285
11-04-77

lh. 1567

ORNL/TM-5843

MASTER

**Supporting Research and Development
on Separations Technology:
Final Report**

B. R. Rodgers
S. Katz
P. R. Westmoreland

OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$6.00; Microfiche \$3.00

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Energy Research and Development Administration/United States Nuclear Regulatory Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Contract No. W-7405-eng-26

COAL TECHNOLOGY PROGRAM

SUPPORTING RESEARCH AND DEVELOPMENT
ON SEPARATIONS TECHNOLOGY:
FINAL REPORT

B. R. Rodgers^a

S. Katz^a

P. R. Westmoreland^a

^aChemical Technology Division

Energy Research and Development Administration
Work Order No. 3 to Agreement No. 14-32-0001-1740

Date Published: October 1977

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

	<u>Page</u>
Abstract	1
1. Summary	1
2. Laboratory-Scale Experiments	3
2.1 Solvent Agglomeration--Fractionation	3
2.1.1 Introduction	3
2.1.2 Description of methods	3
2.1.3 Vacuum filtrations	4
2.1.4 Pressure precoat filtrations	8
2.2 Sedimentation	19
2.2.1 Introduction	19
2.2.2 Theoretical settling rates	20
2.2.3 Settling-filtration combined	20
2.2.4 Settling after thermal agglomeration	23
2.2.5 Settling after additive agglomeration	23
2.3 Precoat Filtration	31
2.3.1 Coal as a precoat	31
2.3.2 Coal as a body feed	31
2.4 Deep-Bed Filtration	33
3. Bench-Scale Experiments	33
3.1 Additive Agglomeration	33
3.2 Solvent Agglomeration	40
3.3 Filtration -- Sintered Metal Filter	43
3.4 Filtration -- Carbonaceous Precoats	47
4. Characterization of SRC Process Streams	55
4.1 Introduction	55
4.2 Electron Microscope Particle Size Distributions	55
4.3 Petrography	60
4.4 Neutron Activation and Spectrochemical Analyses	62
4.5 Viscosity-Temperature Studies	64
4.6 Gel Permeation Chromatography	64
4.7 Aging of SRC-FO and SRC-UFO	65

	<u>Page</u>
4.8 Distillation of SRC Unfiltered and Filtered Oils	72
4.9 Densities of SRC Material	72
4.10 A Comparison of Three SRC Coal Feeds	72
4.11 Characterization Results	77
5. Acknowledgments	78
6. References	78
Appendix A	79

SUPPORTING RESEARCH AND DEVELOPMENT ON SEPARATIONS TECHNOLOGY:
FINAL REPORT

B. R. Rodgers and S. Katz

ABSTRACT

This project for supporting research and development in separations technology for coal conversion systems was sponsored by the Energy Research and Development Administration, Division of Fossil Energy Research. During the first year, the work focused on alternative methods for accomplishing the solid-liquid separations that are required for liquefaction processes. The first phase, completed January 18, 1975, consisted of the review and evaluation of available data. Phase II, reviewed June 30, 1975, consisted of characterization tests of selected process streams and scouting tests for some alternate separations methods. A third phase, which included bench-scale development of agglomeration--settling separations techniques, verification of methods to significantly improve current process filtration rates, and selected characterization and aging tests, ends with this report. Funding in this area was discontinued September 30, 1976.

1. SUMMARY

The first phase of this 2-year project consisted of a review of available literature and an evaluation of the current state of the art in solid-liquid separations for coal liquefaction processes. These results were summarized in a brief topical report which also designated those techniques that would be most likely to meet the needs of commercial coal liquefaction processes for effective, economical separations.

The second phase of the project consisted of a series of laboratory scouting experiments¹ that characterized the separation parameters of solids-containing streams produced by several coal conversion processes under development by ERDA. The purpose of these tests was to determine the separation techniques with the most potential and to supplement

existing data that would help define the range of potentially viable separations processes.

The third phase, begun in October 1975, has consisted of further development of a solvent agglomeration--separations method at bench scale. Under realistic operating conditions, the bench-scale unit, which was designed and fabricated on the basis of the previous studies, has been used to demonstrate the technical viability, limits of operability, preferred operation conditions, and preliminary economics of two proposed separations processes: filtration and settling.

This project has made the following significant contributions to coal conversion technology:

1. Laboratory precoat filtrations have shown that the use of crushed coal and/or char as a precoat and body feed can improve filtration rates and can significantly increase the fuel value of collected solids. Preliminary economic evaluation shows a savings over conventional precoats of about \$16 million/year for a 30,000-ton/day plant.
2. Thermal agglomeration has been shown to increase settling rates at high temperatures. Solvent agglomeration, coupled with thermal agglomeration and followed by settling at elevated temperatures and pressures, has been shown to be a viable alternative to filtration. A preliminary economic evaluation shows that this process has the potential to reduce current filtration costs by as much as 75%. A bench-scale evaluation of the process should be made.
3. Certain additives produce a clarified upper fraction after a settling time of 1 hr or less. In some cases, the clarified fraction will meet EPA guidelines for direct combustion as a boiler fuel. Preliminary economics have not yet been determined, but it is possible that additive agglomeration at low concentrations (< 1000 ppm) will be the least expensive of the proposed separations techniques.

4. Studies of both Solvent Refined Coal (SRC) and Char Oil Energy Development (COED) process stream characteristics have added significantly to the coal liquefaction data base. The electron microscope was used to characterize process solids by particle size distributions. The accumulation of physical and chemical property data, petrographic analyses, neutron activation analyses, and photon emission spectroscopy data also contributed to the data base. Aging tests have determined the effects of sampling and storing SRC-unfiltered oil under various conditions.

2. LABORATORY-SCALE EXPERIMENTS

2.1 Solvent Agglomeration--Fractionation

2.1.1 Introduction

Solvent agglomeration--fractionation (SAF) followed by vacuum filtration has been shown to be a viable scheme^{1,2} for separating char and ash particles from coal liquids. Further studies have shown that SAF followed by settling at elevated temperatures and pressures also shows promise as a solids separation scheme for Solvent Refined Coal (SRC) and similar processes. Settling appears to be most rapid in the temperature range 300 to 350°C, and, in most cases, the filtrates meet the guidelines³ for ash and sulfur content set by the Environmental Protection Agency (EPA). A preliminary economic evaluation⁴ (Appendix 1) showed that SAF followed by settling and filtration of the settled bottoms material would have a product cost advantage of \$3.50/bbl over conventional rotary drum filtration for the SRC process (3/1 solvent-to-oil ratio). For other processes not containing natural solvent, the cost advantage would be approximately \$1.00/bbl of product if settling proved to be applicable.

2.1.2 Description of methods

The standard "Millipore" procedure⁵ was used for vacuum filtration studies. Prior to transfer to the Millipore apparatus, 8 g of unfiltered

oil (UFO) from either the SRC or the Char Oil Energy Development (COED) process was slowly dissolved in 100 cc of solvent at room temperature. The results reported previously¹ did not include certain solvents because they reacted with the Millipore filter paper. "Solvinert," a solvent-resistant filter paper made by Millipore Corporation, was used to obtain the results reported here.

Pressurized precoat filtrations were used to evaluate optimum solvent/oil (S/O) ratios for the toluene--SRC-UFO system. After blending to the desired solvent concentration at room temperature, the mixture was filtered at 100°C and 50-psi (345 kN/m²) overpressure in the apparatus shown in Fig. 2.1.

Settling tests were made by adding the desired amount of solvent to 175 g of UFO at room temperature, and transferring the mixture to a 2.4-cm-ID by 43.5-cm-high stainless steel tube with approximately 20 cc of void space above the liquid phase. The tube was placed in a silicone oil bath which was heated to the test temperature. After settling for a prescribed period, the tubes were chilled and the product was removed in ten fractions of approximately 17.5 g each. Ash and sulfur analyses were made on selected fractions, and these analyses were used to identify the settled zones, as shown in Fig. 2.2.

2.1.3 Vacuum filtrations

The results obtained with the "solvinert" filters are shown in Table 2.1. The following generalizations can be made from these data:

1. COED filtration rates are two to six times as fast as SRC filtrations.
2. The amount of insoluble material (solids) from the COED oil was the same for all four solvents.
3. Pyridine and quinoline dissolved the most SRC oil, and acetone precipitated the largest amount of solids.
4. The quantity of liquid holdup was less for the COED oil.

ORNL DWG 75-5145R2

Fig. 2.1. Laboratory-scale filtering apparatus.

ORNL DWG. 75-8510

- Generally:
1. Clarified zone contains particles less than 5μ and has a total solids concentration much less than the UFO.
 2. Transition zone contains a few particles up to 15μ and varies from a low concentration to that of the UFO.
 3. Settled zone contains nearly all large dark particles and has a concentration much greater than UFO.

Fig. 2.2. Settling zone identification.

Table 2.1. Vacuum filtration of COED and SRC oils with 0.5- μ "Solvynert" Millipore filters

Solvent	Unfiltered oil	Average filtration rate (gal/hr·ft ²)	Average dry solids collected (wt % of UFO)	Average ^a liquid holdup (wt % of wet solids)
Acetone	SRC	14	2.0 ^b	56
	COED	66	9.0	11
Pyridine	SRC	9.3	4.6	58
	COED	26	9.0	50
THF	SRC	12	8.6	21
	COED	70	9.1	10
Quinoline	SRC	6.1	4.5	79
	COED	2.5	9.1	60

^a Determined by drying in an oven at 170°C to a constant weight.

^b Acetone plus SRC damaged the filter paper. The accuracy of this number is questionable.

Analyses of the filtrates are shown in Table 2.2. The solvent was removed by vacuum drying at 60°C, and the residue was analyzed for sulfur by the Leco technique.⁶ The residue from the high-temperature ash analysis was titrated to obtain the iron content. The results show that in all cases the ash content of the filtrate was below EPA maximum allowable concentrations.³ The sulfur content of the SRC filtrate also met EPA requirements, but the COED filtrate did not. Analyses of the COED-UFO solids showed significant concentrations of sulfur and ash, but the filtrate sulfur content remained near the level of the original UFO. Although the iron content was much too low to account for the sulfur as FeS or FeS₂, it was much higher than that for SRC filtrate, which indicates that the sulfur in the filtrate may be contained in soluble organic compounds.

