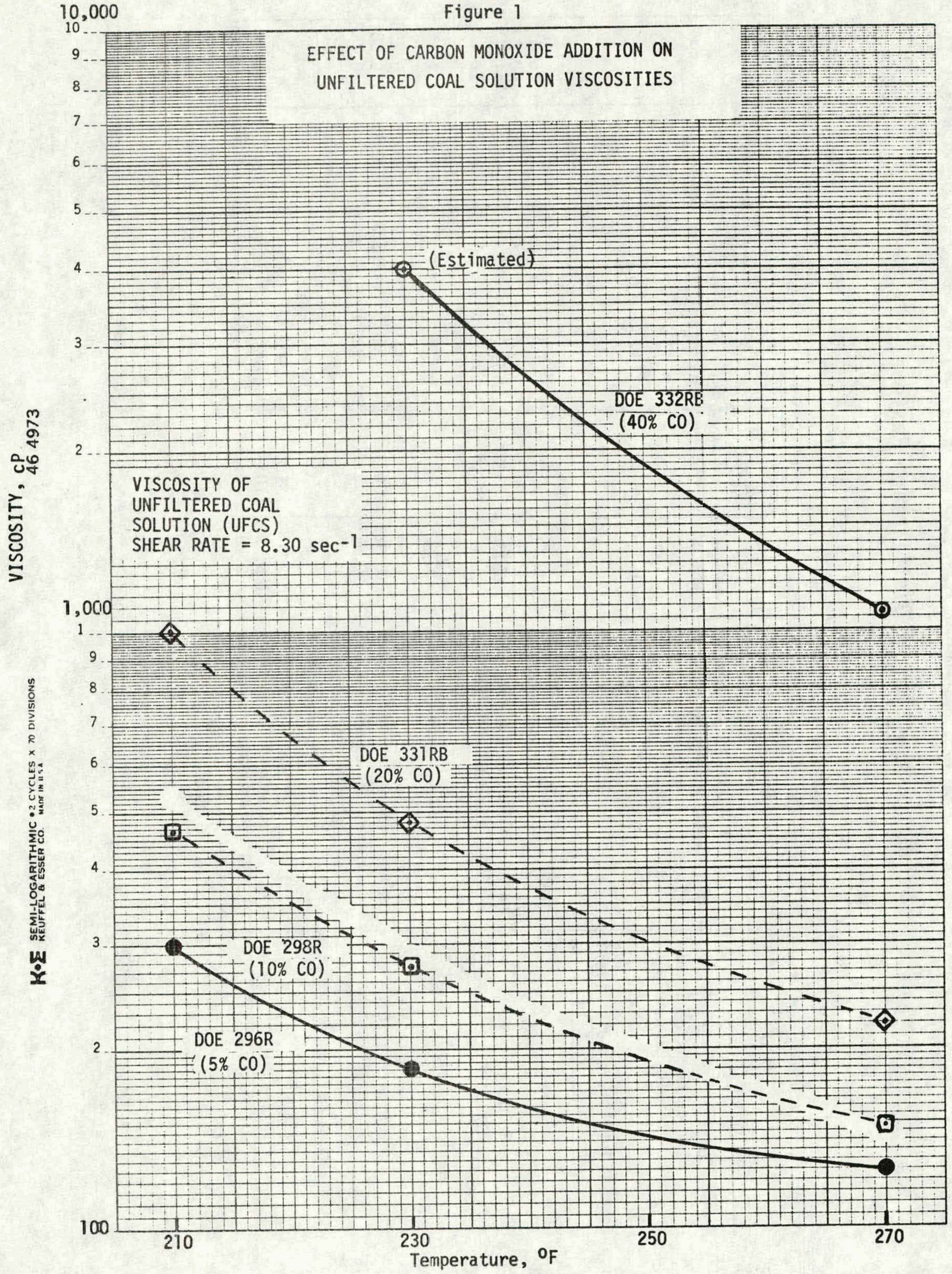
a) Brookfield Model LV viscometer
Spindle #28
Procedure: 45 minutes initial warmup and equilibration;
20-30 minutes equilibration after temperature change;
10 minutes equilibration after shear rate change.

TABLE 12

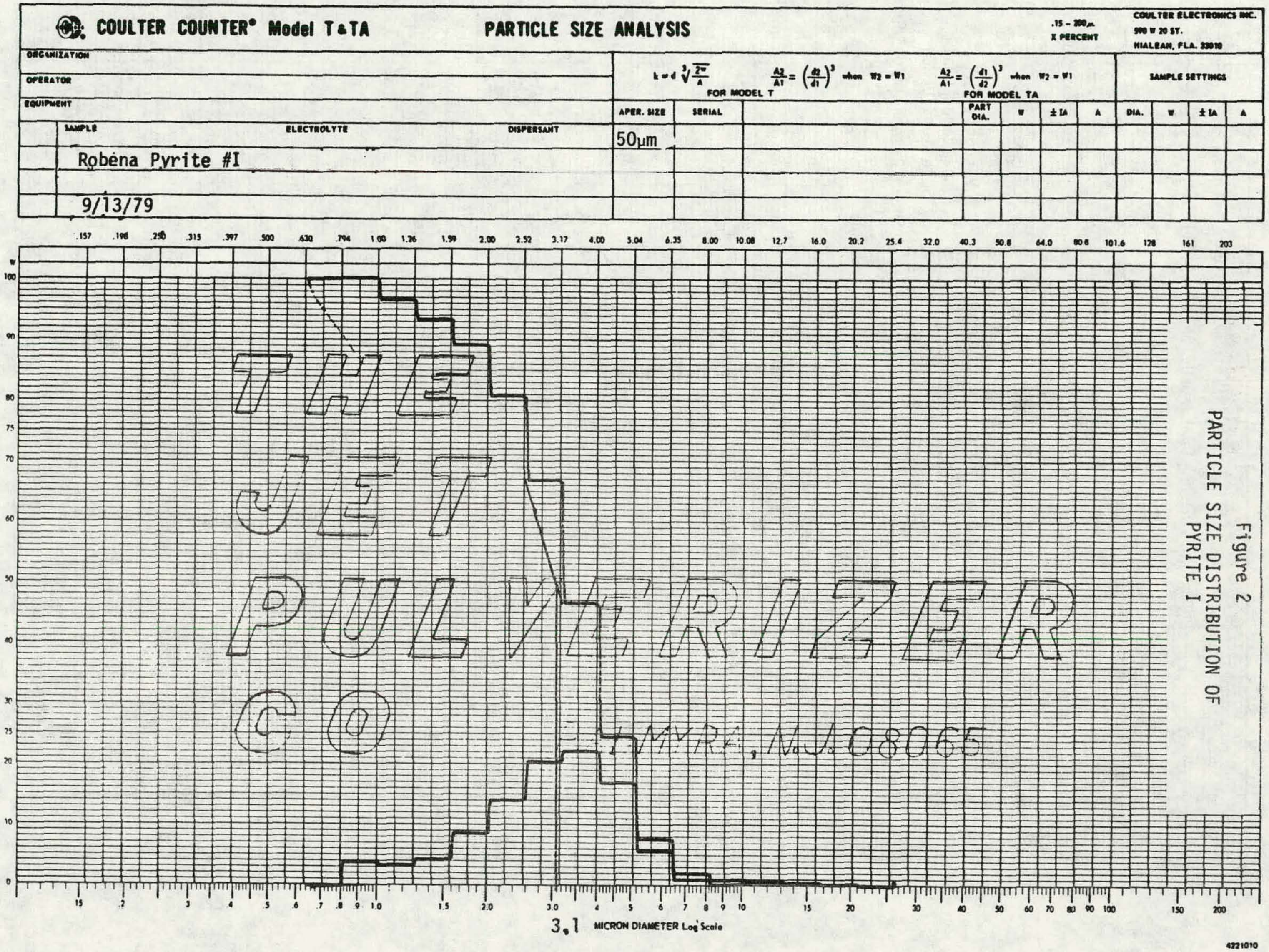
Solvent Extraction of Distillation Residue

