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Ultrafine Coal Cleaning Via Explosive Shattering and Aggregate Flotation Processes

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Final Technical Report to the
Coal Industry Committee, through the
Center for Research on Sulfur in Coal

Contract 1-5-80270

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ILLINOIS STATE GEOLOGICAL SURVEY

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EXECUTIVE SUMMARY

Our overall project objective was to demonstrate that the Illinois Institute of Technology Research Institute (IITRI) Explosive Shattering (ES) process and the Illinois State Geological Survey (ISGS) Aggregate Flotation (AF) process could be used sequentially to produce a high-quality, low-ash fuel that could meet compliance standards for sulfur. In the ES process, coal macerals were selectively broken into particles less than 10 microns in diameter, while mineral particles remained roughly their original size. This was accomplished by briefly bringing the coal to about 800°F and approximately 10,000 psi and then allowing for rapid adiabatic expansion. The product was quenched with a dilute caustic solution to leach and trap the evolved H₂S. The ES product was then subjected to the AF process, which separates the ash-forming minerals and pyrite from the coal by selectively floating coal-air bubble aggregates away from suspended mineral matter via use of selective foaming surfactants, hydrophobic conditioning of the coal macerals, and generation of small air bubbles. We hoped that the final ES/AF product would be of higher quality than that produced from conventional cleaning methods or AF alone.

So far, this ES-AF approach has been unsuccessful. The ES products obtained from the Kentucky No. 11 (KY11) and Illinois Herrin No. 6 (IL6) coals were indeed highly comminuted, but they did not respond well to AF treatment. No significant beneficiation of the ES product could be observed. We concluded that the ES thermal process causes evolution of organic devolatilization products that coat the finely divided macerals and minerals; this causes both particle types to become equally hydrophobic in nature and minimizes physical separation based on differences in surface characteristics. This conclusion is based on extensive chemical and petrographic characterization and experiments involving ES/AF separation and treatments, including changes of pH, ultrasonic treatment, and use of dispersants, electrolytes, microbial treatment, oil agglomeration, flocculation, reverse flotation, and extraction with organic solvents. Analytical techniques such as thermal gravimetric analysis, chemical characterization of organic extracts of ES products, Fischer Assay, chemical analyses for the forms of sulfur, and extensive petrographic analyses were used as characterization methods. Only organic extraction of the ES product showed promise in increasing separation.

Although ES comminution completely liberates mineral matter, the ES product cannot be significantly beneficiated by conventional cleaning methods based on surface property difference.

ABSTRACT

In this study we tested an ultrafine coal cleaning approach combining rapid thermal-chemical comminution and efficient physical separation. The Aggregate Flotation (AF) physical coal cleaning process, developed at the Illinois State Geological Survey (ISGS), was used to treat products obtained from the Explosive Shattering (ES) process, developed at the Illinois Institute of Technology Research Institute (IITRI). The ES process involves subjecting a coal slurry to rapid high pressure and high temperature treatment then allowing rapid adiabatic expansion to occur; this produces an explosive effect that breaks the macerals (organic constituents of coal) into very small particles and frees the unshattered minerals. The AF process efficiently removes the ash and pyrite from the coal by selectively floating coal-air bubble aggregates away from suspended mineral matter via use of selective foaming surfactants, hydrophobic conditioning of the coal macerals, and generation of small air bubbles. The product is a highly beneficiated coal.

We anticipated that the combined approach would significantly reduce ash and pyrite levels to a greater extent than would the AF process alone, because the extensive comminution provided by the ES process liberates more pyrite and ash particles than does attrition grinding only. However, we have been unsuccessful thus far in demonstrating any significant beneficiation with this method for the Herrin coal samples tested. We believe the major problem is that volatile organic compounds produced during the ES process condense and recoat the particles, making all particles hydrophobic and thereby minimizing any separation based on hydrophobic/hydrophilic differences. We are continuing our efforts to further understand and overcome this limitation.