The previous scouting tests to determine the effect of different solvents on agglomeration and filtration of coal liquefaction products used a solvent-to-oil (S/O) ratio of 12/1. This high ratio allowed screening tests to be run at room temperature by maintaining fluidity of the coal liquids; due to short filtration times, it was possible to run a large number of screening tests in a short period. Figure 2.3 shows the effect of reducing this S/O ratio on vacuum filtrations at room temperature. The filtration rates are shown to decrease rapidly as the amount of solvent is decreased, largely due to the increase in viscosity.

2.1.4 Pressure precoat filtrations

Pressure precoat filtration at elevated temperatures, the method employed in current coal liquefaction demonstration plants, was used to evaluate optimum S/O ratios for the toluene--SRC-UFO system. The first set of experiments blended toluene to 50, 20, 10, 7.5, 5, 1, and 0 wt % of the mixture.

During filtration, the settling of agglomerated solids was more rapid than the downward flow of liquid to the filtration interface; this phenomenon resulted in two filtration periods during the high-solvent experiments. The first period represented combined filtration and settling during which the cake of agglomerated solids accumulated

Table 2.2. Analyses of solids and filtrates from vacuum filtrations of solvent fractionated COED and SRC unfiltered oils

Unfiltered oil	Solvent	Solids			Filtered oil		
		Sulfur (wt %)	Ash (wt %)	Iron (wt %)	Sulfur (wt %)	Ash (wt %)	Iron (ppm)
SRC	Acetone	2.62	12.8	6.9	0.98	<0.05	35
SRC	Pyridine	5.34	55.0	6.9	0.73	0.06	35
SRC	Tetrahydrofuran	4.23	33.4	3.9	0.63	0.03	18
SRC	Quinoline	5.75	57.7	8.3	0.64	0.15	32
COED	Acetone	4.57	20.4	13.7	1.65	<0.05	133
COED	Pyridine	4.58	21.0	15.3	1.69	<0.05	258
COED	Tetrahydrofuran	4.60	21.1	14.5	1.76	<0.05	180
COED	Quinoline	4.57	21.5	14.6	1.46	<0.05	199

ORNL DWG. 75-8511R1

Fig. 2.3. The effect of solvent-to-oil ratio on vacuum filtration.
 θ = time, hr; V = volume of filtrate, gal.; A = filtration area, ft².

more rapidly than in the absence of settling. The second period is believed to represent flow of clarified oil through a static bed of filter cake; since no solid buildup occurred during the latter period, the filtration rate was constant. However, the initial filtration rate is the quantity most closely related to filtration rates that would be obtained commercially, since a minimum of settled solids are present at the start of filtration. The steady-state filtration rate during the latter period of the experiment provides information on the characteristics of flow through deposited filter cake of a particular thickness.

The highest initial rates in Table 2.3 indicate at least a four-fold increase in filtration rate over that of SRC-UFO without solvent. Flow through the bed of agglomerated solids near the end of each run is at least three times as great as at the end of a solvent-free SRC-UFO run, at which time approximately the same amount of filter cake is present. Precise optimization of solvent concentration was not possible due to settling effects, but the desired concentration range appears to be 5 to 10% solvent.

Filtrations of SRC-UFO, diluted with various quantities of process recycle solvent at 150°C and 200°C, are shown in Figs. 2.4 and 2.5. Some improvement in filtration of the oil is shown with increasing dilution. In Fig. 2.6, the filtration curve for COED-UFO is compared to a similar curve for SRC-UFO at 150°C; the COED-UFO filtration occurs about 70% faster than the SRC-UFO. This was expected due to the larger particle size distribution of the COED material.¹

2.1.5 Sedimentation

The observed settling of UFO-solvent mixtures during filtration suggested that measurements of ash settling rates after solvent addition could provide a means of judging the degree of agglomeration. Initially, a double tube was used to measure settling rates. Solids were allowed to completely settle in the upper tube and the settled mixture was then filtered in the lower tube. Ideally, this procedure would simulate filtration of settler bottoms and, if continued to completion, would also

Table 2.3. Precoat filtrations of SRC-UFO--toluene mixtures at 100°C and 50 psi

Feed (wt % toluene in mixture with SRC-UFO)	Initial effective ^a filtration rate		Steady state effective ^a filtration rate	
	(g hr ⁻¹ cm ⁻²)	(gal hr ⁻¹ ft ⁻²) ^b	(g hr ⁻¹ cm ⁻²)	(gal hr ⁻¹ ft ⁻²) ^b
50	11.66	2.69	2.21	0.509
	3.34	0.770	1.767	0.408
	3.25	0.750	1.785	0.412
25	18.92	4.37	2.73	0.629
10	20.3	4.68	3.27	0.756
7.5	15.07	3.48	2.37	0.547
5	23.9	5.51	3.29	0.760
	27.3	6.29	3.27	0.756
1	9.48	2.19	1.390	0.321
0	6.14	1.418	1.049	0.242 ^c
	6.30	1.456	1.265	0.292 ^c
	10.09	2.33	0.942	0.217 ^c

^aCalculated on the assumption that filtrate and feed concentration are the same. Rates are given on a toluene-free basis.

^bEstimated filtered oil density of 1.063 g/cm³.

^cNot steady state, but at end of run.

Fig. 2.4. Comparative filtrations of SRC-UFO and dilutions with recycle solvent at 10, 20, and 30% (temp = 150°C).

Fig. 2.5. Comparative filtrations of SRC-UFO and dilutions with recycle solvent at 10, 20, 30, and 40% (temp = 200°C).

Fig. 2.6. Comparative filtrations of COED-UFO and SRC-UFO at 150°C.

provide information on flow of clarified filtrate through a packed filter cake. This technique proved unsatisfactory for the laboratory-scale experiments because of the time required for each experiment (~24 hr). A simple settling at a given temperature, followed by microscopic examination and chemical analyses, was finally adopted as the best method to characterize solvent effects on solids separation. This test proved to be rapid and free from interferences; accurate ash analyses of selected fractions provided a good measure of particle sedimentation.

Table 2.4 presents the results of an 18-hr settling experiment at 200°C. Toluene and recycle solvent are shown to produce reduced sulfur and ash content in the upper 50% of the column to within EPA requirements;³ however, the 18-hr settling time would be excessive for a commercial process. Table 2.5 shows that significant reductions of the contaminants can be achieved in only 1 hr by increasing the temperature to 310°C and using additional process solvent.

A partial matrix of standard 1-hr settling experiments was performed at toluene concentrations of 0, 5, 7.5, 10, 15, and 20% and at temperatures of 150, 200, and 250°C. Chemical analyses of samples from these tests are summarized in Table 2.6. Judging the settling effectiveness by the ash and sulfur content in upper and lower fractions, the best results were obtained at 150°C and 20% toluene, a corner of the matrix. This indicates that better combinations of solvent concentration and temperature may be outside the range of conditions studied in these experiments, and further experiments are necessary to determine optimum conditions.

A temperature-programmed run (approx 2°C/min) using 9 and 20% toluene-SRC mixtures was made at maximum temperatures of 300 and 260°C, respectively. These were followed by a descending temperature program at a similar rate. The resulting mixtures were divided into ten fractions, and selected fractions were analyzed for sulfur, ash, and iron. The results are shown in Table 2.7. The bottom fraction from the 9% mix was a very viscous liquid, but the bottom fraction from the 20% mix was a relatively dry solid. The data, along with the results in Table 2.7, indicate that settling was rapid and complete. The analyses show low

Table 2.4. Analyses of the 200°C, 18-hr sedimentation fractions from SRC-UFO--solvent mixtures

Solvent	Fraction No.	Ash (wt %)	Sulfur (wt %)	Iron (ppm)	Observations with optical microscope
Process recycle solvent, 20 wt %	1	0.03	0.68	15	Excellent clarification
	4	0.03	0.51	18	Excellent clarification
	7	5.66	0.84	6,900	Transition zone
	10	13.88	1.26	15,900	Good settled zone
Toluene, 20 wt %	1	0.04	0.50	250	Excellent clarification
	4	0.14	0.61	150	Good clarification
	7	1.39	0.64	1,900	Upper transition zone
	10	13.41	2.07	15,300	Good settled zone

Table 2.5. Analytical results from settling of SRC-UFO process recycle solvent mixtures in 1 hr at 310°C

Concentration of solvent	Fraction No.	Ash (wt %)	Sulfur (wt %)
5%	1	1.67	0.63
	4	1.52	0.70
	7	1.44	0.67
	10	3.32	0.70
10%	1	1.12	0.59
	4	0.72	0.60
	7	1.22	0.67
	10	3.49	0.75
20%	1	0.33	0.50
	4	0.24	0.54
	7	0.03	0.54

Table 2.6. Matrix of ash and sulfur analyses for toluene--SRC-UFO settling experiments
(Ash % is followed by sulfur % in parentheses. Some duplicate runs are shown.)

Settling temperature (°C)	Depth fraction No.	Toluene concentration in blend with SRC unfiltered oil (wt %)					
		0	5	7.5	10	15	20
150	1				2.56 (0.94)	0.91 (0.65)	<0.03 (0.59)
	2						
	3				2.57	0.87	<0.03
	4						
	5				2.68	0.92	<0.03
	6						
	7						
	8				3.80	5.87	4.43
	9						
	10/11				2.77 (0.93)	4.91 (0.96)	8.38 (1.45)
200	1	2.82 (0.81)	2.08, 2.45 (0.81, 0.82)	2.49 (0.71)	2.46, 2.63 (0.68, 0.77)	2.44, 2.18 (0.74, 0.64)	0.51, 0.07 (0.61, 0.55)
	2						
	3		2.33, 2.48	2.52	2.56, 2.75	2.32, 2.28	0.38, 0.07
	4	2.76					
	5		2.45, 2.46	2.60	2.54, 2.76	2.37, 2.36	0.41, 0.07
	6						
	7	2.99					
	8		2.61, 2.54	2.87	2.67, 2.85	2.48, 2.43 ^a	2.52, 5.53
	9						
	10/11	4.52 (1.00)	3.11, 2.93 (0.86, 0.87)	3.59 (0.84)	3.24, 5.74 (0.74, 0.85)	4.81, 4.54 ^a (0.93, 0.79 ^a)	7.48, 8.06 (1.23, 1.1)
250	1		2.38 (0.80)	2.11 (0.80)	2.75 (0.75)	1.97 (0.66)	
	2						
	3		2.71	4.04	2.81	2.02	
	4						
	5		2.51	2.60	3.59	2.09	
	6						
	7						
	8		2.75	2.70	2.74	2.21	
	9						
	10/11		4.08 (0.85)	4.50 (0.95)	4.31 (0.92)	5.78 (0.92)	

^aNine fractions of oil were removed; analyses 7 and 9 are entered in 3 and 10 slots.

concentrations of ash and sulfur in the upper zones of both runs, and the 20% toluene, temperature-programmed experiment gave specification ash and sulfur values for 50% of the column height.