	DOE 331RB	DOE 332RB	DOE 333R	DOE 335R	DOE 335RB	DOE 336R	DOE 337R	DOE 338R	DOE 339R
Conditions									
Coal	←Powhatan→		←Powhatan→			←Loveridge→			
Carbon Monoxide level in feed gas, mole %	20	40	--	--	--	--	--	--	--
Additive	--	--	--	Pyrite I	Pyrite I	Pyrite I	Pyrite II	Magnetite	--
Solubility of Distillation Residue, wt % in									
Hexane	16.5	10.6	17.8	30.7	23.5	21.9	19.1	17.4	16.3
Benzene	52.6	44.0	51.8	52.3	48.6	50.6	47.7	46.5	40.7
Toluene	54.8	45.6	52.0	51.3	48.2	51.8	51.3	56.4	51.3
Pyridine	61.5	59.6	58.3	56.6	52.5	58.1	59.4	64.6	70.1
Ratio of Solubilities									
Hexane/Pyridine	0.268	0.178	0.303	0.542	0.448	0.377	0.322	0.269	0.233
Benzene/Pyridine	0.855	0.739	0.886	0.925	0.927	0.870	0.803	0.720	0.581
Toluene/Pyridine	0.891	0.765	0.888	0.907	0.919	0.891	0.864	0.873	0.732
Vacuum Residue Properties									
% Ash	27.1	24.5	27.8	32.6	35.8	28.8	28.8	25.6	15.5
Fusion Pt, °C	117	165	150	115	110	118	113	124	149
H/C ratio	0.708	0.681	0.698	0.780	0.754	0.708	0.681	0.715	0.681

Figure 1



EFFECT OF CARBON MONOXIDE ADDITION ON UNFILTERED COAL SOLUTION VISCOSITIES



COULTER COUNTER® Model T&TA PARTICLE SIZE ANALYSIS

.15 – 200µ
X PERCENT

COULTER ELECTRONICS INC.
590 W 20 ST.
HIALEAH, FLA. 33010

ORGANIZATION
OPERATOR
EQUIPMENT

SAMPLE: Robena Pyrite #I
9/13/79

ELECTROLYTE
DISPERSANT

$k = d\sqrt[3]{\frac{2w}{A}}$ $\frac{A2}{A1} = \left(\frac{d2}{d1}\right)^3$ when W2 = W1 FOR MODEL T