INTRODUCTION

The primary goal of this project was to evaluate the feasibility of combining a promising fine-coal cleaning process (ISGS Aggregate Flotation) with an efficient thermal-chemical comminution technique (Consolidated Natural Gas Service/ Illinois Institute of Technology Research Institutes Explosive Shattering) to achieve a clean-coal product low in ash and pyritic sulfur. We used various characterization methods, reagents, and alternate techniques to investigate thoroughly the limitations and possibilities of the approach. The Aggregate Flotation (AF) process has been successful on run-of-mine (ROM) and washed Illinois coals (80% passing 400 mesh, ~37 microns), reducing the ash and pyritic sulfur by 80% to 90% yet retaining up to 80% of the Btu value (Ehrlinger et al, 1986). The Explosive Shattering (ES) process can produce macerals in the range of ~2 microns while the mineral matter particles are retained at their original size (Massey et al, 1980, U.S. Patent 4,313,737). Because the AF process is most effective with very small particles, we believed that the ultrafine ES product could be used as a feed instead of feed produced by conventional comminution techniques such as stirred ball milling. The ability to reduce ash and pyrite content in coals has been shown to be highly dependent on increasing their distributions and degree of liberation, and therefore we thought that the combined ES/AF approach might improve ultrafine coal cleaning.

The ES process involves subjecting a coal slurry to about 800°F and 10,000 psi for a minute or less and then allowing rapid adiabatic expansion to occur. The "trapped" water inside the macerals is allowed to "explode." The expansion breaks the maceral-mineral interfaces, and much smaller particles are formed. The macerals are smaller than the mineral particles, since most minerals are rather impervious to penetration of water vapor. The ES process also attacks organic sulfur in the macerals, and some sulfur is liberated during shattering. (See more detailed description in appendix A.)

Aggregate flotation, an ultrafine coal flotation process, involves conditioning fine-sized coal with a small amount of kerosene to make the macerals more hydrophobic. Combining a foaming surfactant with agitation produces small bubbles that form kerosene-coated coal-air bubble aggregates. These aggregates tend to rise and can be separated; the macerals are floated away, and the minerals remain in solution and are piped off. A detailed overview with supporting data is given in appendix B.

The anticipated product of the combined ES-AF approach would be a coal, low in ash and in both pyritic and organic forms of sulfur, which retains most of its volatile matter. The ES process would remove 10% to 30% of the organic sulfur and the AF process would remove up to 90% of the ash and pyritic sulfur. Neither process alone could achieve the same degree of beneficiation.

The general approach of this study has been to utilize the continuous flow (~100 lbs/hr at 10% slurry) ES unit at IITRI to prepare suitable amounts of feed for the AF separation experiments. Most of the AF separation runs were done at ISGS using a batch procedure rather than the AF continuous method. In general, the ES product obtained for AF treatment was about a 0.3% slurry and was treated both "as received" and in a more concentrated form (15% to 25%). Chemical analyses were generally obtained

TABLE 1. Chemical analysis of feed coal (dry basis)*

%	KY11		IL6	
	CTE	ISGS	CTE	ISGS
Carbon	72.87	73.03	64.54	
Hydrogen	5.18	4.84	4.55	
Nitrogen	1.53	1.49	1.24	
Chlorine	0.07	0.03	0.06	
Sulfur	3.97	3.97	4.72	5.23
Ash	9.13	8.96	16.76	14.97
Oxygen (by diff)	7.25	7.72	8.13	
Volatile matter	40.12	41.4	38.12	
Pyritic S	---	2.34	2.39	
Sulfatic S	---	0.26	0.04	
Organic S	---	1.37	2.29	
Heating value, Btu/lb	13,298	13,048		9963
Free Swelling Index (FSI)	---	5.0	3.5	

* Analyses by Commercial Testing and Engineering (CTE) and ISGS

at each step, and additional petrographic analyses were performed for selected samples. Sulfur, ash, and Btu values of the final product and the starting feed coal were obtained to evaluate the results.

Results so far have shown that the product produced from the ES process is not a suitable feed for the AF process and that the combination of the two processes offers little advantage over AF alone. In fact, AF performed better on conventionally attrition-ground coal than on ES comminuted coal, principally because of the hydrophobic nature of the ES product and possibly because of aggregation of the ultrafine particles from the ES process. The AF process achieved no separation of the resulting ES product. Consequently, most of our effort was subsequently focused on increasing our understanding of the problem and attempting to circumvent it.