Table 2.7. Analyses of fractions from temperature-programmed settling

Toluene content	Fraction No.	Ash (wt %)	Sulfur (wt %)	Iron (ppm)
9	4	0.23	0.67	29
9	7	4.70	1.02	5,200
9	10	7.54	1.10	8,200
20	4	0.04	0.51	22
20	7	0.60	0.55	710
20	10	10.31	1.36	13,900

2.2 Sedimentation

2.2.1 Introduction

The solvent agglomeration studies of the previous section showed that settling is a promising alternate separations technique to filtration. Settling has received little attention as a separations technique for coal liquefaction streams because of the extremely small particles that are formed ($50\% < 1 \mu$) and the long settling times required to separate particles in this size range. In this section, theoretical settling rates are calculated by using electron-microscope particle size distributions of SRC-UFO to provide particle diameters. These calculations show that measured ash settling rates are at least an order of magnitude greater than would be predicted if they were based on the ultimate particle sizes, even after allowing for the effect of the solvent on the viscosity. The difference is believed to be due to an increase in effective particle size due to solvent agglomeration. Two

additional methods of effectively increasing the particle size (i.e., temperature and additives) are also discussed in this section.

2.2.2 Theoretical settling rates

Stokes's law, as applied to sedimentation, is given by:

$$u_t = \frac{gd^2(\rho_p - \rho)}{18\mu}$$

where

u_t = ultimate settling velocity or terminal velocity, cm/hr;

g = acceleration due to gravity, cm/hr²;

d = particle diameter, cm;

ρ_p = particle density, 1.96 g/cc;

ρ = liquid density, 1.097 g/cc; and

μ = liquid viscosity.

Settling velocities were calculated over the range 50 to 300°C for five particle diameters selected from SRC particle size distributions.¹ These diameters represented the upper size limits for particles comprising 1, 10, 50, 90, and 99 vol % of the total solids. Results of the calculated rates are shown in Fig. 2.7. The calculated settling rate for the largest particles (99% < 1.8 μ diam) was 0.25 in./hr at 350°C; the measured rate after the addition of 20% toluene was 9.8 in./hr, which indicates that considerable agglomeration had occurred.

2.2.3 Settling-filtration combined

The third 10% fraction from the top of the settling column was taken from sedimentation tests and subjected to a standard precoat filtration at 50-psi differential pressure and 100°C. The filtration apparatus, shown in Fig. 2.1, was used with 800 mg of "Fibre-Flo" precoat. Figure 2.8 shows that filtration improvement of 30 to 70 times the standard

ORNL DWG. 75-8715 R1

Fig. 2.7. Theoretical settling velocities for different sized particles in SRC oils.

Fig. 2.8. Improvement in filterability as a function of settling time and temperature.

rate (no prior settling) is possible after several hours of sedimentation at 300 and 350°C, or after longer settling periods at lower temperatures.

2.2.4 Settling after thermal agglomeration

The results of ash, sulfur, and iron chemical analyses on fractions from sedimentation runs using neat SRC-UFO are shown in Table 2.8. These data indicate that for long settling times or high temperatures, a specification-level clarified zone may be produced by sedimentation alone. The clarified zones for the high-temperature runs appear to extend to fraction 8. The small transition zones extend to fraction 9, where the settled zone begins. This indicates that settling is nearly complete during the 1- to 3-hr time periods. Settling tests at temperatures higher than 350°C (or for times greater than 1 hr at 350°C) were hampered by gas evolution and viscosity increases, which may rule out settling at these temperatures.

The results also indicate that particle enlargement occurred during settling at the higher temperatures. To verify that particle growth was due to the high temperatures, a 10-g sample of SRC-UFO, heated in a capsule at 300°C for 1 hr, was remixed before preparing slides for optical microscopy. Significant aggregates of submicron particles measuring 20 to 30 μ could be seen at 1000X. Electron microscope studies, shown in Figs. 2.9 and 2.10, show that the particles are more agglomerated, and also that the sharp curves present in the original UFO become more rounded, perhaps indicating recrystallization.

2.2.5 Settling after additive agglomeration

A screening study of the use of chemical additives to improve the agglomeration-settling process was suggested previously⁷ and was begun in April 1975. Since very little was known about the mechanism by which these agents operate, initial results were interpreted by the use of the short settling test described earlier. This test produced little settling for SRC-UFO alone; thus, any measured improvement had to be due to the additive.

Table 2.8. Analytical results for settling tests on neat SRC-UFO

Temp (°C)	Settling time (hr)	Fraction No.	Ash (wt %)	Sulfur (wt %)	Iron (ppm)
310	3	1	0.08	0.70	104
		4	0.09	0.64	99
		7	0.08	0.70	109
		8	0.69	0.63	
		9	4.13	0.78	
		10	10.13	1.43	
		11	10.63	1.61	
350	1	1	0.17	0.67	
		4	0.13	0.66	
		7	0.12	0.64	
		8	0.24	0.62	
		9	4.53	0.79	
		10	9.59	1.34	
		11	10.08	1.02	14,200
400	1	1	1.05	0.73	1,370
		4	0.53	0.71	659
		7	0.95	0.70	1,220
		11	9.06	1.15	12,600
345	3	1	0.34	0.57	403
		4	0.36	0.59	451
		7	1.50	0.72	1,990
		10	8.75	1.30	2,380
200	3	1	0.20	0.72	195
		4	2.81	0.88	3,300
		7	3.07	1.01	2,100
		10	5.12	1.06	7,100
200	16	1	0.88	0.76	35
		4	0.020	0.73	140
		7	0.14	0.72	120
		10	7.99	1.00	11,400
200	18	4	0.053	0.79	50
		7	0.38	0.68	215
		10	12.5	1.28	9,100

Fig. 2.9. Unfiltered SRC oil: Electronmicrograph, 24,000X.

Fig. 2.10. Heat treated unfiltered SRC oil: Electronmicrograph, 24,000X.

The following solid materials gave results that were comparable to SRC-UFO without additive: Polox WSR-301 (Monsanto Company); Tween-80 (ICI America, Incorporated); CAL-FLOC Coagulant (Calgon Company); 2C-304 (Zimmerite Corporation); ENDCOR-4622 (Dearborn Chemical Company); Sodium Nitrate-Borate (Calgon Company); Aerosol OT, sodium phosphate, potassium carbonate, calcium sulfate, ammonium borate, sulfur, and -200 +250 mesh Illinois No. 6 coal. Subsequent chemical analyses showed that the sulfur, Polyox, or coal additives did not cause any additional settling to occur. For the other additives tested, the bottom fractions were as much as 2.5% higher in ash, which indicated that some settling had occurred. The lower fraction ash analysis was highest for the ammonium borate additive (5.27%), followed by potassium carbonate (4.25%), and Tween-80 (4.15%).

Screening studies were continued with the testing of 24 liquid additives provided by the Tretolite Division of Petrolite Corporation. Three broad classifications of additives were studied: anionic, cationic, and nonionic. Ash analyses of selected fractions from each of the 24 tests were used to determine the degree of settling. The results produced by the most promising additives after 60 min of settling are shown in Table 2.9. Excellent separations can be observed at additive concentrations as low as 500 ppm. The most promising additive, 771-119, appears to provide at least a factor of 5 improvement over the agglomeration-settling time of untreated oils at the same temperature.

Table 2.9. Settling of SRC-UFO treated with petroleum additive^a at 280°C for 60 min; ash concentrations in the top fractions

Additive No.	Additive concentration		
	4000 ppm	1000 ppm	500 ppm
771-139	0.18	0.11	0.11
771-119	0.023	<0.05	0.05
772-237	0.032	0.88	0.36
772-232	0.093	0.21	

^aFrom the Tretolite Division of Petrolite Corporation.

The settling results for different values of concentration, temperature, and reduced settling times are shown in Table 2.10. Although they appear consistent, repeatability was poor, and further substantiation of the absolute values is necessary. An effort to verify these results on the bench-scale apparatus is described later in this report.

Table 2.10. Temperature and concentration effects on settling of additive 771-119 and SRC-UFO mixtures for 48 min

Temperature (°C)	Ash in the top fraction for the concentrations of additive shown (wt %)			
	1000 ppm	500 ppm	250 ppm	0 ppm
210	0.04	4.79	5.61	2.60
245	0.04	3.85	5.39	2.49
280	0.03	2.44	5.35	2.02
315	0.02	0.06	1.56	2.38
350	0.04	0.06	2.50	2.50

Figure 2.11 shows the results of three pairs of sedimentation tests using the 771-119 additive at 4000 ppm. The control was run before each additive test, with the six tests being made in a single sequence to minimize experimental variations. A significantly lower ash content was noted for fractions 1 through 7; as anticipated, a larger ash content was observed for the bottom fraction.

For the three additive tests, the ash content in the first three fractions was low; it gradually increased up to the seventh fraction and then rose sharply thereafter. Two of these runs were 48 min, and one run was 30 min. These figures include the time required to bring the sample to test conditions; therefore, the actual settling time at the given temperature was less than that shown. Each fraction represents a depth of about 3.5 cm; thus, the settling rate for the smallest particle appears to be about 20 cm/hr (or nearly 8 in./hr).

Fig. 2.11. Comparative laboratory-scale settling tests using additive 771-119.

Additional inorganic additives were tested and aluminum sulfate, ammonium sulfate, and ammonium hydrogen sulfate were apparently as effective as the organic additives. Aluminum phosphate, a good settling accelerator, seemed to perform better at temperatures near 340°C while ammonium monohydrogen phosphate seemed to be less effective. Phosphoric acid, phosphoric anhydride, and sulfuric acid appeared to be most effective at higher concentrations (e.g., 10,000 ppm), but they also seemed to be effective at temperatures as low as 200°C; phase separation in the matrix material, and possibly flocculation, were noted even at this low temperature.

Table 2.11 lists some possible mechanisms based on these observations. Since a wide range of particle types and compositions exist as a suspension in a variable matrix, several settling mechanisms may be operating simultaneously. Agglomeration is known to occur both after solvent dilution and upon the application of heat. The extent to which charge, melting, or chemical conversion occurs to promote agglomeration has not yet been established. Electron-microscope studies of before and after heat treatment indicate that particle reformation does occur. It implies some solubility of the organic species in the matrix organic materials at the test conditions.