$\frac{A2}{A1} = \left(\frac{d1}{d2}\right)^3$ when W2 = W1 FOR MODEL TA

SAMPLE SETTINGS

APER. SIZE: 50µm

SERIAL

PART DIA. | W | ± IA | A

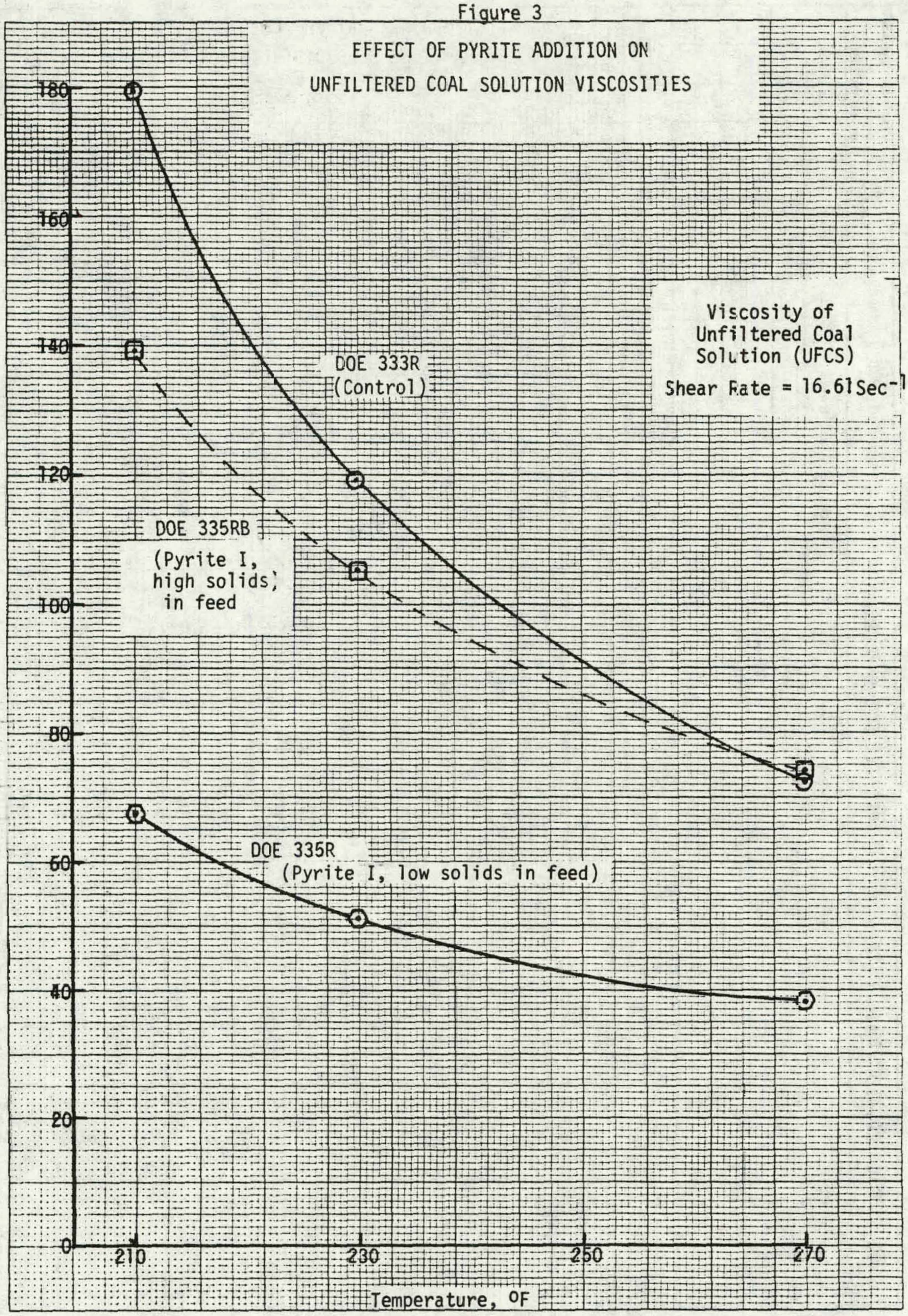
DIA. | W | ± IA | A

THE JET PULVERIZER CO
PALMYRA, N.J. 08065

3.1

Figure 2
PARTICLE SIZE DISTRIBUTION OF
PYRITE I

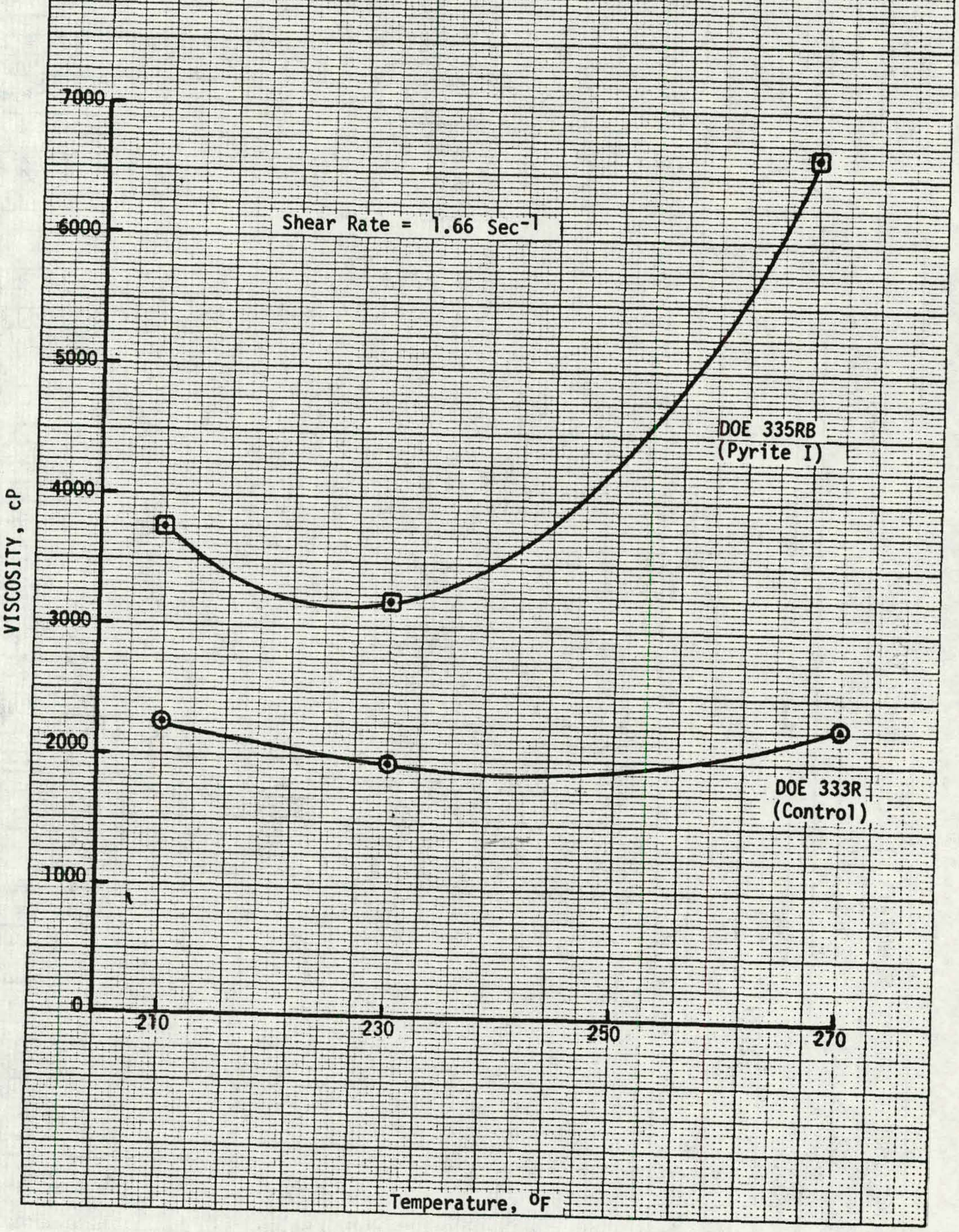
Figure 3

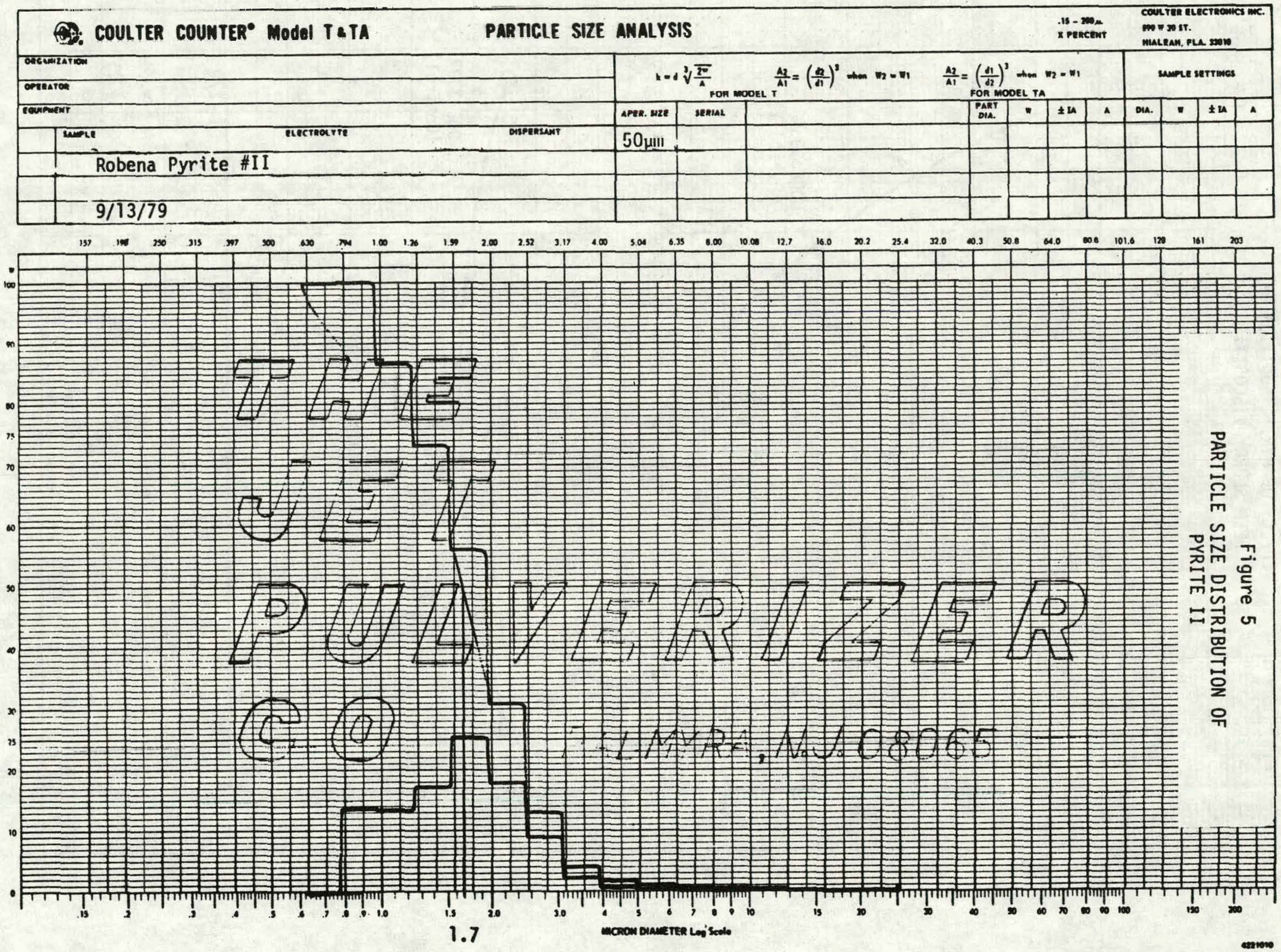


EFFECT OF PYRITE ADDITION ON UNFILTERED COAL SOLUTION VISCOSITIES

Figure 4

EFFECT OF PYRITE ADDITION ON
FEED SLURRY VISCOSITIES





$k = d\sqrt[3]{\frac{2w}{A}}$ $\frac{A_2}{A_1} = \left(\frac{d_2}{d_1}\right)^3$ when $W_2 = W_1$ FOR MODEL T

