DOE/PC/90

DOE/PC/90178--T4

DE92 004910

SELECTIVE FLOTATION OF FOSSIL RESIN FROM WESTERN COAL

DOE Contract DE-AC22-90PC90178

Quarterly Report for June 1, 1991 to August 31, 1991

Submitted by:

Gordon F. Jensen, Director
 Utah Engineering Experimental Station
 University of Utah
 Salt Lake City, Utah 84112

and

Jan D. Miller, Professor
 Department of Metallurgical Engineering
 University of Utah
 Salt Lake City, Utah 84112

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.

October 15, 1991

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Technical activities for the fourth quarter of DOE contract DE-AC22-90PC90178, "Selective Flotation of Fossil Resin from Western Coal," involved efforts by both the University of Utah and Advanced Processing Technologies, Inc. Laboratory research at the University of Utah was primarily concerned with surface chemistry/resin characterization. APT's major activities included proof-of-concept plant testing of the fossil resin flotation circuit.

SURFACE CHEMISTRY/RESIN CHARACTERIZATION

Surface chemistry/resin characterization work at the University of Utah during the past quarter has emphasized FTIR analysis. FTIR spectra of resin samples (Hiawatha seam, Wasatch Plateau coal field) were obtained on a Digilab FTS-40 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a model 3240-SPC data-processing system. The software capability of the instrument includes base-line correction, deconvolution, and subtraction of the primary spectra.

Transmission spectra of the resin types were obtained in a KBr matrix. An accurately weighed sample was mixed (~3%) with KBr in a Wig-L-Bug for 5 minutes, and a portion of the mixture (150 mg) was pressed into a disk (13 mm diameter) under 20,000 psi. For the purposes of quantitative comparisons, the accurate composition of the mixture and the weight of the disk were recorded. Since more than 90% of the sample disk is exposed to the source beam, small differences in the distribution of resin in the KBr matrix were observed to cause a difference of no more than 5% in quantitative comparisons. Further uncertainties were minimized by the preparation of the disks with equal weights of the components. Primary spectra of the samples were obtained from 256 scans with a nominal resolution of 4 cm^{-1} in the range 4000-700 cm^{-1} .

In comparison to ^{13}C NMR (please refer to second quarterly report), FTIR spectroscopy offers more information on the nature of the compounds comprising these resin types, as a result

of its high sensitivity. This FTIR technique provides information on the nature of the chemical bonds present by virtue of their vibrational energy patterns. However, unlike in NMR spectroscopy, absorption bands in a given FTIR spectrum cannot be quantitatively compared, as the intensity of each band depends on its characteristic absorption coefficients. Infrared spectroscopy has been widely used to characterize related resin compound derived from different sources. A number of spectral features have been found to be common for all resins.

Fossil resins derived from Wasatch Plateau coal show some distinct spectral characteristics. A typical spectrum of hexane-extracted coal resin is presented in Figure 1. Among the notable features of this spectrum is the presence of an intense peak at 2954 cm^{-1} , which is attributed to the asymmetric C-H stretching of the methyl group. It is a common observation in most cases involving natural mixtures such as these, that the C-H stretching region is dominated by a peak at 2930 cm^{-1} , which corresponds to asymmetrical C-H stretching of methylene groups, and that the C-H stretching of the methyl group is of relatively low intensity at 2954 cm^{-1} . Of course this is due to the fact that normally the terminal methyl groups are small in number when compared to the methylene groups. In this regard, the rather unusual occurrence of the high-intensity band at 2954 cm^{-1} in the hexane-extracted resin indicates the presence of a large number of methyl groups and leads to the speculation that extensive branching is present in the compounds which constitute fossil resins. The same conclusion is sustained from the examination of the corresponding deformation modes of vibration observed in the spectral region $1450\text{-}1350\text{ cm}^{-1}$. Splitting of the 1375 cm^{-1} band into three distinct peaks at wave numbers 1383 cm^{-1} , 1377 cm^{-1} , and 1368 cm^{-1} strongly indicates the presence of tertiary and quaternary methyl groups.