Table 2.11. Possible events leading to more rapid settling

Initial events	Final events
Neutralization of zeta potential	Agglomeration
Melting away of hard organic surface layer	Particle enlargement through recrystallization
Chemical conversion of surface	Flocculation
Phase separation	

2.3 Precoat Filtration

2.3.1 Coal as a precoat

Previous studies¹ reported that when sized fractions of pulverized Illinois No. 6 coal are used as a precoat, they provided filtration curves similar to those obtained with Johns-Manville "Fibre-Flo." In addition, the filtered oil met EPA ash and sulfur guidelines.³ At temperatures above 480°F (250°C), the coal precoat tended to soften and resistance to flow developed as expected. Using experimental techniques similar to those described previously, the tendency for coal to soften was examined for a minimum of 2 hr at 410, 433, and 453°F (210, 233, and 234°C). At both 410 and 433°F (210 and 223°C), the flow of oil through the 2-g coal bed (-150 +170 mesh) with 50-psi driving pressure continued at an unchanged rate for over 2 hr. In each case there was no indication of bed plugging. At 450°F (230°C), the flow of oil through the bed slowed continuously throughout the 2-hr period. The final flow rate was about 40% of the initial flow rate. These data show that Illinois No. 6 coal can be used as a precoat during a typical filtration cycle of 1-1/2 hr (Funda filter at SRC-Wilsonville) if the temperature is below 400°F (200°C). Other coal materials such as anthracite, less volatile coals, and devolatilized coal products (e.g., char and coke) can extend this temperature range where required.

2.3.2 Coal as a body feed

Filtration tests to study the use of coal as a body-feed material were performed at 150°C with 50-psi differential pressure using three different fractions of coal at 10% concentrations in the SRC-UFO. The results are shown in Fig. 2.12. The -80 +100-mesh coal did not measurably affect the filtration. Use of the -170 +200-mesh coal resulted in a filtration improvement of ~10%, and a filtration improvement of ~5% was realized with the <325-mesh coal.

ORNL DWG. 75-8433 R 2

Fig. 2.12. Comparative filtrations varying the mesh of 10% suspensions of coal in SRC-UFO. Conditions: 50 psi, 80 mg of precoat, 150°C.

2.4 Deep-Bed Filtrations

Deep-bed filtrations of SRC-UFO were examined briefly as a part of the scouting program (see Table 2.12). Filtration rates through beds of Ottawa sand decreased with increasing bed depth, but leveled out at about $88 \text{ gal hr}^{-1} \text{ ft}^{-2}$; however, the sulfur and ash content of the effluent were not reduced to acceptable levels.

Filtration through beds of Illinois No. 6 coal produced some improvement in sulfur and ash levels. The -85 +100-mesh coal acted as a precoat; thus, the filtration proceeded as a filter-cake process instead of a deep-bed process. Increasing the bed porosity by use of -65 +80 or -42 +65-mesh coal increased filtration rates, but the sulfur was only reduced by about one-third and the ash by about two-thirds. Using coal particles larger than -42 +65 mesh produced very open beds which failed to filter.

In conclusion, deep-bed sand filtrations were unsatisfactory. Deep-bed coal filters were marginally successful at reducing the sulfur and ash content, but not to acceptable EPA levels. At best, deep-bed filtration could be employed to reduce the solids content and would have to be followed by a polishing filter.

3. BENCH-SCALE EXPERIMENTS

3.1 Additive Agglomeration

The bench-scale apparatus shown in Figs. 3.1-3.3 was debugged and pressure tested to 330 psig of air pressure. Initial tests with SRC-filtered oil (SRC-FO) demonstrated operability.

Sixteen runs were made on the bench-scale apparatus using a Tretolite additive at concentrations of 500 to 4000 ppm and at temperatures of 200°C to 315°C . In most cases, a 30 to 50% clarified product was obtained in 90 to 150 min, as shown in Table 3.1. Tests using the more promising inorganic additives, as determined by the laboratory-scale apparatus, gave results similar to those obtained with the Tretolite additive.

Table 2.12. Deep-bed filtrations (SRC-unfiltered oils) at 150°C

Run No.	Nominal bed depth (in.)	Media	Average filtration rate at pressure drop		Solids ^a removed (%)	Filtrate analysis ^b (wt %)		
			gal hr ⁻¹ ft ⁻²	psi		Sulfur	Ash	Iron
1	0.5	Ottawa sand	486	1	19	0.93		
2	1	Ottawa sand	336	1	5	1.04		
3	1.5	Ottawa sand	265	1	0	0.90		
4	2	Ottawa sand	88	1	0	0.71	2.01	0.24
5	5	Ottawa sand	87	1	9	0.71	2.29	0.27
6	2	Coal (-85 +100 mesh)	1.4	50	84	0.64	0.02	0.004
7	5	Coal (-85 +100 mesh)	1.4	50	84	0.60	0.03	0.006
8	5	Coal (-65 +80 mesh)	6.9	50	27	0.59	0.63	0.082
9	5	Coal (-42 +65 mesh)	6.0	50	37	0.61	0.69	0.091
10	10	Coal (-32 +42 mesh)	1400	50	0	0.81	3.22	0.47
11	10	Coal (-32 +42 mesh)	287	10	17	0.87	2.95	0.42
12	10	Coal (-32 +42 mesh)	5.2	1	0	0.86	2.86	0.42

^aBased on cresol insolubles.^bFor unfiltered oil: sulfur = 0.90; ash = 3.20; iron = 0.47.

Fig. 3.1. Coal solid-liquid separations facility (west elevation).

ORNL-DWG 76-157

Fig. 3.2. Diagram of bench-scale settling chamber (1-1/2 in. diam).

Fig. 3.3. Section A.-A. of 3-in. plate filter.

Table 3.1. Bench-scale settling of SRC-UFO using Tretolite additive 119 as agglomerator

Concentration (ppm)	Temperature (°F)	Number of runs included in average	Average ash concentration (wt %) of the upper 30% fraction after the time (min) shown				
			30	60	90	120	150
0	530	7	1.44 ± 0.60 ^a	1.13 ± 0.58 ^a	0.90 ± 0.52 ^a	0.40 ± 0.34 ^a	0.20 ± 0.14 ^a
500	530	1	1.47	1.20	1.01	0.53	0.14
1500	530	1	1.61	1.25	0.81	0.51	0.22
1500	600	1	0.54	1.30	0.08		
1500	390	2	1.45	1.76	0.76		
2500	530	3	1.48	0.96	0.56	0.30 ^b	0.05 ^b
4000	600	1	1.31	0.58	0.21		

^a ± figures are standard deviations of the seven runs.

^b From one run only.

The standard operating procedure for these runs consisted of injecting the additive into a stirred autoclave, bringing the autoclave to temperature, and transferring the mixture to the settler, which was maintained at the same temperature. This procedure is closer to field conditions than the laboratory-scale experiments in which the additive is mixed in a sealed tube and inserted into a heated silicone bath. However, for a given set of conditions, the laboratory-scale experiments produced a clarified product in shorter times, as previously reported.² A number of changes in bench-scale operating procedures were made in an attempt to increase settling rates:

1. Instead of using the stirred autoclave, the mixtures were heated in the settler without stirring.
2. Instead of injecting directly into the stirred autoclave, the additive was mixed in the feed pot.

Neither of these changes improved settling rates significantly.

After 23 runs, the settling apparatus was dismantled and thoroughly cleaned. Very little accumulation of material was noted on the walls of the apparatus, but some solids accumulation had occurred in the sample valves. Following this discovery, new sample valves were installed that permitted samples to be withdrawn from the center of the settler, rather than the walls. The valves were provided with straight-through connections and could be cleaned with a wire brush after each run, consequently eliminating solids accumulation between runs. However, subsequent results were similar to those obtained prior to cleaning the apparatus and installing the new valves, indicating that the disparity of results with the laboratory-scale apparatus was not due to accumulation of solids within the equipment. Next, it was postulated that the slower settling in the bench-scale apparatus could be due to the production of convection currents by uneven heating. These currents would tend to mix the solids

and maintain the smaller particles in suspension. To counter this effect, the settler, including Calrod heaters, was sprayed with a conductive layer of copper, and the Calrods were imbedded in a heat transfer cement (Thermon). Six additional thermocouples were also installed to provide better temperature control.

The results that follow were obtained using the modified settler. An accurate estimate of the settling rate in the bench-scale apparatus was obtained with a full settler charge of 1.8 liters (height ~52 in.) of neat UFO, which was held at 530°F (275°C) for 4.5 hr. The settling rate is determined by the dotted line in Fig. 3.4 as 7.5 in./hr, and compares to the average value of all laboratory-scale runs with petroleum additive, which is 7.47 in./hr. Also, no appreciable differences were found between additive and nonadditive UFO settling characteristics in the bench-scale settler. It is concluded from these data that no appreciable change in rate occurs with the petroleum additive, but that the settling rate of neat UFO is much higher at these temperatures than previously reported.

3.2 Solvent Agglomeration

Figure 3.5 compares settling of UFO containing various solvents, including two process solvents from the SRC process at Ft. Lewis, Washington. Although settling rates are considerably improved for all

Fig. 3.4. Settling of SRC-UFO at 530°F.

Fig. 3.5. Settling of SRC-UFO mixture at 530°F.

solvents shown, it is particularly true for the light oil process solvent and decane. However, a considerable increase in the solids content of the mixture occurred with decane addition, and the increased solids load on the process may not be desirable. For instance, the underflow in a commercial process would typically feed a carbonizer or gasifier and the cost of treatment of additional solids in this step would have to be examined.

To quantify the solids increase with the addition of solvent, 1.2- μ Millipore vacuum filtrations were run using room temperature mixtures of UFO containing the above solvents. Figure 3.6 shows the results obtained after drying the collected solids to a constant temperature at 170°C. At 20 wt % solvent, the solids content of the neat UFO (6.8 wt %) was increased to 17.8 wt % by the addition of decane, but the addition of toluene and light oil increased the solids content to only 8.3 wt %. Wash solvent did not increase the solids content. All values are on a solvent-free basis.