$\frac{A_2}{A_1} = \left(\frac{d_1}{d_2}\right)^3$ when $W_2 = W_1$ FOR MODEL TA

50µm

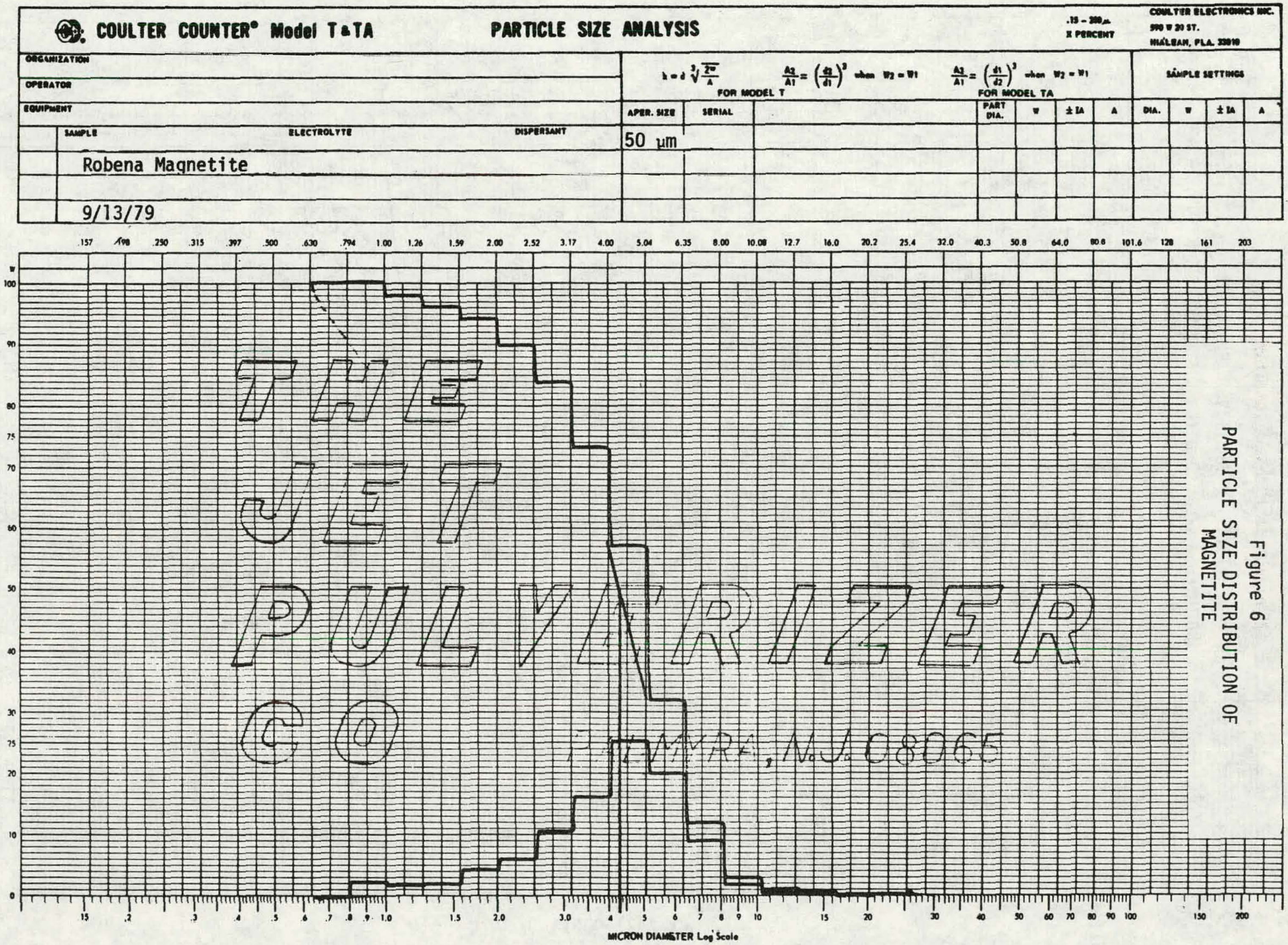
Robena Pyrite #II

9/13/79

1.7

THE JET PULVERIZER CO. PALMYRA, N.J. 08065

Figure 5
PARTICLE SIZE DISTRIBUTION OF PYRITE II



COULTER COUNTER® Model T&TA

PARTICLE SIZE ANALYSIS

COULTER ELECTRONICS INC.
590 W 20 ST.
HIALEAH, FLA. 33010

ORGANIZATION	
OPERATOR	
EQUIPMENT	
SAMPLE	Robena Magnetite
	9/13/79
APER. SIZE	50 µm