In addition to the C-H stretching and bending vibrational bands of the methyl and

Figure 1. FTIR spectrum of the hexane-extracted fossil resin from Hiawatha seam coal, Utah.

methylene groups, the spectra of fossil resins are characterized by the presence of two distinct bands at 1711 cm^{-1} and 1741 cm^{-1} . These bands indicate the presence of carbonyl groups in the resinous compounds. These groups could be from carboxylic acids, esters, ketones, or aldehydes. It is also possible that a mixture of these compounds could exist in the fossil resins. However, a strong contribution from carboxylic acids can be discounted on the basis that there is no corresponding O-H vibrational band either at 3640 cm^{-1} (free O-H) or 3400 cm^{-1} (hydrogen-bonded O-H). The absence of aldehydes can also be established by the argument that there is no moderately intense band observed at 2720 cm^{-1} , which is characteristic of C-H stretching mode when the same carbon atom is attached to an oxygen atom by a double bond. Using this simple deduction, one is led to the inevitable conclusion that the two observed bands, viz., at 1711 cm^{-1} and 1741 cm^{-1} , are due to ketones and esters. It is known that esters formed from saturated monocarboxylic acids and saturated alcohols absorb in the region $1735\text{-}1740\text{ cm}^{-1}$, and α,β -unsaturated ketones absorb in the region $1690\text{-}1707\text{ cm}^{-1}$. A possibility also exists that the band at 1741 cm^{-1} may be due to polycyclic ketones, with the carbonyl group in a six-membered ring. In view of this, the suggested assignments are considered to be speculative. In the assignment of both carbonyl bands, aromatic ketones and esters are not taken into consideration as there is no significant indication of the presence of aromatic compounds in the resins. This latter statement can be strengthened by the absence of bands with moderate intensities in regions such as $\sim 3030\text{ cm}^{-1}$, $\sim 1600\text{ cm}^{-1}$, and $740\text{-}950\text{ cm}^{-1}$, which are characteristic regions of aromatic C-H stretching, conjugated C=C stretching, and aromatic C-H out-of-plane bending vibrations, respectively.

The hexane-extracted resin spectrum also contains numerous low-intensity bands. These and others with probable assignments are outlined in Table 1. The band at $\sim 1600\text{ cm}^{-1}$ is

Table 1. Typical FTIR Absorbance Bands in the Mid-Infrared Region of Fossil Resins Derived from Hiawatha Bituminous Coal

Wave Number, cm ⁻¹	Band Designation
3450-3200	O-H and N-H stretching
2954	C-H stretching (asymmetrical) in -CH ₃
2930	C-H stretching (asymmetrical) in -CH ₂
2870	C-H stretching (asymmetrical) in -CH ₃
2723	C=O stretching of bridge-head carbon
1741	C=O stretching in esters and cyclic ketones
1711	C=O stretching in unsaturated ketones
1604	C=C stretching (conjugated) and skeletal ring vibration
1564	C=C stretching in arenes
1456	C-H deformation in -CH ₂
1383-1368	C-H deformation in -CH ₃
1234	C-H wagging in cycloparaffins
1168	C-O-C vibrations in esters
972	C-H deformation in trans-olefins
824-808	C=C deformation in cis olefins
728-720	C-H wagging

attributed to the aromatic and conjugated C=C stretching. The band observed at 1168 cm^{-1} has been interpreted to be due to saturated isoprenoid by some authors, while others attribute it to the C-O-C vibrations in esters. A band at 972 cm^{-1} , which is observed in all of the fossil resins, is assigned to C-H deformation of a trans-olefinic isomer.