EXPERIMENTAL METHODS AND RESULTS

Characterization of feed coals

Two Herrin seam feed coals were used in this study--a Kentucky No. 11 (KY11) and an Illinois No. 6 (IL6) coal. Because the IL6 coal was not received until late November, 1986, most of the research was performed only with the KY11 coal. Both coals were obtained and used by IITRI in conjunction with their ongoing USDOE project (DE-AC22-85FC80753). The coals were ground to pass 80 mesh (~177 micron) so they would pass through the exit orifice in the ES apparatus, and then stored under a nitrogen atmosphere. A summary of chemical, sieve, and particle-size analyses of these feed coals and the ES product is shown in tables 1-5.

Description of ES/AF runs

Delayed AF separation on ES product (3/27/86 IITRI sample). The first AF run was conducted using the ES product (~90 g at 25% solids), which was received one week after ES treatment. The product was diluted to about

TABLE 2. Particle-size distribution (%) of feed and ES products (KY11)*

Particle-size range (microns)	Feed	ES**						
		After perl mill grinding			ES shattered coal			
		5 min	10 min	20 min	3/4/86	3/27/86	4/15/86	6/10/86
176-125	9.7	1.6	0	0.2	5.4	0.6	0	0
125-88	8.6	0	0	0	0	0	0	0
88-62	14.3	3.3	1.1	0	.1	1.0	0	0
62-44	16.6	6.9	0.8	1.8	5.4	0	0	0
44-31	9.5	10.8	2.6	5.1	11.5	4.4	0	0
31-22	10.7	16.9	12.7	12.6	17.1	15.3	1.8	0.7
22-16	10.0	17.5	18.8	18.6	19.3	21.3	7.8	7.8
16-11	5.3	13.1	16.9	16.8	14.9	18.9	11.9	10.3
11-7.8	2.7	6.0	10.1	14.8	10.7	9.8	14.9	14.9
7.8-5.5	2.7	6.0	10.1	10.6	5.4	9.8	14.8	16.1
5.5-3.9	2.8	5.8	9.5	8.4	4.4	7.5	17.6	19.1
3.9-2.8	2.3	4.6	7.3	6.5	3.5	4.5	15.4	16.5
2.8-1.9	1.0	1.9	3.9	2.9	1.1	2.0	10.4	9.8
-1.9	0.5	0.9	1.9	1.4	0.5	1.0	5.2	4.8
Mean particle size (microns)	53.3	24.1	14.2	12.1	27.3	16.4	7.6	7.2

* Analyses performed at IITRI via Leeds and Northrup Microtrac Analyzer

** ES conditions: 3/4/86, 750°F, 6000 psi; 3/27/86, 765°F, 7100 psi; 4/15/86, 835°F, 7500 psi; 6/10/86, 820°F, 6000 psi

TABLE 3. Particle-size distribution (%) of feed and ES shattered samples* (IL6)

Particle-size range (microns)	Feed	ES Shattered Coal**		
		Drum 1 11/14/86	Drum 2 11/14/86	Cyclone trap sample
176-125	10.8	0	0	0
125-88	10.5	0	0	0
88-62	19.0	0.4	0	0.1
62-44	16.2	0	0.2	0
44-31	13.2	0	0	0.1
31-22	11.7	4.8	3.1	6.4
22-16	8.7	11.9	12.1	15.8
16-11	4.3	14.9	15.9	16.9
11-7.8	2.6	16.9	16.1	16.4
7.8-3.9	1.9	29.8	29.3	27.0
3.9-2.8	1.1	11.3	12.4	10.0
2.8-1.9	0	6.7	7.3	4.9
-1.9	0	3.3	3.6	2.4
Mean particle size (microns)	60.7	9.6	9.1	8.9

* Analyses performed at IITRI via Leeds and Northrup Microtrac Analyzer

** ES conditions: 11/14/86 Drum 1, 835°F, 7400 psi; 11/14/86 Drum 2, 830°F, 7050 psi; 11/18/86 cyclone trap, 835°F, 7500 psi

2.2% solids (by weight) and subjected to AF, using a Wilfley-Weber Cell (4 liters). Splits of the slurry were submitted for chemical and petrographic analyses. Chemical results (table 6) indicate that AF separation of the ES product produced no significant reduction of sulfur and only a very minor reduction in ash. The Btu, total sulfur, and pyritic sulfur values remained about the same for both concentrate and tails of the AF run. Although petrographic examination (fig. 4) of the ES product shows that the shattering process indeed frees pyrite and ash from the macerals,

TABLE 4. Chemical analysis of ES products (dry basis)