4.3

Figure 6
PARTICLE SIZE DISTRIBUTION OF MAGNETITE

Figure 7

EFFECT OF ADDITIVES ON
UNFILTERED COAL SOLUTION VISCOSITIES

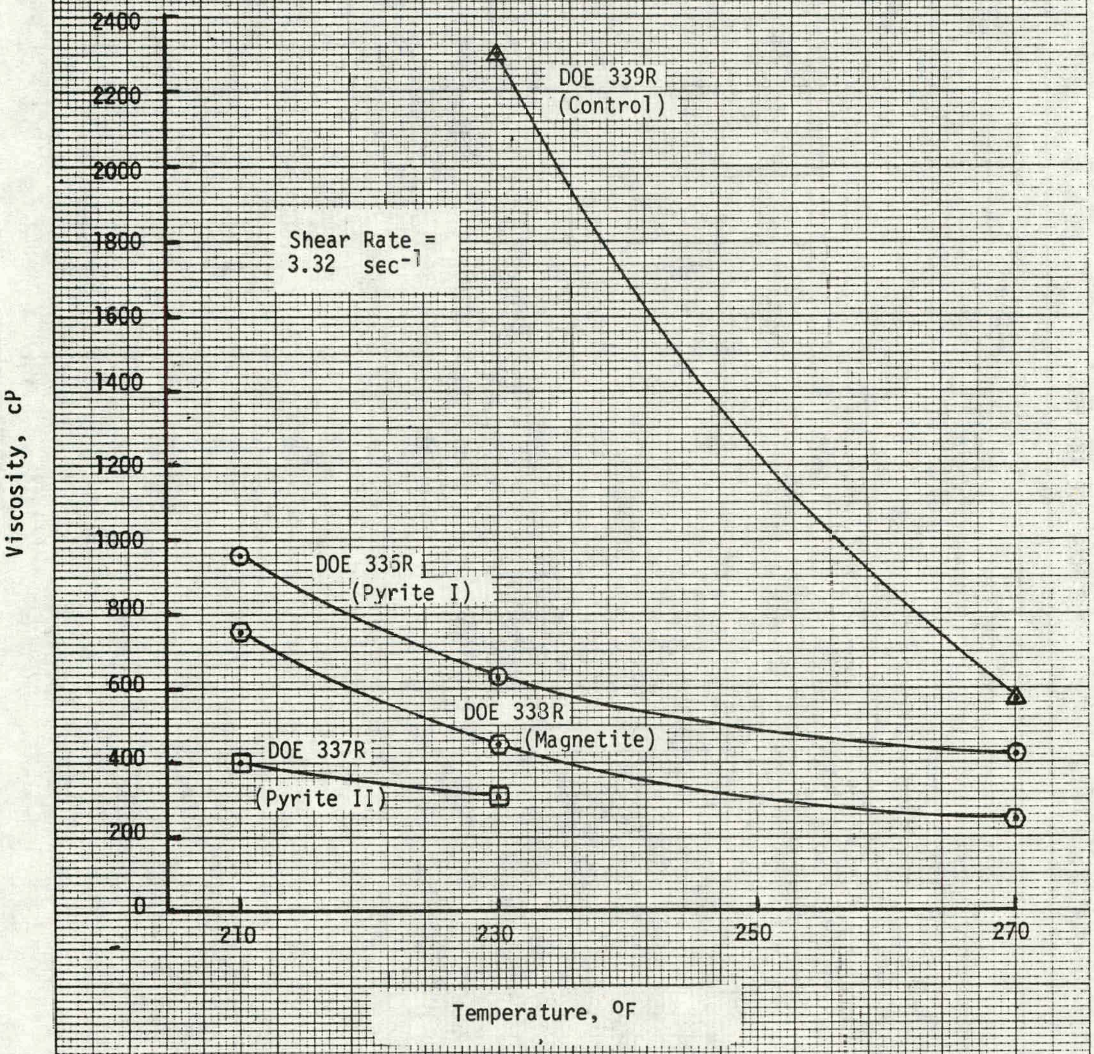


Figure 8

EFFECT OF SHEAR RATE ON FEED SLURRY VISCOSITY

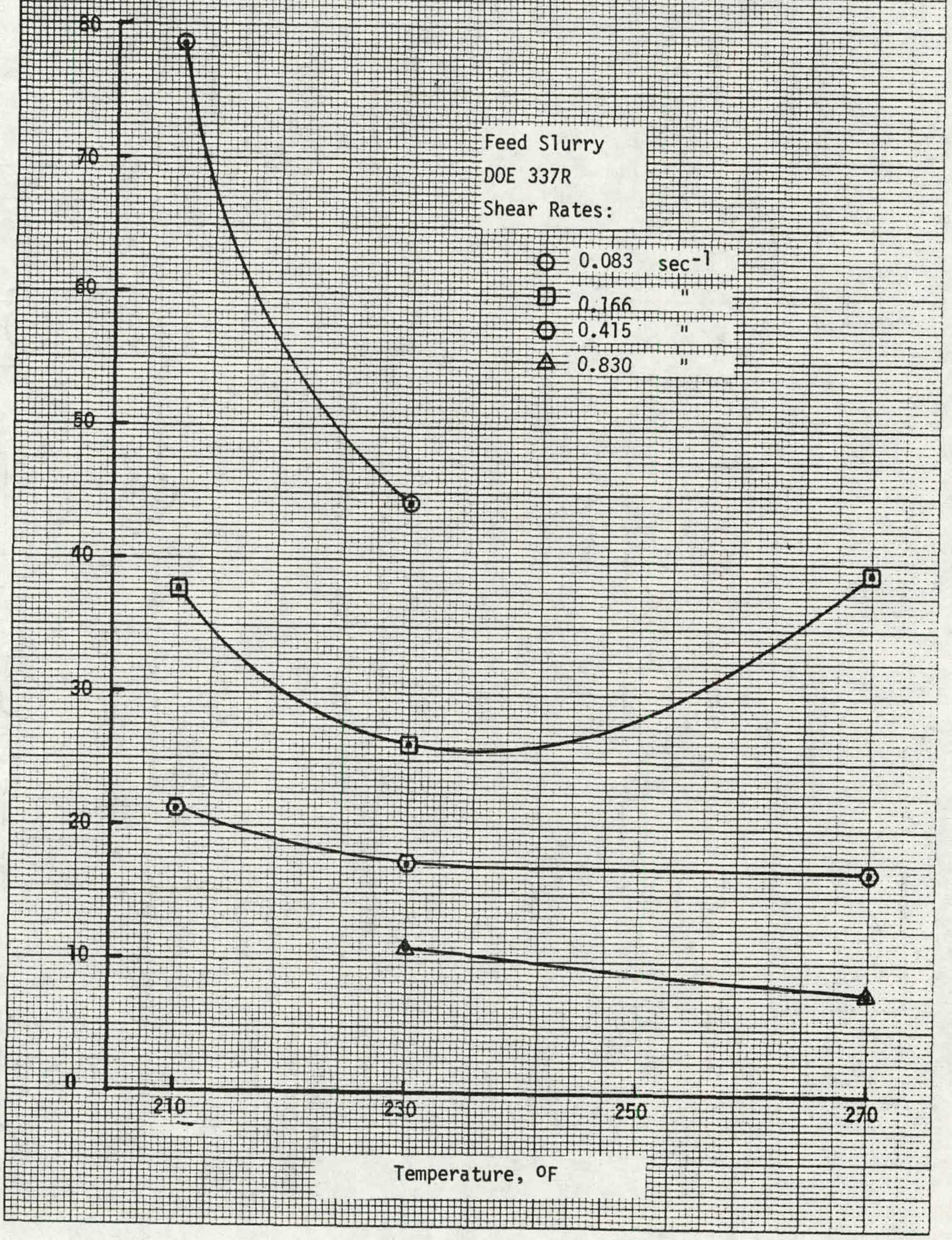


Figure 9

SLURRY MIXING, PUMPING AND METERING SYSTEM

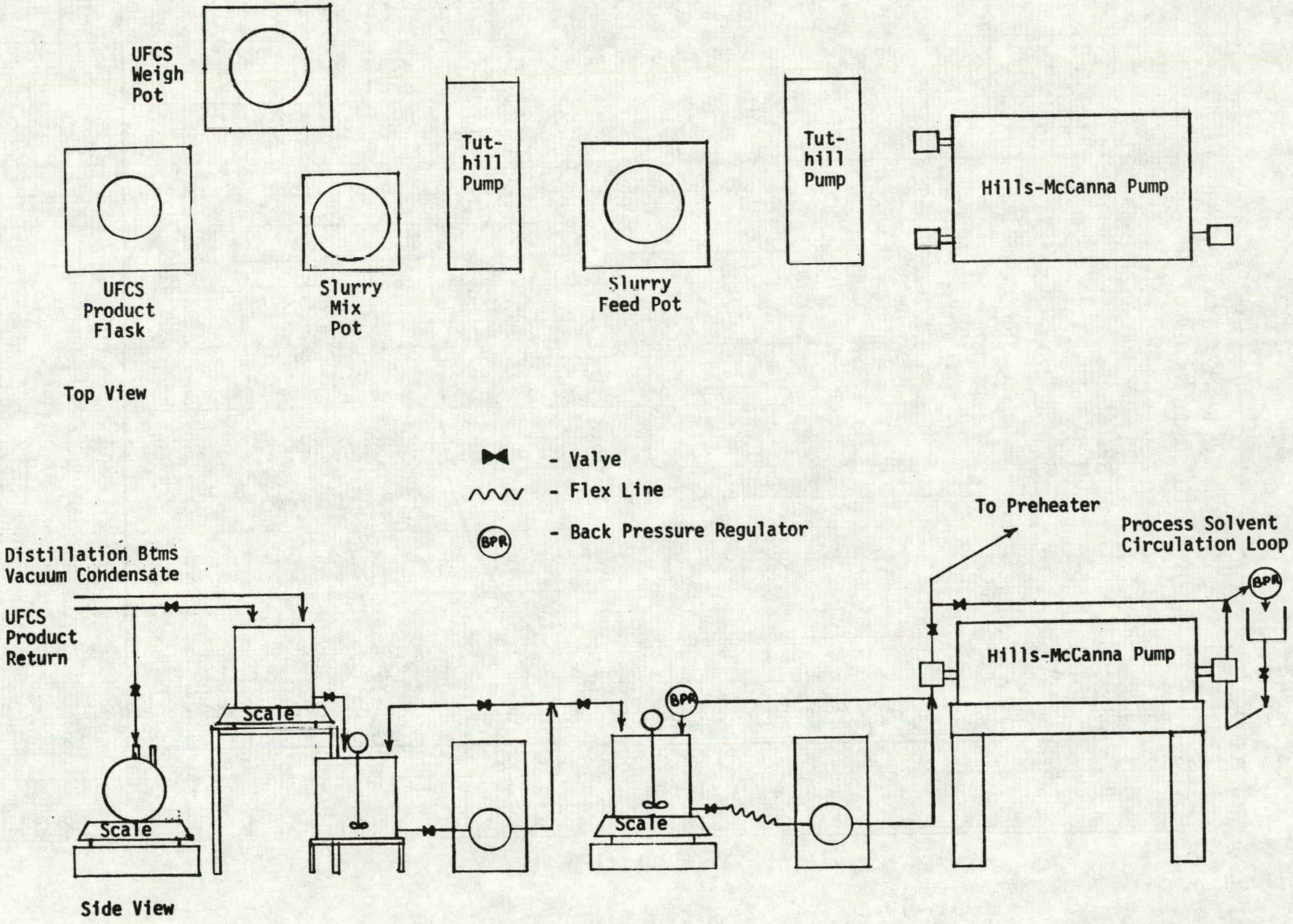
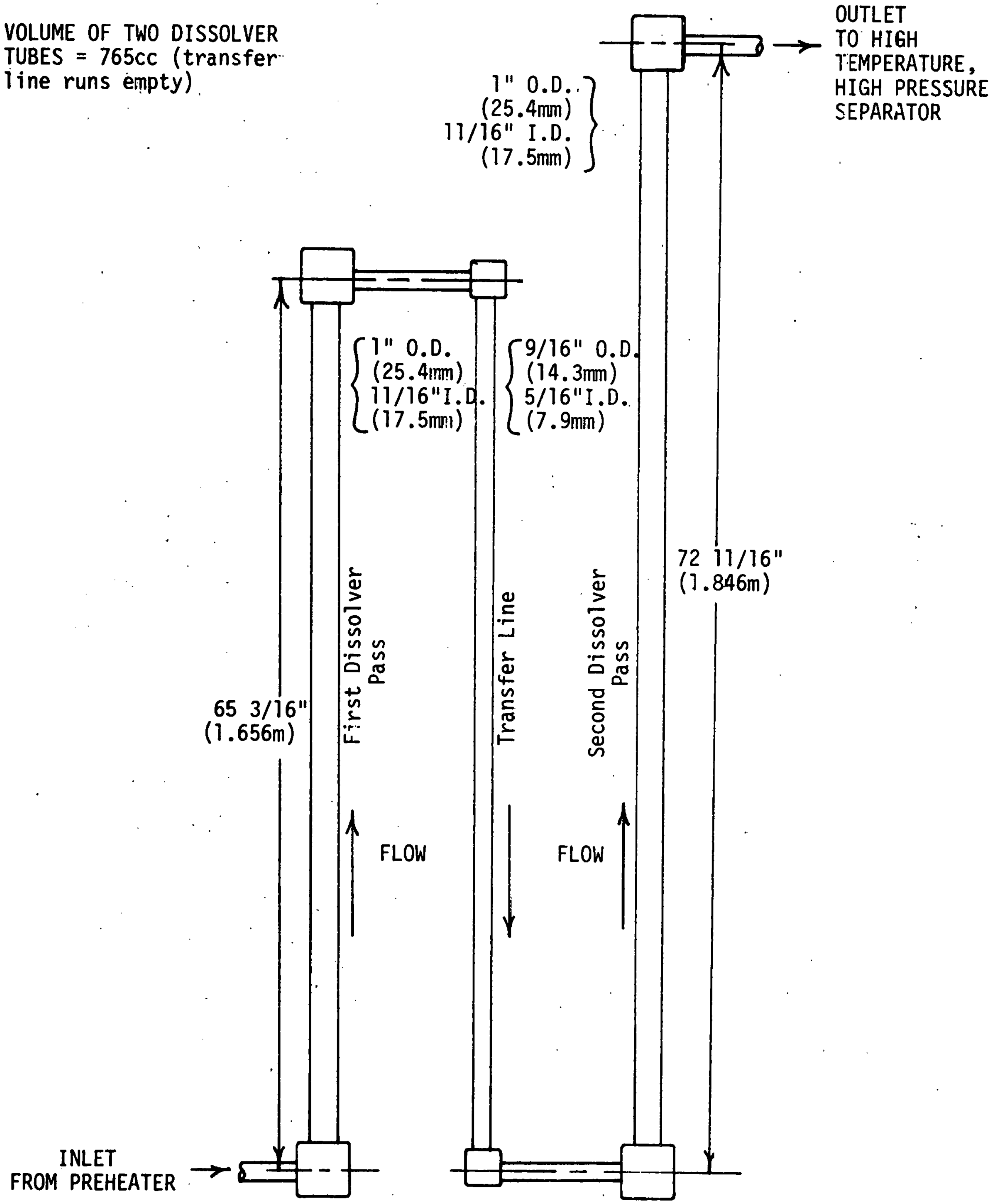