Obtaining a set of curves such as those shown in Fig. 3.5 for different overflow rates, and curves similar to those shown in Fig. 3.6 to characterize the corresponding underflow solids load, would allow optimization of separations for a particular process such as SRC. One such proposed scheme is shown in Fig. 3.7. The percent liquid in the underflow, which determines pumpability, and the filtration and gasification characteristics of the bottoms from the sedimentation steps would have to be determined by further experimentation. Also, more precise distillation cuts should be evaluated to find a material which would increase the sedimentation rate. Figure 3.8 shows the alternate schemes that should be examined in any test program to optimize solid-liquid separations from coal liquids.

3.3 Filtration — Sintered Metal Filter

Three shakedown runs were made in the bench-scale filter using a 40- μ nominal pore opening, sintered metal plate filter. At 390°F (200°C) and 12-psi pressure drop, filtered oil (FO) from the PAMCO-SRC process gave an initial filtration rate of 464 lb/hr·ft², which dropped to

ORNL DWG 76-14656R1

Fig. 3.6. Millipore filtrations of SRC-UFO.

Fig. 3.7. Solids-liquid separation scheme proposed by ORNL.

Fig. 3.3. Alternate schemes for solids-liquid separation:

100 lb/hr·ft² near the end of the filtration period, and an overall average filtration rate of 168 lb/hr·ft². The rate reduction with time is surprising, since the filtered oil contained only 0.06 wt % ash; small organic particles may have plugged some of the filter pores. Near the end of the run, increasing the pressure by a factor of 4 increased the filtration rate by a factor of 2.5, indicating a moderately compressible filter cake.

Unfiltered oil from the PAMCO-SRC process was filtered as described above at 390 (200°C) and 500°F (260°C). At 200°C and 50 psi pressure drop, the initial filtration rate was 118 lb/hr·ft²; this decreased to 10 lb/hr·ft² after 1 hr. Doubling the pressure after this time increased the rate by a factor 1.7, indicating a highly incompressible cake with high-flow resistance. At 260°C and 20 psi pressure drop, the initial rate was 165 lb/hr·ft², and the rate fell to 56 lb/hr·ft² after 7 min. There was considerable vapor loss in the atmospheric filtrate receiver during this run due to the vapor pressure at 260°C (~ 20 psi), but the vapor pressure losses at 200°C (~ 2 psi) were minimal.

Because high-filtrate vapor losses occurred during filtration at elevated temperatures, it was necessary to design, construct, and install the filtrate receiver shown in Fig. 3.9. The main components of the weighing system are a Statham strain gage and a universal transducer.

3.4 Filtration — Carbonaceous Precoats

Figure 3.10 shows the comparative results obtained from filtrations of SRC-UFO at 300°F (150°C) using precoats of diatomaceous earth, coal, and char from the ORNL hydrocarbonizer. These results confirmed the laboratory-scale results reported previously,¹ which showed that coal is an acceptable alternate to diatomaceous earth at temperatures below 400°F (200°C). The previous findings are extended by including char to eliminate any high-temperature deficiencies of the coal precoats; additional experiments near 530°F (275°C) have confirmed the high-temperature stability of char.⁸

Fig. 3.9. Bench-scale sealed filtrate receiver.

ORNL DWG 76-17443 RI

Fig. 3.10. Bench-scale precoat filtrations of SRC-UFO at 300°F, 50 psi.

For the above runs, the filtrate receiver was at atmospheric pressure and, consequently, some vapor was lost. The data points in Fig. 3.10 show the actual amount of filtrate that was collected. The lower curve is a plot of an equation which adequately represents the poorest filtration rate case, but it does not consider vapor losses. It is represented by:

$$m_f = 340 + 4\theta - 340 e^{-0.1\theta}, \quad (1)$$

where

m_f = weight of filtrate, g

θ = time, min.

The upper curve results if a correction is made by adding the liquid loss (caused by vaporization and drying) to the filtrate, and the high-initial rate case is assumed. The upper curve is described by:

$$m_f^c = 340 + 5.24\theta - 340 e^{-0.3\theta}, \quad (2)$$

where

m_f^c = corrected weight of filtrate, g.

Equation 2 is the recommended equation for use with plate filtrations of this type and applies specifically to SRC-UFO. The corrected rate in grams per minute, R_f^c , is obtained by:

$$\frac{dm_f^c}{d\theta} = R_f^c = 5.24 + 102 e^{-0.3\theta}. \quad (3)$$

For the 3-in. plate filter in $\text{gal/hr}\cdot\text{ft}^2$, $R_f^c = 1.45 + 28.3 e^{-0.3\theta}$.

The filter cake thickness in inches, t , at a given time is represented by:

$$t = \frac{R_f^c \theta}{2.54A\rho} = \frac{m_f}{2.54A\rho},$$

where

A = area, cm^2 ,

ρ = density, g/cm^3 .

For the 3-in. bench-scale plate filter used in these experiments, the corrected thickness in inches is $t^c = 6.44 (10^{-4}) m_f^c$; substituting Eq. (2) yields:

$$t^c = 0.219 + 0.003380 - 0.219 e^{-0.30} \quad (4)$$

Calculations using Eqs. (3) and (4) are given in Table 3.2 and illustrate the rapid decline of filtration rate with thickness of filter cake.

Table 3.2. Decline in filtration rate with filter cake thickness

Thickness (in.)	Rate (gal/hr·ft ²)
0.06	22
0.11	17
0.17	10
0.20	6.1
0.23	4.0
0.64	1.5

These rates are typical of those obtained in SRC pilot plants and show the importance of maintaining a very thin filter cake.

Equation (3) also shows that the maximum filtration rate that can be obtained with this system is 30 gal/hr·ft² (276 lb/hr·ft²). Using diatomaceous earth, these rates are unacceptable for economic reasons. However, with coal or char precoats, the economics can be improved by at least a factor of 5. This is a practical finding that can aid current coal conversion pilot plants. However, some method of agglomerating these small particles prior to settling and/or filtration is necessary so that economic feasibility can be demonstrated on a commercial scale, for filtration as well as sedimentation.

In the preceding filtrations, the cakes were dried "in situ" by applying heated nitrogen before they were removed from the bench-scale apparatus. This produced the surface cracking shown in Fig. 3.11. The interface between the coal precoat and the filter cake collected on top can be seen in Fig. 3.12. The collected solids are packed very tightly and appear to be a continuous solid; the porous nature of the coal precoat can be seen below the filter cake. The precoats in these experiments were ~1 in. thick and the collected solids were 1/2 to 5/8 in. thick.

In conclusion, bench-scale filtrations at 200°C have verified previous laboratory-scale filtrations which showed that coal makes a suitable precoat and also improves process economics. These results were extended to include char precoats, thereby eliminating problems that might occur with the carbonaceous precoats at higher temperatures. Equations are given which adequately represent the batch filtration data. These equations are useful as a model for a leaf-type filtration of SRC-UFO, in which it is assumed that the bench-scale filter is equivalent to a 3-in.-diam plug from a pressure leaf. The equations are also useful as an indicator of the filtration rates that can be expected for a given filter cake thickness and, consequently, are useful for a rotary drum-type filter; however, more information on precoat cutting characteristics is needed. Qualitatively, the carbonaceous precoats cut smoothly and without gouging.

Fig. 3.11. Filter assembly showing filter cake and Illinois No. 6 coal precoat.

PHOTO 5812-76

Fig. 3.12. Interface of coal precoat with collected solids.

4. CHARACTERIZATION OF SRC PROCESS STREAMS

4.1 Introduction

Although analyses of coal liquefaction process streams have engendered large quantities of data, not much is known about the effects of sampling techniques and aging. These effects were determined by bimonthly analyses of filtered and unfiltered samples from the SRC-UFO (Wilsonville) process plant. The effect of storing the samples in steel cans under ordinary air at 0°C, 20°C, and 60°C, and at 20°C under a nitrogen blanket was determined over a 1-year period. Other characterization studies of SRC filtered and unfiltered oils included electron microscope particle size distributions, gel permeation chromatography, viscosity-temperature relationships, petrography, and elemental analyses.

4.2 Electron Microscope Particle Size Distributions

Figure 4.1 is an electron micrograph of the particles contained in Wilsonville SRC-UFO derived from a Pittsburgh No. 8 coal. Figure 4.2 shows the particle size distribution of these solids. Although 90% of the particles have diameters less than $2.7\ \mu$, this sample contained larger particles than the SRC-UFO from Illinois No. 6 coal.¹ Particles in the latter sample were distributed as follows: 90% < $1.61\ \mu$; 50% < $0.99\ \mu$; and 10% < $0.25\ \mu$.

Figure 4.3 shows the solids contained in UFO from the PAMCO-SRC process magnified 7908X, and Fig. 4.4 indicates the particle size distribution as determined from a similar photograph using a Zeis counter with computer analysis. The particles shown here are only slightly larger than those found in Wilsonville SRC-UFO from Illinois No. 6 coal, and slightly smaller than those found in Wilsonville SRC-UFO from Pittsburgh No. 8 coal. It should be noted that 50% of the particles by volume have diameters less than $1\ \mu$.

An attempt was made to determine the effect of thermal agglomeration on the ultimate (not agglomerated) particle size distribution of solids from the SRC process. Samples from a 250°C settling run were redispersed

9254 x

ORNL-DWG 76-122

Fig. 4.1. Electron micrograph of solids contained in SRC-UFO from Pittsburgh No. 8 coal.

Fig. 4.2. Particle size distribution of SRC-UFO from Pittsburgh No. 8 coal by electron microscope.

ORNL DWG 76-873

0 1 2 3 MICRONS

Fig. 4.3. Electron micrograph of solids in PAMCO-SRC unfiltered oil.
7908X.

Fig. 4.4. Particle size distribution of SRC-UFO from the PAMCO process.

for electron microscopy by using collodion and amyl acetate. The results shown in Table 4.1 indicate that the lower fractions do not contain large particles, except possibly for the short (3 hr) settling time. The results also show a decrease in particle size with settling time for nearly all fractions and lend credence to the mechanism by which agglomeration of small particles produces rapid settling (i.e., the small particles shown here cannot account for the degree of observed settling). A slight reduction is indicated in the true particle size, probably due to surface melting during extended times at the elevated temperatures.

4.3 Petrography

L. A. Harris, of the Metals and Ceramics Division, prepared a sample of the filtered solids from the toluene fractionation of COED-UFO for standard coal petrography. The analyses determined the volume percent and size frequency of pyrite, as follows:

Pyrite = 0.11 vol %.