%	KY11		IL6*
	3/27/86	6/10/86	11/14/86 Drum 2
Carbon	74.81		
Hydrogen	4.85		
Nitrogen	1.58		
Chlorine	0.16		
Sulfur	2.74	3.87	2.53
Ash	10.0	12.2	9.25
Oxygen (by diff)	6.04		
Volatile matter	40.2		
Pyritic S	1.45	2.47	
Sulfatic S	0.02	0.0	
Organic S	1.27	1.40	
FSI	1.0		
Heating value (Btu/lb)	11,975	13,100	12,513

*IITRI analyses on different split are 4.14% total sulfur, 1.04% pyritic sulfur

TABLE 5. Sieve analysis of KY11 feed coal

Fraction mesh size	Sample number	%				
		Weight	Ash	Total sulfur	Pyritic sulfur	Btu
+150	C-24587	7.81	6.75	3.28	1.75	13537
150x200	C-24588	16.72	6.69	3.22	1.87	13540
200x270	C-24589	18.31	6.45	3.29	1.93	13538
270x400	C-24591	42.91	12.29	4.69	3.08	13452
-400	C-24591	42.91	12.29	4.69	3.08	12466
Feed (Calc)*	---	---	9.05	3.89	2.40	13066

* Calculated

most of the particles appear to recombine into aggregates 200 to 500 microns in size. This aggregation may have been caused by petrographic sample preparation; however, it should be noted that the feed coal does not aggregate during petrographic sample preparation.

Comparison of chemical analyses of the feed coal with the IITRI ES product (table 6) indicates that no significant organic sulfur was lost during this particular run. (Values for "other" sulfur, derived by subtracting all forms of sulfur from total S, were compared with the organic S values for C-24386.) Values for sulfidic ($S^{=}$) and elemental (S°) forms of sulfur may be in error because of incomplete extraction. The procedure for determining $S^{=}$ and S° concentrations (appendix C) is still being developed and refined for this type of coal-derived sample under CRSC contract 1-5-90249.

Data generated by G. Sresty under U.S. DOE Contract DE-AC22-85FC80753 (appendix D) indicate that about 16% to 37% of the organic sulfur in similar samples (KY11 coal) was removed by the ES process. ISGS data indicate that the decrease in total sulfur in the ES product appears to be at the expense of the formation of pyrrhotite and H_2S . Appreciable sulfide (~25 ppm) was noted in the filtrate of the first sample, a 0.4% slurry received from IITRI.

TABLE 6. Chemical analysis of separation products of IITRI sample (3/27/86)
(Mineral Free basis)

	Feed coal (C-24386) (%)	ES product* (C-24637) (%)	ES/AF concentrate (C-24638) (%)	ES/AF rougher tails (C-24639) (%)	ES/AF cleaner tails (C-24640) (%)
Total S	3.97	2.78	2.72	2.54	2.62
Pyritic S	2.34	1.37	1.52	1.64	1.37
Sulfate S	0.26	0.00	0.01	0.00	0.00
Organic*** (Other)S	1.37	(1.39)	(1.16)	(0.88)	(1.25)
Sulfidic S	---	0.01**	0.02**	0.01**	---
Elemental S	---	0.01**	0.01**	0.01**	---
Ash	9.0	8.2	7.7	9.3	8.1
Btu	13,048	13,032	13,248	13,072	13,110
Wt (g)	---	---	55	21	14

* Made at 765°F and 7100 psi

** Procedures being developed for these analyses are described in appendix C.

*** Organic (or other) sulfur is calculated by difference

Flotation conditions: Pulp density, 2.2 wt%; Cell-Wilfley Weber (4 liters)
Air-B scfh; rpm-500; collector, kerosene (3.7 lbs/ton); surfactant, Airfoam
(1.85 lbs active/ton); initial pH-8.1. Flotation taken to completion in both
separations (cleaner and recleaner).