Figure 10

Modified GU5 Dissolver



APPENDIX A

EXTRACTION ANALYSES OF DISTILLATION RESIDUES FROM SRC PROCESSES

Introduction

The method which follows is intended for general inspection of vacuum distillation residues from either SRC I or SRC II process studies. The solubility is determined by extraction of weighed samples using hexane, benzene, toluene, and pyridine.

Solvents

In the work to be presented, a number of substitutions in solvent have been considered. It is usual to separate oils by use of pentane. This material is too low boiling for routine use in our laboratory, however, and normal hexane has been used instead. The toxicity of benzene renders it a problem to use; therefore, substitution of toluene has been proposed. Correlation studies have been made with benzene and toluene in the work to be discussed. Finally, pyridine has been used as the correlating solvent which is assumed to dissolve coal products normally soluble in hot solvent derived in either the SRC I or the SRC II process. (Insoluble organic matter, or IOM, in our operations is defined as material not soluble in hot pyridine and this has been found to correlate well with the material actually insoluble in hot coal derived process solvents.)

Samples

Samples are to be selected from the lined out portion of an experiment and should be as near to average for the period in question as is practical. In this regard, the fusion point, the ash in the vacuum bottoms, and any elemental analysis results available should be considered in selection of a sample. In addition, the vapor temperatures and pot temperatures for the vacuum distillation should have been normal (or average for the run in question) for the sample chosen for analysis. In the event that unusual results are obtained on the first sample chosen, a second sample should be extracted to see if the unusual pattern holds for other samples from the experiment.

All samples should be ground and sifted to pass a 100 mesh screen before use in the solubility measurement procedure.

Equipment

Extractions with benzene, toluene, or pyridine are done in a medium size Soxhlet extractor, Corning #3740 (Scientific Products Cat. No. E6260-2), with a 45/50 standard taper joint at the top and a 24/40 standard taper at the bottom. A Corning #3840 condenser is used to return the refluxing solvent to the extractor. A one liter round bottom flask is used as the solvent boiler and is situated in an electrical heating mantle.

The preferred thimble is the Norton AL 889 Alundum thimble (34 X 100 mm) of medium porosity. The round bottom style (Scientific Products Cat. No. E6465-5) has been used for this work. A Whatman paper thimble of the same approximate dimensions is useable but is difficult to bring to constant weight in humid weather.

It has been observed that the temperature of the refluxing solvent as it accumulates in the extraction thimble may vary with the reflux rate and the design of the extractor. Therefore, it appears necessary to standardize the type of extractor and to reproduce the distillation rate of solvent from one setup to the next.

Hexane extractions have been done in a modified extractor designed to suspend the thimble chamber and the siphon tube in the solvent vapors in order to maintain the temperature of the extraction constant at the boiling point of the solvent. The same thimble type is used for all extractions.

Procedure

1. When an Alundum thimble is used repeatedly, it is necessary to clean it before use. Remove any extraction residue which can be brushed or scraped out by use of a spatula. Put the thimble in a cool muffle furnace and heat to 750-800°C by allowing the furnace to heat up at its natural rate. When the thimble is burned clean, turn off the power and allow the furnace to cool well below red heat before removing the thimble. Because of the time required, it is best to clean thimbles in batches before use. Since thimbles do not stand abrupt thermal shock well, this method of cleaning is preferred to placing thimbles in a preheated furnace.

2. When thimbles are used with filtered samples, the ash residue is quite small and the ignition will produce a perfectly clean white thimble for reuse. When recycle (SRC II) materials are run, the residue in the thimble will contain ash and a residue rich in iron will be observed. This will stain the thimble red. When the residue is blown out with compressed air, the thimble will be discolored but free of any loose material, and the residue remaining will not impair the flow of solvent through the thimble. In any case, it appears practical to reuse the thimble many times without any additional cleaning other than ignition of the residue.

3. Grind a 5 gram portion of the vacuum distillation residue and sift it to pass a 100 mesh sieve for each extraction. The extraction is done on a separate sample for each solvent.

4. Write the sample number and extraction solvent to be used on the Alundum thimble using a lead pencil. Weigh the thimble and record its empty weight.

5. Use a weighing paper to introduce a 5 gram sample into the weighed thimble. The powdered sample should be well down in the thimble before it slips off the weighing paper in order to minimize dusting of the sample into the air. Reweigh the thimble plus the sample. The sample weight is then obtained by difference.

6. Carefully slide the thimble into the extractor and put the extractor in place on a clamp on a ringstand or other suitable rack which can hold the heating mantle, flask, and extractor in place. Add

500 ml of the solvent to be used and a few boiling chips to the one liter flask. It is preferable to set this up in a hood; for benzene it is mandatory.

7. Assemble the flask, extractor and condenser on the rack using no stopcock grease on the joints. This prevents contamination of the extract solution in case it is to be used for further studies.

8. Repeat the procedure, preparing an extraction apparatus with hexane, benzene, toluene and pyridine as extraction solvents.

9. Attach the heating mantle to a variac power supply and heat the solvent to boiling. Adjust the reflux rate to produce a steady return of solvent from the condenser to the extractor and to cause the extractor to fill and empty in a few minutes time. Allow the extractor to run for 18 to 20 hours (overnight) then turn off the heat and allow the extractor to cool.

10. Use forceps to remove the extraction thimble. Place this in a clean beaker in the hood to allow the residual solvent to drain out of the thimble. This can be facilitated by placing a Kimwipe or paper towel in the beaker to draw out solvent by capillary action. By definition, any material which migrates from the inside of the thimble to the outside is considered to have been extracted. On this basis, the outer surface of the thimble is to be wiped clean of precipitated matter which often develops in the latter stages of the extraction.

11. When the contents of the thimble are free of liquid, place the thimble in a clean beaker and put it in a drying oven at 100 to 105°C. Allow the thimble to dry until it is free of solvent odor (normally four to six hours will be required). Cool and weigh.

12. Calculate the percentage of the sample which has been extracted by the solvent in question. For SRC II type samples, an appreciable amount of mineral matter and insoluble organic matter will remain in the thimble used for pyridine extraction. For SRC I type samples, the pyridine extraction will normally dissolve substantially all of the filtered material. SRC II samples may be compared to other kinds of samples by stating the relative amount of soluble material in a fraction compared to the pyridine solubility of the sample in question.