Size frequency of pyrite:

<u>Size range</u> (μ)	<u>No. of</u> <u>particles</u>	<u>% of</u> <u>particles</u>
0-1.05	622	0.70
1.05-2.1	169	0.19
2.1-3.2	59	0.07
3.2-4.3	22	0.02
4.3-5.3	9	0.01
5.3-10.5	4	0.01
10.5-50	0	

In addition to the pyrite analyses, many nonreactive coal constituents (inertinites) were present in the sample. A cursory analysis showed that 20 to 30 vol % of the sample was composed of this material, which suggests the concentration of inertinites in these solids.

A similar sample was subjected to low-temperature ashing, which consists of oxidizing the organic constituent while concentrating the mineral matter. Although the process did not go to completion, a petrographic analysis of this sample was made using transmitted light. The minerals

Table 4.1. Summary of electron microscope determinations of particle size distributions for the 250°C settling fractions of SRC-UFO

Settling time (hr)	Fraction	Volume of particles less than the diameters given below (%)		
		90	50	10
3	1	1.55	0.99	0.17
3	4	1.57	0.78	0.20
3	7	3.03	2.31	0.94
3	10	3.38	1.83	0.69
	Average	2.38	1.48	0.50
7	1	0.52	0.32	0.10
7	4	1.22	0.86	0.26
7	7	1.09	0.70	0.24
7	10	0.97	0.66	0.18
	Average	0.95	0.64	0.20
21	1	0.76	0.36	0.09
21	4	0.78	0.30	0.12
21	7	0.94	0.39	0.16
21	10	0.92	0.48	0.19
	Average	0.85	0.38	0.14
	Overall average	1.39	0.83	0.28
	Starting material	1.61	0.99	0.25

were generally $<10 \mu$ in size, with a large portion falling in the $<2 \mu$ range. The limits of optical resolution (0.6μ) did not permit analysis of the very fine material.

4.4 Neutron Activation and Spectrochemical Analyses

Neutron activation is an analytical tool that is more accurate than emission spectroscopy for determination of low concentrations of some elements. The improved accuracy makes the application of this tool to differential separation of inorganic components possible, and it thereby provides an insight into separative mechanisms. Results of neutron activation analyses of SRC-UFO from the pilot plant at Wilsonville, Alabama, are shown in Table 4.2. The coal feed during this period was Illinois No. 6. These values compare favorably with those of COED-UFO using spark-source mass spectrometry, although there are notable differences.

Table 4.3 shows the results of excitation spectrochemical analyses of two coal feeds used at the SRC plant at Wilsonville, Alabama: Illinois No. 6 coal, and Pittsburgh No. 8 coal. Although some differences are noted, the elemental content of both samples is similar. All coal elemental values reported here are higher than for the UFO, since the latter material contained process solvent.

Table 4.2 Analyses of an SRC-UFO by neutron activation.

Element	Concentration (ppm)	Element	Concentration (ppm)
Na	90	As	1.3
Mg	490	Br	0.6
Al	3500	Mo	4
Cl	98	Sb	0.3
K	630	Ba	16
Ca	500	La	1.8
Sc	0.9	Th	0.2
Ti	142	Ce	4
V	13	Mn	12
Fe	4800	Co	1.8
Cr	8.5		

Table 4.3. Spectrochemical analyses of two coal feeds to the SRC plant at Wilsonville, Alabama. Values are in parts per million

	Illinois No. 6	Pittsburgh No. 8		Illinois No. 6	Pittsburgh No. 8
Al	5000	5000	Mn	75	50
As	5	7	Mo	7	3
B	400	200	Na	400	300
Ba	50	100	Nb	1	2
Be	1	0.5	Ni	20	20
Bi	5	3	P	50	100
Ca	>10,000	>10,000	Pb	30	10
Cd	2	1	Rb	50	50
Co	1	3	Sc	0.5	0.5
Cr	30	30	Si	>10,000	>10,000
Cs	3	3	Sr	50	100
Cu	10	7	Th	2	2
Fe	10,000	10,000	Tl	1300	1500
Ga	2	5	U	3	2
Ge	7	5	V	100	50
F	20	30	W	3	1
K	1000	500	Zn	400	300
Li	50	20	Zr	20	20
Mg	700	1000			

4.5 Viscosity-Temperature Studies

A reverse flow kinematic viscometer was used to measure the viscosity of filtered and unfiltered SRC oil over the range of 38 to 93°C. Viscosities of 5 to 15% toluene in SRC-UFO mixtures were also determined. Figure 4.5 shows considerable differences between the viscosities of FO and UFO. The viscosity of SRC-UFO is greatly reduced upon the addition of 5% toluene. The viscosity reduction of FO after the addition of toluene is less pronounced, indicating that the effect of toluene on the particles in the UFO is important to the solution viscosity.

4.6 Gel Permeation Chromatography

Figure 4.6 shows the molecular size distribution of the "as received" SRC-UFO and FO derived from Pittsburgh No. 8 coal. Although the curves are similar in shape, there were some differences between the UFO and FO; the percent of molecules greater than 10 Å was 46% for UFO and 37% for FO, and the small peak maximums were shifted slightly to higher molecular sizes for the UFO. More data will be required to determine if the differences between FO and UFO are significant. After the SRC-FO was stored for 2 months at 140°F (60°C), 39% of the molecules were greater than 10 Å; this difference is believed to be insignificant.

4.7 Aging of SRC-FO and SRC-UFO

The averaged results and standard deviations of four determinations made on SRC-FO at the beginning of the aging period (September 1975) are shown in the first column of Table 4.4. Also shown are results of tests after aging these samples for 2 months under various conditions. The FO analyses that varied by more than twice the standard deviation (σ) are indicated by a footnote. Little overall change was observed, but significant decreases (greater than $\pm 2\sigma$) occurred in the hydrogen, nitrogen, and sulfur contents, as well as in the density. Significant increases were recorded in the viscosity, acetone isolubles, and calorific values. A significant increase was also noted in the oxygen content of the sample stored at 30°F (-1.1°C). The UFO from the Pittsburgh No. 8 coal had a higher carbon/hydrogen ratio than the FO. This was also true for the oils from

ORNL-DWG 76-125RI

Fig. 4.5. The effect of solvent concentration on SRC oil viscosity. (UFO - unfiltered oil; FO - filtered oil; T - toluene.)

Fig. 4.6. Molecular size distribution of SRC oils.

Table 4.4. Analyses of oils from the SRC process

	FO-P#8 ^a	FO-P#8	FO-P#8	FO-P#8	FO-P#8	FO-I#6 ^a	UFO-P#8	UFO-I#6 ^a
Storage time (months)	0	2	2	2	2	0	0	0
Storage condition ^b	as received	140-A	30-A	70-A	70-N	as received	as received	as received
Carbon ^c (wt %)	88.1 ± 0.3 ^d	88.5	87.8	88.2	88.6	89.0	86.3	88.0
Hydrogen ^c (wt %)	8.05 ± 0.21	8.02	7.60*	7.73*	7.79*	7.46	7.14	6.71
C/H	11.0 ± 0.3	11.0	11.6*	11.4	11.4	11.9	12.1	13.1
Nitrogen ^c (wt %)	0.82 ± 0.01	0.73*	0.81	0.81	0.78*	0.66	0.93	1.04
Oxygen ^c (wt %)	2.66 ± 0.50	2.45	3.44	3.00	2.49	2.43	4.97	3.35
Total sulfur ^c (wt %)	0.42 ± 0.03	0.34*	0.32*	0.31*	0.34*	0.45	0.65	0.93
Sulfate sulfur (wt %)	<0.003	0.004	<0.003	<0.003	0.003	-	<0.02	-
Sulfide sulfur (wt %)	0.011	0.007	0.006	0.005	0.004	-	0.13	-
Ash (wt %)	0.02	0.02	0.02	0.02	0.02	<0.05	2.52	3.19
Density (g/cc)	1.056 ± 0.001	1.054	1.052*	1.052*	1.053*	-	1.114	1.141
Viscosity (cP @ 250°F)	1.441 ± 0.003	1.468*	1.450*	1.458*	1.450*	-	52.7 @ 100°F	295 @ 100°F
Solids - acetone insolubles (wt %)	2.60 ± 0.49	3.84*	4.00*	4.97*	3.98*	-	12.63	-
Solids - cresol insolubles (wt %)	0.06	0.06	0.01	<0.01	<0.01	-	4.36	4.0
Calorific value (Btu/lb)	16,782 ± 34	16,371*	16,826*	16,855*	16,855*	16,700	15,958	15,815

^aFO = filtered oil, P#8 = Pittsburgh #8 coal-derived oil, I#6 = Illinois #6 coal-derived oil.

^bStorage condition = temperature (°F), followed by gas blanket in vapor space (N or A for nitrogen or air). All samples are stored in individual 1-pint screw-top steel cans and taken to Analytical Chemistry on alternating months.

^cUltimate analyses are on MAF basis.

^dStandard deviations are ± figures.

*Value exceeds plus or minus two times the standard deviation.

Illinois No. 6 coal, which were not as saturated as the oils from the Pittsburgh coal, and which had higher viscosities and densities than oils from the Pittsburgh coal. The sample of Pittsburgh No. 8 UFO contained 1 to 2% water, which was probably due to contamination during sampling or storage.

Analyses of SRC-FO after 8 months of aging, and SRC-UFO after 4 months of aging under various storage conditions are shown in Tables 4.5 and 4.6. The FO analyses are very similar to previous results and indicate that SRC-FO is stable under most storage conditions. Analyses of the UFO showed that storage at 140°F (60°C) lowers the percentage of carbon and hydrogen with a corresponding gain in oxygen and solids content (as determined by acetone insolubles and cresol insolubles). This indicates that some oxidation is occurring in the presence of air at the higher storage temperature. Since a similar phenomenon did not occur with the FO, the solids present in the UFO may have influenced oxidation.

Observations of the ash and cresol insoluble results for UFO suggest that some analyses may have been performed on samples that were not properly homogenized with respect to solids. Some settling had occurred even at room temperature over long periods of time; consequently, samples must be thoroughly mixed before withdrawing a subsample for analyses. Otherwise, samples from the settled portion will show higher ash and cresol insoluble contents with correspondingly lower carbon and hydrogen values and higher oxygen values. The latter is due to the difference method by which oxygen is obtained.

$$[\text{Oxygen} = 100 - (\text{C} + \text{H} + \text{N} + \text{S} + \text{ash})]$$

The data for the 60°C UFO samples are consistent with sampling in a more settled lower section, and data for the 20°C nitrogen UFO samples are consistent with sampling from the less settled upper portion of the master sample. This illustrates the difficulty of obtaining representative coal liquid samples for testing. Extra care was taken with subsequent samples to ensure proper homogenization.