Immediate AF separation on ES product (6/10/86 IITRI sample). To determine whether reaggregation of the ES product was caused by aging, the AF equipment was taken to the IITRI site, and the separation was performed immediately after the ES product was produced. The ES product slurry (0.3 wt% and ~64°C) was transferred directly to a 70-liter Wilfley-Weber cell. Flotation of the ES solids readily commenced upon addition of air into the cell. This result was unexpected and could have been due to either a lack of solubility of gas bubbles in hot water or to oils produced during the ES process that functioned as in-situ collectors. After this naturally floating material was collected, 0.5 cc (2.6 lb/ton) of Airfoam was added; this addition produced a second concentrate. The results of this test (table 7, float A) indicate that the total sulfur, ash, and Btu values are about equal for concentrates and tails, again indicating that no beneficiation occurred. Organic sulfur concentration in the product is lower than that in the tails. The pyritic sulfur concentration appears to be slightly less in the tails than in the product; this was unexpected and has not yet been accounted for.

Immediate AF separation (using dispersant) on ES product (6/10/86 IITRI Sample). In this run (float B), which was similar to float A (table 7), 1000 ppm (based on volume) of a commercial dispersant, sodium hexametaphosphate (SHMP), was added to the ES slurry along with 0.5 cc (3 lb/ton) of Airfoam. We suspected that addition of the dispersant might facilitate separation of reaggregated mineral/coal particles during flotation. It appeared, however, that the yield of concentrate was reduced (table 7) and no beneficiation occurred. In fact, a slightly higher ash and total sulfur concentration was obtained in the product concentrate relative to that in the tails. The pyritic sulfur content in the concentrate is distinctly higher (2.14% vs 1.05%) than the pyritic sulfur in the tails. It is also curious that the Btu values of the concentrate and tails are roughly equivalent (13,132 vs 13,390).

TABLE 7. On-site tests for ES/AF as-received ES product (6/10/86)

	Sample (No.)	%						Btu
		WT	Ash	PS	OS	TS		
IITRI Feed Coal	C-25044	---	8.6	1.40	2.47	3.86	13100	
IITRI ES Product	C-25043	---	12.2	0.90	2.03	2.94	12622	
Float A	Conc 1	C-25040	14.4	11.0	0.67	2.12	2.79	13060
	Conc 2	C-25041	65.6	10.4	0.49	2.20	2.69	13013
	Tails	C-25266	20.0	10.5	1.13	1.64	2.77	12946
	Calc Feed			10.5	0.64	2.08	2.72	13006
Float B	Conc 1	C-25042	51.7	9.8	0.82	2.14	2.96	13132
	Tails	C-25267	48.3	8.6	1.28	1.05	2.33	13390
	Calc feed			9.2	1.05	1.61	2.66	13256

Conditions: (Float A): Conc 1, no foamer added; Conc 2, 2.6 lbs/t Airfoam added
 (Float B): 3.0 lbs/t Airfoam added plus 1000 ppm SHMP
 PS=pyritic sulfur, OS=Organic sulfur, TS=total sulfur

TABLE 8. Electrolyte and methanol wash treatment of 4/15/86 ES product before AF separation

%	Aluminum sulfate addition*			Methanol extraction**		
	Feed (Calc)	14 lbs/Tds Conc (C-24800)	85 lbs/Tds Conc (C-24802)	Feed	Conc (C-24804)	Tails
Total S	2.73	2.88	3.08	3.02	1.99	3.37
Ash	10.0	9.9	10.9	12.0	7.3	13.6
Pyritic S		2.86	2.79	2.33	1.21	2.27
Recovery		44.2			25.4	74.5
Btu	13,042	13,077	12,413	12,674	13,335	12,451

Conditions:

* 1.5 lbs active airfoam/ton, 4-liter Denver cell, 1075 rpm, 8 scfh flow rate

** 1.4 lbs active airfoam/ton, 4-liter Denver cell, 1075 rpm, 8 scfh flow rate ES
 Product washed with 6:1 (w/w) methanol/coal on a dry solids basis.

These results (floats A and B) indicate unexpected trends and show that no beneficiation can be expected by direct combination of ES and AF. In order to achieve separation, some procedure must be used that utilizes the "free" particles before reagglomeration occurs.

When the actual versus calculated ES feeds are compared (table 7) it appears that the mass balances are off, possibly because of sampling problems or because of the occurrence of segregation. During the ES run significant leaks in the IITRI unit were observed, which may have caused process conditions to vary.

Special exploratory runs

In an attempt to effect a separation the following experiments were run.