    When any solvent which dissolves an appreciable fraction of the sample is allowed to cool, part of the dissolved material normally precipitates. This is an indication that results will be temperature sensitive (and hence may vary with barometric pressure and the altitude of the laboratory, for example). The precipitated material is quite difficult to recover quantitatively; therefore, the difference between the solubility hot and at room temperature would be difficult to use as the basis for an additional separation step.

    It is possible to recover samples of the soluble material for subsequent investigation by carefully evaporating the solvent away.

Complete transfer from flasks and extraction equipment is difficult and the quantitative removal of solvent is, at least, time consuming. At this time, the procedure is not generally used because of time required.

Precision

Once the method had been run enough times to develop a standardized routine and to determine the main causes of difference, a set of trials was run with toluene as the extraction solvent to determine the precision obtained by a single analyst with matched extraction equipment. Data are presented below for a typical SRC I process vacuum distillation residue sample.

Precision Obtained by a Single Analyst

Trial No.	Percent Extracted
1	60.87
2	63.74
3	60.93
4	63.20
5	62.09
6	62.69
7	63.41
8	62.57
9	61.28
Mean	62.31
Standard Deviation =	1.08

In this study, all thimbles had been previously used with distillation residues containing ash. In addition, the study used a set of three thimbles twice and a separate set of three thimbles. Presence of residual ash causes variable weights in the used thimbles but the presence of the finely divided ash seems to cause no problems in the operation of the extractor. Good precision was obtained as indicated by a standard deviation just over one percent absolute or one and three quarters percent relative.

In a second study, one analyst ran a series of extractions using hexane, toluene, and pyridine. A second analyst ran a similar set of extractions using benzene, toluene and pyridine. In this manner, a long set of duplicate trials using toluene on different samples, including both SRC I and SRC II runs, was obtained. In addition, a second set of comparisons with pyridine on SRC II materials is available. Since pyridine dissolves essentially all of the SRC I (filtered) product, the comparisons with pyridine using this type of sample are of little interest. The following pairs of data are available from SRC I type samples.

Deviation in Results Between Two Analysts

Sample	Percent Soluble in Toluene		
	Analyst A	Analyst B	Deviation
A	60.33	58.48	1.85
B	56.09	56.28	0.19
C	58.94	58.52	0.42
D	59.26	57.82	1.44
E	52.98	52.80	0.18
F	49.62	64.02	14.40
G	58.58	68.70	10.12
H	63.61	60.62	2.99

Precision studies with hexane or benzene have not been done, but it is expected that results with toluene or pyridine will be typical for other solvents as well.

For the most part, duplication was good in the samples analyzed once the procedure had been reasonably well established. In two cases, samples F and G, the difference between analysts was unaccountably large. In both of these cases, available sample was insufficient to allow enough repeat work to settle the question of which value should be preferred. For experiment F, a separate sample was run with benzene and the solubility of 62.64% used to justify discarding the 49.62% value. In the case of sample G, the value from benzene extraction was 65.45% which seems to justify discarding the lower toluene solubility value.

The sample used in computing the precision obtained by a single analyst above was from the same run as sample G. The two samples were six product periods apart. The difference observed in toluene solubility (68.70 versus 62.31 percent) is probably significant and illustrates the variation that can occur between samples during a given lined-out period. In particular, the vacuum distillation is difficult to reproduce due to possible reversion of product to higher molecular weight material. The results above suggest that a single sample can be extracted with a standard deviation of about 1.1%, but inclusion of separate samples will spread this deviation appreciably. Deviations between separate samples are smaller for SRC II operation (discussed below).

The comparison was continued for the extraction of SRC II products. In this case, comparisons are available both with toluene and pyridine as extraction solvent. These results are given on the table below:

DUPLICATION OF RESULTS USING SRC II VACUUM DISTILLATION RESIDUE SAMPLES

Sample Number	Toluene Solubility Analyst A	 Analyst B	Deviation	Pyridine Solubility Analyst A	 Analyst B	Deviation
DOE 330RB-51	49.56	50.32	0.76	61.43	62.16	0.73
DOE 331RB-43	55.17	54.40	0.77	61.18	61.77	0.59
DOE 332RB-36	45.11	46.03	0.91	59.82	59.36	0.46
DOE 333R-30	53.28	53.08	0.20	55.94	59.11	3.17
DOE 333R-40		49.56	(3.62)		60.55	(3.03)
DOE 335R-25	51.91		(0.59)	55.11		(1.49)
DOE 335R-32	49.92	52.72	2.80	56.73	56.47	0.26
DOE 335RB-60	47.16	49.25	2.09	52.39	52.55	0.16
DOE 336R-40	51.39	52.13	0.74	58.03	58.14	0.11
DOE 337R-62	49.76	52.79	3.03	59.38	59.32	0.06
DOE 338R-45	57.33			65.01		
DOE 338R-51		55.37	(1.96)		64.15	(0.86)
DOE 339R-25	54.76		(3.50)	71.03		(0.98)
DOE 339R-31		53.50	(2.24)		70.24	(0.19)
DOE 339R-38	50.99	51.54	0.55	69.69	70.41	0.72

Note: Values in brackets ( ) compare the average of duplicate results on one sample with another sample from the same run.

In this table enough information is available to allow comparison of the precision between analysts for the extraction of the same sample and to gain some information about the increase in spread when different samples are included in the comparison. For toluene extraction, the standard deviation is 1.74 for comparison of results on the same sample and increases to 2.94 when data for different samples is considered (in each case these values are determined by two analysts using separate equipment). For the pyridine extraction the standard deviation is 1.21 when the data for the same sample is considered. This increases to 1.81 when the values for different samples is considered. (Various combinations of data from different analysts are considered in the pyridine results.) Thus, the pattern assumed by the data appears normal. That is, a single operator can achieve better precision than several, and real differences are present from sample to sample within the same run.

APPENDIX B

ANALYSIS OF TUBING FAILURE

In the section of failed pipe, approximately two feet long and threaded on both ends, a longitudinal crack, approximately 1 cm long, was located partly in the threads and partly in the main section of the pipe at one end (Figures B-1 and B-2). The pipe, which carried the vapor effluent from the intermediate temperature separator, operated in a vertical orientation with the failed end next to the separator. The pipe was made of 316 stainless steel.

In the main section of the pipe, the crack appeared to have propagated from the O.D. to the I.D. Several shorter cracks were found starting at the O.D. very near the main crack. However, some pits at the I.D. also had cracks initiating from them. In the threaded section of pipe, the crack initiated at the I.D. surface (Figure B-3). About half of the I.D. surface in the threaded section was covered with a black adherent scale and the main crack, and a number of shorter cracks, appeared to have started under the scale. Several very short cracks started at the O.D. very near the main crack. In general, the cracks were branched and transgranular; typical of chloride stress corrosion cracks (Figures B-3 and B-4). The pipe was heavily cold worked, particularly at the threads. Chlorides were found in the crack, and the combination of residual stresses from cold work and chlorides (probably from the process stream) led to the failure.

It is not clear whether cracking started at the I.D. or the O.D. If cracking started at the I.D., the main crack could have leaked effluent to the O.D. and caused cracking there. On the other hand, if there were chlorides in the heavily cold worked threads (for instance, if the fitting wasn't properly cleaned) it could easily have started cracks from the O.D.

The use of 316 stainless steel in the solution annealed condition should minimize future chloride stress corrosion cracking failures. If the problem persists, Incoloy 800H can be used to prevent chloride stress corrosion cracking.