As observed with other properties of the resin types, the differences among them are very small and are found only in moderate to less-intense bands. For a close examination of the differences, portions of the spectra are displayed in Figures 2 and 3. Perhaps the largest difference with smooth gradation is found in the band at 1741 cm^{-1} (Figure 2). This band, which was suggested previously to represent ester groups (or polycyclic ketones), is seen to gradually increase its intensity from yellow to dark-brown resin. Also noticeable in the same figure is the gradual change in the feeble and relatively broad band characteristic of aromatic or conjugated C=C at 1604 cm^{-1} . These two observations imply that the polarity of the resin fractions increase in the same manner as the band intensities. In addition, a band at 1564 cm^{-1} , the presence of which may indicate arenes, is also seen to vary with the resin type, though not in an orderly fashion. This band is weakest in the dark-brown resin and appears to vary randomly with the other color fractions.

Further differences are found at wave numbers 1234 cm^{-1} and 728 cm^{-1} (Figure 3), both of which are attributed to the methylene C-H wagging in cycloparaffins such as cyclopentane in the former case and cyclohexane in the latter. Here again these bands decrease from yellow to dark-brown resin.

Figure 2. Comparison of FTIR spectra of the four fossil resin types from the Hiawatha seam coal, Utah in the region 1850-1525 cm^{-1} .

Figure 3. Comparison of FTIR spectra of the four fossil resin types from the Hiawatha seam coal, Utah in the region 1300-700 cm^{-1} .

PROOF-OF-CONCEPT PLANT TESTING

Research work conducted during the past quarter by Advanced Processing Technologies, Inc., (APT) has involved operation of the resin flotation circuit as described in previous quarterly reports. Efforts are being made to establish the optimum fossil resin recovery and resin concentrate quality from the circuit.

Size-By-Size Analysis of Resin Flotation Circuit Performance

Size-by-size screening tests have been carried out with flotation products from the fossil resin flotation circuit to determine the flotation performance of the circuit as a function of particle size. With the flotation circuit operating at steady state, a sufficient amount of feed (hydrosizer overflow), resin circuit cleaner concentrate product, and resin circuit rougher tailing reject were collected, screened, and analyzed. These samples were collected from a high solids concentration test (about 12% solids by weight). In the test, the cleaner flotation was controlled at about pH 10.9 and at a reagent addition of about 0.7 kg/ton. The analysis from the composite material showed a resin flotation recovery of about 91% from the overall resin flotation circuit at a concentrate product grade of about 42%.

Results from the screen analysis for these products are given in Table 2. As shown in the table, fossil resin recovery from the flotation circuit is satisfactory for relatively fine sizes with recoveries at 97.8%, 87.8%, and 82.8% for -200 mesh, 100/200 mesh, and 48/100 mesh, respectively. However, for the 30/48 mesh fraction, a flotation recovery of only 71.8% was obtained and the recovery decreases further to about 52% for particles coarser than 30 mesh. In this view, although the hydrosizer can effectively recover coarse liberated resin particles up to 16 mesh for feed to the flotation circuit (please refer to the second quarterly report for operation

**Table 2. Size by Size Analysis of Resin Grade and Distribution from the Flotation Circuit).
(UPL Coal, sample collected from high solids concentration run, pH 10.9, reagent 0.7 kg/ton).**

Size(mesh)	FEED MATERIALS			CLEANER CELL PRODUCT			ROUGHER TAIL REJECTS			Size-by-Size Recovery(%)	
	Weight Data		Resin Analy.	Weight Data		Resin Analy.	Weight Data		Resin Analy.		
	gram	(%)		gram	(%)		gram	(%)			gram
+30	22.0	1.9	1.90	4.4	0.8	34.95	10.7	2.2	0.93	5.80	52.45
30x48	283.8	24.5	1.52	12.4	2.3	38.64	177.6	36.6	0.44	45.53	71.87
48x100	257.0	22.2	1.83	11.3	2.1	84.26	157.8	32.6	0.32	29.42	82.83
100x200	143.4	12.4	2.31	20.3	3.8	70.58	49.3	10.2	0.29	8.33	87.81
-200	451.9	39.0	7.96	483.7	90.9	42.78	89.3	18.4	0.21	10.93	97.84
Composite	1158.1	100.0	4.21	532.1	100.0	44.56	484.7	100.0	0.35	100.00	92.32

performance of the hydrosizer), these coarse resin particles are relatively difficult to be recovered by flotation under the current operating conditions. It is evident that further work is still needed to improve flotation recovery of these coarse resin particles. Fortunately, the coarse resin fraction does not contribute significantly to the overall recovery.