Figure 4.7 shows the distillation of SRC-UFO and -FO from the Wilsonville plant (Pittsburgh No. 8 coal feed) after various periods of aging. Results of the product oil distillations are remarkably similar after storage under

Table 4.5. Results^a of aging on SRC-FO samples

Condition	Filtered oil								
	AS ^b	140-A ^b		15-A ^b		70-A ^b		70-N ^b	
	Time (months)	0	4	8	4	8	4	8	4
C	88.1	88.1	88.3	88.1	88.0	88.4	88.2	88.1	88.1
H	8.05	7.52	7.53	7.49	7.31	7.51	7.40	7.55	7.51
C/H	11.0	11.7	11.7	11.8	12.0	11.8	11.9	11.7	11.7
N	0.82	0.72	0.83	0.80	0.76	0.76	0.84	0.69	0.78
O	2.66	3.30	2.93	3.31	3.55	3.02	3.16	3.35	3.28
S _{Total}	0.42	0.36	0.41	0.35	0.40	0.36	0.39	0.35	0.36
S _{sulfide}	0.011	<0.005 pyritic	0.02	<0.005 pyritic	0.02	<0.005 pyritic	0.02	<0.005 pyritic	0.01
Ash	0.02	0.02	0.01	0.02	0.02	0.02	0.04	0.02	0.01
ρ @ 25°C	1.056	1.052	1.054	1.052	1.053	1.052	1.052	1.052	1.053
μ @ 250°C	1.441	1.418	1.54	1.464	1.59	1.454	1.53	1.441	1.52
Solids (acetone)	2.60	3.93	3.20	3.45	3.17	3.72	2.21	3.84	3.62
Solids (cresol)	0.06	0.01	0.03	0.01	0.03	0.02	0.04	0.02	0.02
Heat	16,782	16,851		16,887	16,827	16,767	16,843	16,850	16,847

^aWeight percent, except ρ = g/cm³, μ = cSt, heat = Btu/lb.

^bStorage key: AS = as received.
 140-A = 140°F in air atmosphere.
 15-A = 15°F in air atmosphere.
 70-A = 70°F in air atmosphere.
 70-N = 70°F in nitrogen atmosphere.

Table 4.6. Results^a of aging on SRC-UFO samples

Condition	Unfiltered oil					
	AS ^b	140-A ^b		15-A ^b	70-A ^b	70-N ^b
	Time (months)	0	2	4	4	4
C	86.3	84.7	83.6	85.6	86.0	86.9
H	7.14	6.89	6.73	6.93	6.85	6.87
C/H	12.1	12.3	12.4	12.4	12.6	12.6
N	0.93	0.96	0.96	0.93	0.95	0.88
O	2.46	4.17	4.80	4.18	3.41	3.40
S _{Total}	0.65	0.71	0.79	0.71	0.67	0.70
S _{sulfide}	0.13		0.24	0.18	0.20	0.08
Ash	2.52	2.57	3.15	2.65	2.09	1.32
ρ @ 25°C	1.114	1.116	1.125	1.109	1.108	1.107
μ @ 100°C	52.7		62.2	81.5	52.1	49.4
Solids (acetone)	12.6	12.9	13.5	11.2	11.5	10.8
Solids (cresol)	4.36	4.62	6.75	3.67	2.77	3.60
Heat	15,958	15,886	15,762	16,098	16,275	16,322

^aWeight percent, except ρ = g/cm³, μ = cSt, heat = Btu/lb.

^bStorage key: AS = as received
 140-A = 140°F in air atmosphere.
 15-A = 15°F in air atmosphere.
 70-A = 70°F in air atmosphere.
 70-N = 70°F in nitrogen atmosphere.

Fig. 4.7. Distillation of Wilsonville-SRC.

a variety of conditions; the four curves shown for FO after 6 months under different storage conditions are indistinguishable and serve as an example of the repeatability of the method. Since the sample that was stored for 6 months at 140°F (60°C) showed no change, the change in the sample stored for 4 months at 60°C is probably due to a faulty seal. More data are needed to determine if the lower volatility shown for the UFO is due to the nature of the sample or to a faulty seal. The PAMCO SRC-UFO and -FO are shown to be less volatile than the Wilsonville SRC (Fig. 4.8).

4.8 Distillation of SRC Process Streams

It naturally follows from the success of using pure solvents to aid in the separation of solids from coal liquids that process-derived solvents can be identified that will accomplish the same task. For example, there are three streams in the SRC process that could yield a solvent material suitable for solids precipitation: wash solvent, process solvent, and light oil. Table 4.7 shows the gross distillation characteristics of each material along with that of UFO. The cuts that yielded sufficient material should be used at a concentration of 20% in UFO to determine their efficacy for accelerating solids agglomeration and settling (see Sect. 3.2). A lower concentration should be used for the materials that are successful at the concentration level of 20%.

4.9 Densities of SRC Material

The densities of materials used in the PAMCO process are shown in Table 4.8. Figure 4.9 shows the change of densities with temperature for SRC-UFO from the Southern Services SRC plant at Wilsonville, Alabama.

4.10 A Comparison of Three SRC Coal Feeds

A comparison of coals, as fed to the SRC-Wilsonville process, was made to determine the effect of feed on some observed operating differences. The results of chemical and physical analyses are shown in Table 4.9. On November 21, 1974, high conversions (90 to 95%) were obtained by the process, and on April 3, 1975, low conversions (80 to 90%)

Fig. 4.8. Distillation of PAMCO-SRC.

Table 4.7. Distillation of SRC process streams

Process stream	Percent distilled					
	Boiling point range (°F)					
	RT 200	200- 300	300- 400	400- 500	500- 600	>600
Wash solvent	<0.3	0.4	30.2	67.3	1.67	
Process solvent	1.7	1.7	1.7	1.7	38.3	58.3
Light oil	3.1	73.1	20.6	1.4		
Unfiltered oil				0.4	54.5	42.3

Table 4.8. Densities of PAMCO SRC-UFO at 25°C

Material	Density (g/cm ³)
Wash solvent	0.958
300-400°F cut	0.935
400-500°F cut	0.970
Light oil	0.786
200-300°F cut	0.771
300-400°F cut	0.847
Unfiltered oil	1.114
Filtered oil	1.056

Fig. 4.9. Dependence of the density of Wilsonville SRC-UFO (S/O - 3/1) on temperature.

Table 4.9. Comparison of three coal feeds in the
SRC-Wilsonville process

	Illinois No. 6	Illinois No. 6	Pittsburgh No. 8
Date sampled	11/21/74	4/3/75	8/7/75
Elemental analyses, wt %			
C ^a	65.8	72.0	83.1
H ^a	5.06	5.32	5.81
N ^a	1.32	1.43	1.55
S ^a	3.08	3.50	3.04
O ^a	9.90	12.44	6.52
Fe ^a	1.23	1.17	
Ash	10.53	10.43	8.22
Moisture	4.32	4.63	1.07
Volatile	36.6	37.0	39.4
Fixed carbon	48.6	48.0	51.3
Calorific value, Btu/lb	11,805	13,780	15,040

^aMAF basis; others are on as received basis.

were obtained. The Illinois No. 6 coals were not significantly different and could not fully account for the differences in conversions; however, the higher content of nitrogen, sulfur, and oxygen, and the lower content of iron could have had some effect. The Pittsburgh No. 8 coal feed at Wilsonville is a more volatile material with less oxygen, ash, and moisture, but with more fixed carbon and nitrogen.

4.11 Characterization Results

The iron value of 4800 ppm (Table 4.2), as determined by neutron activation analyses, compared favorably with the value of 4700 ppm that was obtained by ashing followed by atomic adsorption. These iron values, along with those obtained from the most settled fraction from the sedimentation studies (Table 2.8), allow an estimation to be made of the ratio of inorganic to organic sulfur in the original UFO. The necessary assumption that all the inorganic sulfur has settled is supported by the high-iron values in the lower fractions (shown in Table 2.8), and by the low-ash values in the upper fractions. The clarified zones for all runs contained approximately 0.7 wt % sulfur, as compared to 0.9 wt % sulfur for UFO. These data indicate that three-fourths of the sulfur in the UFO is organic and cannot be separated by de-ashing techniques. The iron/sulfur ratio in the settled fractions is near 1, suggesting that most of the sulfur originally present as FeS_2 has been converted to FeS during the dissolution process.

Another important result to be gleaned from the analytical data is that some of the organic sulfur remaining in the clarified zones could be precipitated (or agglomerated) by the addition of solvents. Process recycle solvent reduced the clarified-zone sulfur content to 0.50 wt % at 310°C, and toluene reduced the sulfur content to 0.50 wt % at 200°C (Tables 2.5 and 2.6). This technique effectively removed a total of 56% of the starting sulfur, including 30% of the organic sulfur.

5. ACKNOWLEDGMENTS

The assistance of the following is gratefully acknowledged: M. H. Eager, Y-12, for particle size distributions; L. D. Hulett, F. L. Ball, H. W. Dunn, W. R. Laing, and L. J. Brady, of the Analytical Chemistry Division, for numerous characterization analyses; L. A. Harris, of the Metals and Ceramics Division, for petrographic analyses; and D. A. McWhirter, of the Chemical Technology Division, for general laboratory measurements.

6. REFERENCES

1. B. R. Rodgers and S. Katz, Supporting Research and Development on Separations Technology - Phase II Report: Scouting Experiments, ORNL/TM-4968 (October 1975).
2. J. P. Nichols (Program Director), Coal Technology Program Quarterly Progress Report for the Period Ending September 30, 1975, ORNL-5093 (December 1975).
3. Code of Federal Regulations, No. 40, Sect. 60.42-60.44 (Dec. 23, 1971).
4. B. R. Rodgers to E. Schmetz (ERDA), personal communication, Sept. 19, 1975.
5. 1967 Book of ASTM Standards, Part 17, pp. 839-54, American Society for Testing and Materials, Philadelphia, 1967.
6. "Standard Method of Test for Sulfur in Petroleum Products (High-Temperature Method)," 1975 Book of ASTM Standards, Part 23, Method D-1552, American Society for Testing and Materials, Philadelphia, 1975.
7. M. S. Edwards, B. R. Rodgers, and R. Salmon, Coal Technology Program Supporting Research and Development on Separation Technology: Phase I Report, ORNL/TM-4801 (March 1975).
8. B. R. Rodgers, "Filtration of Micron-Sized Particles from Coal Liquids: Carbonaceous Precoats," presented at the Second Pacific Area Chemical Engineering Conference (Pachec '77), Denver, Colorado, August 1977.