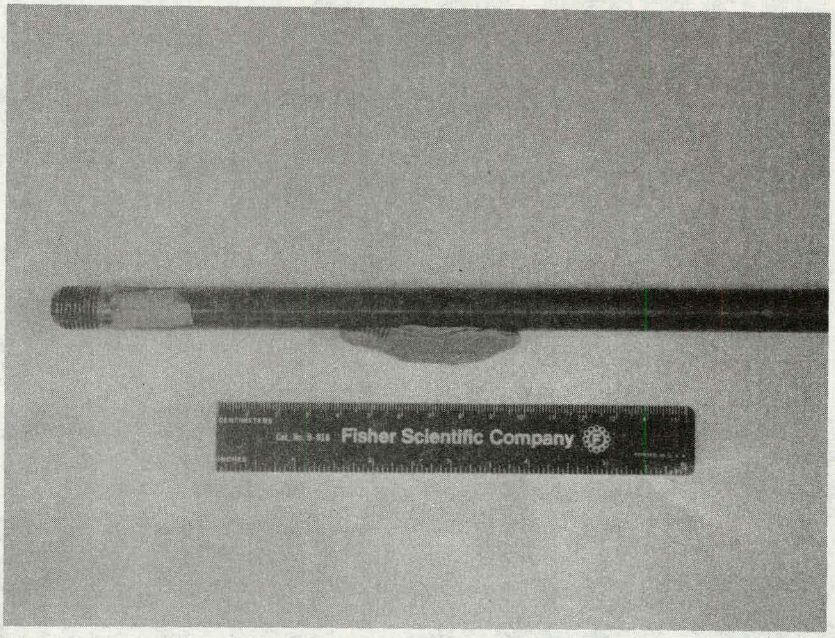


Figure B-1

Piece of failed pipe from the vapor outlet of the intermediate temperature separator.

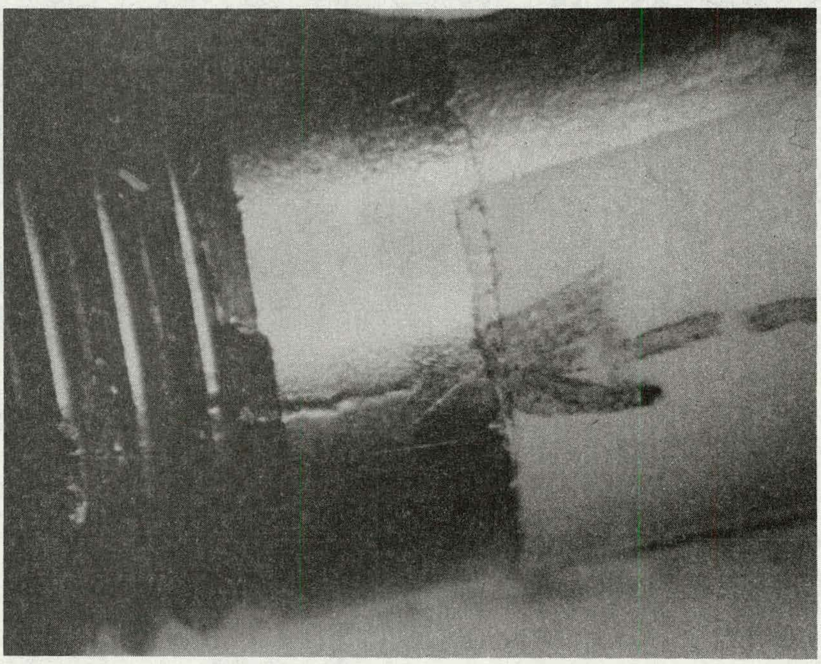
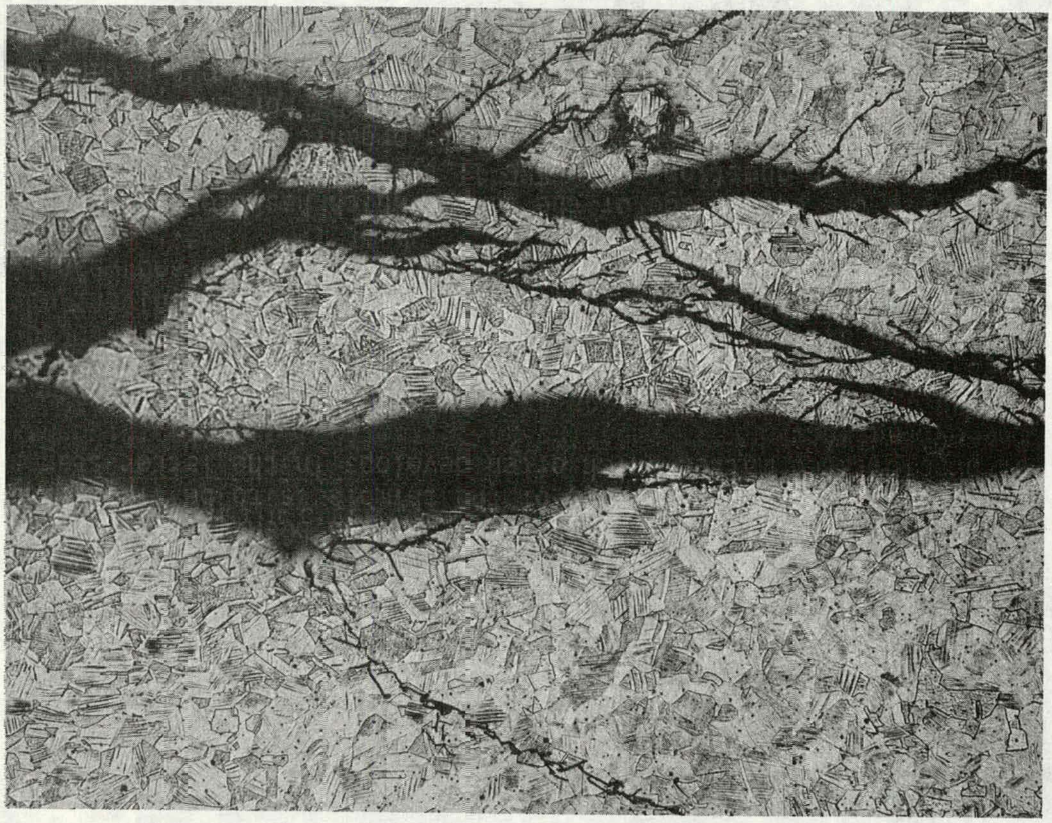


Figure B-2

Close-up of the crack in the pipe. 6X

ID



OD

150X

Figure B-3

Section of the main crack showing branched, transgranular morphology.

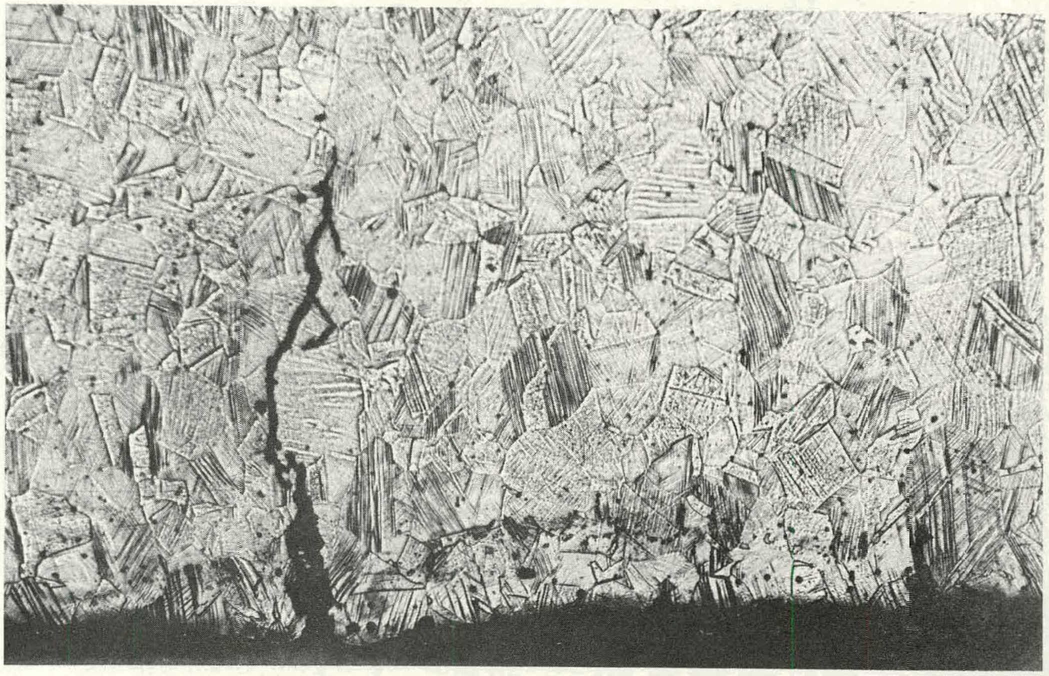


Figure B-4

Cracks starting at ID of pipe. Note parallel deformation lines in grains indicating cold work. 300X

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