Effect of Flotation pH

Effect of flotation pH on flotation performance has been carried out during the past quarter. Three pH values (10, 10.5, and 11) have been examined. The testing was carried out with a reagent addition of 0.5 kg/ton. Experimental Results are given in Table 3.

Table 3. Effect of pH on Fossil Resin Flotation (Continuous Flotation).

<u>Sample ID</u>	<u>Flotation pH Value and Resin Grade(%)</u>		
	<u>10</u>	<u>10.5</u>	<u>11</u>
Feed	5.41	5.12	5.56
Rougher Conc.	25.42	27.46	39.50
Rougher Tails	0.83	1.12	1.44
Cleaner Conc.	64.88	69.87	78.93
Recovery (%)	85.76	79.4	75.48

From the table, it is clear that the higher the flotation pH, the higher the concentrate grade

(%resin), and the lower the flotation recovery. These results are consistent with early laboratory research carried out at the University of Utah.

Effect of Solids Concentration

Effect of solids concentration on flotation performance has also been carried out during the past quarter. In this test, the solids concentration entering into the rougher flotation cell was measured at 1.6%, 3.0%, 5.1%, and 12.1%, respectively (these levels were to be controlled at 1.5, 3.0, 5.0 and 12.0%) The reagent addition was 0.5-0.6 kg/ton. The flotation pH was maintained from pH 10.8 to 11. The experimental results are given in Table 4.

Table 4. Effect of Solids Concentration on Fossil Resin Flotation (Continuous Flotation).

	<u>%Solids In Rougher Cell & Resin Grade</u>			
<u>Sample ID</u>	<u>1.6</u>	<u>2.97</u>	<u>5.12</u>	<u>12.1</u>
Feed	5.53	4.91	5.40	3.77
Rougher C	32.04	20.01	15.31	16.71
Rougher T	1.78	1.17	0.81	0.33
Cleaner C	82.48	68.54	60.01	48.06
Cleaner T	25.77	16.67	10.97	12.28
Recovery(%)	69.31	77.49	86.16	91.87

As clearly demonstrated in the table, when the solids concentration increases, the overall flotation recovery of the fossil resin also increases from about 69% to 91%. The cleaner concentrate grade, however, decreases from about 82% to 48%. This phenomenon indicates that the froth stability and characteristics (as affected by solids concentration) have a significant role on selective fossil resin flotation from coal. More about this will be discussed in future reports and publications.

Locked Water Recycle Test

The effect of water recycle on the performance of the resin flotation circuit was carried out during the past quarter. The major purpose of this test was to simulate the plant conditions which recycle the water discharged from the flotation circuit. The recycled water discharged from flotation circuit contains a certain amount of residual flotation reagents and suspended solids. The primary concern is that these residual flotation reagents may adsorb on coal particles prior to flotation and thus might affect the separation efficiency and the recovery of fossil resin from coal. In this view, the results are of particular importance to the commercialization of the fossil resin flotation technology.

In this test, the flotation tails rejected from the resin circuit were settled in a thickener. The overflow water was then recycled and reused throughout the testing. The flotation circuit pH was kept constant at about pH 10.5. The frother addition was also kept constant at about 0.7 kg/ton. The test was run for about 8 hours and samples were collected at different time intervals and later analyzed so that the effect of residual reagents could be evaluated through comparison of recoveries and concentrate grades as collected at different time intervals.