APPENDIX A

APPENDIX A: PRELIMINARY ECONOMIC EVALUATION OF A SOLID-LIQUID SEPARATION PROCESS FOR SRC

With the exception of a few isolated attempts to utilize classification, hydrocloning, or centrifugation techniques, all of the current coal liquefaction projects rely upon pressure precoat filtration to effect solid-liquid separations. Consideration of processing alternatives for these separations must therefore be based upon a comparison of the economics of such alternatives with that of pressure precoat filtration.

Preliminary experimental data have been used to evaluate the economics of a different solid-liquid separation process for SRC which entails the addition of toluene to unfiltered SRC process liquids (solvent addition promotes agglomeration of solids and precipitation of certain sulfur-containing organics). As shown in Fig. A.1, the mixture of solvent and unfiltered oil is flashed to effect solvent recovery. Agglomerated solids in the liquid stream are then concentrated by continuous sedimentation and finally removed by rotary drum filtration. The filtrate is mixed with clarified overflow from the thickeners and is further processed for product recovery.

Results of these preliminary economic calculations show a cost advantage for the proposed process over pressure precoat filtration of approximately \$3.40 per barrel of product. The basis on which these calculations were made is presented in Table A.1; details of processing costs (with underlying assumptions) are given in Table A.2.

Clearly, many assumptions are involved in this estimate, but in most cases, the conditions chosen were conservative. Data concerning filtration rates, precoat requirements, stream concentrations, physical properties, etc., were based upon operating experience with COED and SRC processes. Certain costs are expected to be similar (or negligible) for both processes and were thus neglected. Our own experimental data on SRC unfiltered oil were used to estimate settling rates for agglomerated solids and to set the solvent requirement. Figure A.2 shows how the computed cost advantage of the proposed process varies with both total solvent requirement and recovery efficiency. Even at solvent-to-UFO ratios of 1/5 and with losses of 4%, the process remains superior to filtration alone.

Fig. A.1. Processing alternatives for SRC solid-liquid separations.

Table A.1. Basis of economic evaluation of solid-liquid separation techniques for SRC

Process variable	Assumed value
Coal feed rate (Illinois No. 6)	30,000 tons/day
Solvent/coal ratio	3/1
Gas production	2,000 tons/day
Solids content of unfiltered oil	6.8 wt %
Product SRC	16,500 tons/day (80,000 bbl/day)

Table A.2. Comparison of processing costs for SRC solid-liquid separation by (1) pressure precoat (rotary drum) filtration, and (2) solvent agglomeration followed by sedimentation and pressure precoat filtration of thickener underflow

(Basis: 30,000 tons per day of coal feed)

	Millions of dollars	
	Rotary drum filtration	Proposed process
<u>Capital equipment</u>		
Solvent recovery vessel		7.8
Continuous sedimentation vessels ^a		34.8
Filtration equipment ^b	342	10.0
Total capital investment	342	51.6
<u>Operating costs</u>		
Capital costs ^c	82.1	12.4
Precoat material	33.9	1.57
Makeup solvent ^d		3.88
Total annual costs	116	17.9

^aThirteen thickeners operating at 590°F and 150 psig. Sized at 200-ft diameter by 7 ft deep with pressure vessel enclosure.

^bIn each case, 700-ft² rotary drum filters will be utilized with the following operating specification:

- (1) 1.1 cycles/day with downtime of 15%,
 - (2) precoat requirement is 3.5 lb of Johns-Manville "Super-Cel" per cycle per ft²,
 - (3) filtration rate is proportional to the weight ratio of solids in the slurry to liquids in the slurry, and
 - (4) liquid holdup in filter cake is 60 wt % of the solids.
- The number of filters required for solid-liquid separation by filtration alone and by the proposed process are 171 and 8, respectively.

^cCapital costs are taken to be 24% per year of the total capital investment.

^dTotal solvent requirement is assumed to be 5 wt % of the unfiltered SRC process liquids with losses at 1%.

Fig. A.2. Dependence on solvent losses of overall cost advantages for the proposed process.

INTERNAL DISTRIBUTION

1. M. Bender	26. W. R. Laing
2. C. R. Boston	27. R. S. Livingston
3. C. H. Brown	28. A. P. Malinauskas
4. D. A. Canonico	29. L. E. McNeese
5. B. R. Clark	30. J. R. McWherter
6. H. D. Cochran, Jr.	31. J. P. Nichols
7. F. L. Culler	32. T. W. Pickel
8. V. A. DeCarlo	33. W. W. Pitt
9. M. S. Edwards	34. H. Postma
10. D. M. Eissenberg	35-60. B. R. Rodgers
11. J. L. Epler	61. M. W. Rosenthal
12. D. E. Ferguson	62. R. Salmon
13. L. M. Ferris	63. C. D. Scott
14. R. C. Forrester	64. W. D. Shults
15. W. R. Gambill	65. S. P. N. Singh
16. C. W. Gehrs	66. G. P. Smith
17. J. B. Gibson	67. E. G. St. Clair
18. M. R. Guerin	68. O. K. Tallent
19. C. W. Hancher	69. D. B. Trauger
20. L. A. Harris	70. W. C. Ulrich
21. J. R. Hightower	71. J. S. Watson
22. J. M. Holmes	72. P. R. Westmoreland
23. J. K. Huffstetler	73. R. G. Wymer
24. D. S. Joy	74. Patent Office
25. O. L. Keller	75. Lab. Records-RC
	76-80. Lab. Records
	81-83. Central Research Library
	84. Document Reference Section

EXTERNAL DISTRIBUTION

ERDA, Oak Ridge Operations

85. Research and Technical Support Division

ERDA, San Francisco Operations Office, 1333 Broadway, San Francisco, CA 94102

86. N. S. Hagen

ERDA, Washington

87. W. Bakker, MER	97. T. Cox, MER
88. D. Ballantine, DBER	98. P. Duhamel, MER
89. N. F. Barr, DTO	99. C. W. Edington, DBER
90. J. D. Batchelor, CCU	100. J. Forst, MER
91. T. Beresovski, RD&D	101. H. Frankel, MER
92. L. M. Burman, OG&ST	102. R. Franklin, DBER
93. C. E. Carter, DBER	103. S. I. Freedman, CCU
94. E. L. Clark, CCU	104. D. Garrett, MFPM
95. N. P. Cochran, MFPM	105. S. W. Gouse, AFE
96. R. C. Corey, MER	106. W. S. Harmon, MFPM

107.	R. M. Jameson, DBER	125.	J. L. Powell, MFPM
108.	H. R. Johnson, FE/OPPA	126.	M. Reilly, FE/OPPA
109.	H. Jones, MFPM	127.	M. Schulman, DBER
110.	L. Kindley, MER	128.	J. Shen, MER
111.	C. Knudsen, FE/OPPA	129.	A. P. Sikri, OG&ST
112.	T. K. Lau, CCU	130.	D. H. Slade, DBER
113.	R. W. A. LeGassie, APA	131.	J. Smith, MER
114.	J. L. Liverman, AES	132.	D. K. Stevens, DPR
115.	W. G. McDaniel, MFPM	133.	J. W. Watkins, OG&ST
116-121.	G. A. Mills, MER	134.	D. O. Webb, Off. Cong. Rel.
122.	W. E. Mott, DBER	135.	P. R. Wieber, OG&ST
123.	E. S. Pierce, DPR	136.	R. W. Wood, DBER
124.	H. E. Podall, MFPM		
-
137. G. S. Leighton, Department of Housing and Urban Development, 451 7th St., S.W., Washington, DC 20410
 138. J. H. Rothenberg, Department of Housing and Urban Development, 451 7th St., S.W., Washington, DC 20410
 139. R. S. Goor, National Science Foundation, 1800 G Street, N.W., Washington, DC 20550
 140. Robert Rabin, National Science Foundation, 1800 G Street, N.W., Washington, DC 20550
 141. Charles B. Sedman, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711
 142. N. S. Boodman, Section Supervisor, U.S. Steel Corporation Applied Research Laboratory, 125 Jamison Lane, Monroeville, PA 15146
 143. Theresa Wiley, Institute Librarian, University of Kentucky, Institute for Mining and Materials Research, 213 Bradley Hall, Lexington, KY 40506
 144. O. J. Haun, University of Kentucky, Institute for Mining and Materials Research, 213 Bradley Hall, Lexington, KY 40506
 145. J. K. Shou, University of Kentucky, Institute for Mining and Materials Research, 213 Bradley Hall, Lexington, KY 40506
 146. A. W. Decora, ERDA Laramie Energy Research Center, P.O. Box 3395, University Station, Laramie, WY 82071
 147. C. F. Brandenburg, ERDA Laramie Energy Research Center, P.O. Box 3395, University Station, Laramie, WY 82071
 148. R. E. Poulson, ERDA Laramie Energy Research Center, P.O. Box 3395, University Station, Laramie, WY 82071
 149. K. A. Schrider, ERDA Morgantown Energy Research Center, P.O. Box 800, Morgantown, WV 26506
 150. John W. Larson, Department of Chemistry, University of Tennessee, Knoxville, TN 37916
 151. William A. Peters, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139
 152. Donald Hanson, Department of Chemical Engineering, University of California, Berkeley, CA 94720
 153. S. E. Wellborn, Manager, Feedstocks Development, E.I. du Pont de Nemours & Co., Inc., Wilmington, DE 19898
 154. S. K. Chakrabartty, Alberta Research Council, Fuel Sciences Div., 11315-87th Ave., Edmonton, Alberta, Canada T6G 2C2
 155. William C. Liu, Sr. Research Engineer, Technetics Division, Brunswick Corporation, 1 Brunswick Plaza, Skokie, IL 60076

- 156. E. H. Reichl, President, Conoco Coal Development Co., High Ridge Park, Stamford, CT 06904
- 157. T. C. Vogt, Mobil Research and Development Corp., P.O. Box 900, Dallas, Texas 75221
- 158. D. A. Northrup, Sandia Laboratories, Livermore, CA 94550
- 159. R. Wolk, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94304
- 160. Clark H. Ice (Consultant)
- 161. Elmer L. Gaden, Jr. (Consultant)
- 162. Larry E. Swabb, Jr. (Consultant)
- 163-447. Distribution as shown in TID-4500 under UC-90d, Coal Conversion and Utilization - Liquefaction Category (25 copies - NTIS)