Table 5 provides the experimental results from this test. As clearly shown in the table,

the effect of residual reagents on the flotation separation of fossil resin from coal indeed exists but the effect is minimal. Only slight decrease in concentrate grade (%resin) has occurred after 8 hours. However, this effect can be considered as minimal in view of other effects that might be expected in actual plant operation, such as, variation of feed solids concentration, change of surface properties of feed materials, etc.

Table 5. Experimental Results From Water Recycle Testing (Rougher and Cleaner Flotation, Feed: 5.28% Resin).

<u>Run Time (hrs)</u>	<u>Resin Grade (%)</u>	<u>Recovery (%)</u>
0.5	64.9	93.7
1.0	62.6	97.7
1.5	64.4	90.0
2.0	58.8	88.3
2.5	57.3	92.6
3.0	61.7	94.4
3.5	53.0	99.5
4.0	50.3	85.3
4.5	53.8	89.4
5.0	47.0	99.1
5.5	48.6	97.0
6.0	53.5	85.4
6.5	51.0	94.8
7.0	51.3	96.3
7.5	52.8	97.5
8.0	55.4	93.3

Fine Coal Flotation Separation

During the past quarter, fine coal flotation of the tailings rejected from the resin flotation

circuit has also been carried out. Please refer to our previous quarterly reports for the flowsheet. This phase of work has undertaken to evaluate the possibility of fine coal cleaning for ash removal.

Again, please refer to previous quarterly reports for the circuit configuration. In this testing, the tailings stream discharged from the rougher resin flotation cells was fed to two Galigher Agitair flotation cells (cell volume 1.6 ft³ each). These two cells were connected with the rougher resin cells through a junction box (with a weir, bars, and an adjustable sand gate). Diesel oil at a dosage of approximately 0.5 kg/ton was added to the junction box as a promoter for fine coal flotation.

Table 6 gives experimental results for the test. The feed to coal cells (rougher resin tailings) contains about 20% ash. With only one stage of flotation, a fine coal product containing 7.6% ash at a recovery of 84% is obtained. From a commercial standpoint, this cleaned fine coal product could be filtered, dried and then blended into the coarse fraction (+1/4" from screen, please refer to plant circuit configuration in previous quarterly reports) for power generation. The overall benefit is a totally reduced ash content and a controlled (consistent) moisture level.

Table 6. Fine Coal Flotation Testing of Rougher Resin Tailings.

Feed : Rougher Tails from Resin Flotation Circuit.

Feed Ash (%):	20.75
Clean Coal Ash (%):	7.61
Tails Ash (%):	54.52
Combustible Recovery (%):	84.05

Improved Plant Configuration and Economic Analysis

Based on the experimental data obtained in all phases of proof-of-concept testing, a better (and more detailed) fossil resin flotation plant has been prepared. See Figure 4. The flowsheet has been modified from the early conceptual plant given in previous quarterly reports. In the flowsheet, run-of-mine coal is first dry-screened. The plus 2 mesh portion is directly sent for power generation. Minus 2 mesh material is mixed with water and re-screened on a 6 mesh screen. Oversize (2x6 mesh) is dewatered by centrifugation and sent for power generation. Undersize (-6 mesh) is pumped into a hydrosizer. The hydrosizer underflow is then cleaned by spirals to remove coarse mineral matter and pyrite. After such gravity separation, cleaned coal particles will be dewatered by centrifugation and sent for power generation. Hydrosizer overflow (-30 mesh material with a high resin content) is sent to the resin flotation circuit which consists of rougher flotation, cleaner flotation and recleaner flotation. The resin concentrate thus produced is filtered and delivered to the refinery for final processing. Tailings rejected from the resin flotation circuit are subject cleaning by fine coal flotation. The recovered fine coal concentrate is then filtered, dried, and sent for power generation.

Table 7 provides the mass balances for each of the streams in the flowsheet given in Figure 4. Two general assumptions are

- a) Feed: 500,000 tons coal per year;
- b) Size distribution and resin content as follows:

<u>size</u>	<u>Wt(%)</u>	<u>resin content (%)</u>
+ 1/2"	34.7	1.91
1/2" x 1/4"	18.8	1.87
1/4" x 50 mesh	37.5	1.51
< 50 mesh	9.0	14.21

These two assumptions actually are the true coal characteristics for the coal obtained from Co-Op Mining Co during the proof-of-concept testing. The plant would produce 18 million pounds of fossil resin per year at a concentrate grade of 78.5%. Economical analysis with respect to the proposed circuit has been carried out during the past quarter and is still in progress. The detailed information regarding capital investment, operating cost, profitability, etc., will be given in the last quarterly report when additional consideration has been given to this phase of the work.

Fossil Resin Recovery Plant Configuration

Table 7 Mass Balances For An 18 Million Pounds Fossil Resin Production Plant Give In Figure 4 Based On Experimental Data Obtained From The Proof-Of-Concept Testing Program (300 Working Days Per Year At 24 Hours Per Day).

Stream	Solids lb/min	Water lb/min	Percent Resin	Percent Ash	Percent Solids	GPM Pulp
FU1	13333.33	1481.48			90.00	
FC1	2314.81	257.20			90.00	
FC1a	802.31	89.15			90.00	
FC1b	1512.50	168.06			90.00	
FW1		751.13				
FC3	1512.50	1008.33			60.00	234.25
FC4	435.88	108.97			80.00	45.73
FC5	1076.62	899.36			54.49	188.52
FP1	435.88	37.90			92.00	37.21
FF1	418.98	4818.29	9.03		8.00	609.13
FF2	94.34	377.38			20.00	52.32
FF3	62.90	251.58			20.00	34.88
FF4	41.93	62.90	78.50		40.00	10.68
FF5	377.05	5148.49	0.80		6.82	645.58
FF6		55.50				6.65
FF7	41.93	7.40			85.00	4.03
FW7		235.86				28.28
FW6		157.24				18.85
FA1	0.01	0.01			50.00	7.37
FC4	435.88	108.97			80.00	45.73
FP1	435.88	32.81			93.00	36.60
FL1		76.16				9.13
FC5	1076.62	899.36			54.49	188.52
FW2		4722.70				566.27
FP2	657.64	803.78			45.00	145.66
FP3	657.64	1972.92			25.00	285.84
FW3		1169.14				140.18
FP4	558.99	1852.35			23.18	264.00

FP5	98.65	120.57		45.00	21.85
FW4		175.37			21.03
FP6	98.65	295.94		25.00	42.88
FP7	32.88	215.56		13.24	28.31
FP8	65.76	80.38		45.00	14.57
FP9	65.76	3.46		95.00	5.34
FL3		76.92			9.22
FP10	591.88	2067.91		22.25	292.31
FP11	591.88	51.47		92.00	50.53
FL2		2016.44			241.78
FP12	1954.50	146.23		93.04	

FL1		76.16			9.13
FL2		2016.44			241.78
FL3		76.92			9.22
FF5	377.05	5148.49		6.82	645.58
FF6		55.50			6.65
FS1	377.05	460.84		45.00	83.51
FS2		335.16			40.19
FS3	377.05	125.68		75.00	43.33
FS4	124.43	41.48	0.33	75.00	14.30
FS5	252.62	84.21		75.00	29.03
FS6	252.62	20.48		92.50	21.39
FW9		63.72			7.64
FT1		0.00			
FT2		7247.82			869.04

FW0		7104.20			851.82
FW1		751.13			90.06
FW2		4722.70			566.27
FW3		1169.14			140.18
FW4		175.37			21.03
FW5		-143.62			-17.22
FW6		157.24			18.85
FW7		235.86			28.28
FW8		157.24			18.85
FW9		63.72			7.64
FW10		50.00			6.00
FW11		13.62			1.63
FA1		0.01			0.00
FT2		7247.82			869.04
FW12		800.00			95.92
FW13		800.00			95.92

END

DATE
FILMED
2 120192

I