Aluminum sulfate addition to ES product (4/15/86 sample) before AF separation. A limited amount of ES product (~400 g slurry at 20.8% solids), derived from the KY11 coal under conditions of 7500 psi and 835°F,

TABLE 9. Analyses of organic solvent-washed ES product

	%				Btu	Sample number
	Ash	PS	OS	TS		
IITRI KY11 feed coal (6/10)	8.6	2.47	1.40	3.86	13100	C-25044
IITRI ES product (6/10)	12.2	2.03	0.90	2.94	12622	C-25043

(A) Solvent wash on concentrated ES product

MeOH wash feed	14.5	2.07	0.61	2.68	12240	C-25196
THF wash feed	10.8	---	---	2.17	13127	C-25197
THF/H ₂ O wash feed	10.9	---	---	2.19	13048	C-25198
Acetone wash feed	14.4	---	---	2.45	12072	C-25199

ES product washed 6:1 (w/w) with solvents, agitated in a blender for 5 minutes, then filtered.

(B) Ultrasonic treatment of MeOH washed, concentrated ES product

	13.3	1.50	1.15	2.64	12748	C-25265
--	------	------	------	------	-------	---------

Conditions: 20% solid ES product slurry mixed with 3:1 methanol for 60 seconds. Mixture then placed in Bronson ultrasonic bath for 30 minutes at full power (Model DHA-1000).

PS=pyritic sulfur; OS=organic sulfur; TS=total sulfur

was treated with several different concentrations of an electrolyte (aluminum sulfate) prior to AF separation. The conditions and results are shown in table 8. The data indicate that no beneficiation occurred at these levels of electrolyte addition and suggests that clumping may not be primarily an electrostatic phenomenon.

Extraction (solvent wash) of ES product (4/15/86 sample) with methanol before AF separation. An AF separation was made on a reconstituted slurry of ES product that had been extracted with methanol, then filtered. Results shown in table 8 indicate that the extraction (solvent wash) produced some AF beneficiation. The methanol washing helped considerably, indicating that a methanol-soluble "oil" may have bound the liberated particles together, causing all particles (macerals and minerals) to be hydrophobic. A later experiment involved extraction of the ES product and chemical examination of the extract. A noticeable oil-like smell was discernible in all ES slurries when received; this most likely was a by-product of the short-term high-temperature and high-pressure conditions, which tended to cause some degradation of the organic structure in the macerals. The explanation for the reaggregation is probably quite complex, involving an oil by-product, and possibly is time dependent. Most certainly, concentrating and drying the solids would tend to promote reaggregation. The ES samples taken for particle-size analyses at IITRI were not concentrated (-0.5% to 1% solids) and were treated with a dispersant soon after ES treatment.

Extraction of ES product (6/10/86 sample) with various solvents. About 1 1/2 barrels (55 gal) of 0.3% ES product slurry was obtained during the 6/10/86 IITRI continuous flow run and shipped to IGS for further studies. Table 9(A) shows the results of extraction at room temperature separately

TABLE 10. AF separation of organic solvent-washed ES product

		%					Btu	Sample number
		Wt	Ash	PS	OS	TS		
IITRI KY11 feed coal (6/10)	---	8.6	2.47	1.40	3.86	13100	C-25044	
IITRI ES product (6/10)	---	12.2	2.03	0.90	2.94	12622	C-25043	

AF on MeOH-washed concentrated ES productDosage

5.3 lbs/t A.F.	Conc 1	17.0	9.1	---	---	2.07	13170	C-25074
10.5 lbs/t A.F.	Conc 2	51.5	12.5	2.06	0.48	2.54	12502	C-25075
	Tails	31.5	19.6	2.86	0.71	3.61	---	C-25076
	Calc feed		14.2			2.80	---	

AF on MeOH/THF-washed concentrated ES productDosage

9.5 lbs/t A.F.	Conc 1	59.9	10.5	---	---	2.60	13083	C-25200
10.0 lbs/t K	Tails	40.1	13.3	---	---	2.54	11876	C-25201
	Calc feed		11.6			2.58	12579	

AF on MeOH/THF-washed concentrated ES productDosage

5.0 lbs/t A.F.	Conc 1	25.0	11.7	---	---	2.32	12603	C-25202
3.0 lbs/t K								
5.0 lbs/t A.F.	Conc 2	64.6	14.1	---	---	1.91	12347	C-25203
3.0 lbs/t K								
3.0 lbs/K	Conc 3	8.2	16.2	---	---	2.36	12739	C-25204
	Tails	2.2	34.1	---	---	---	---	C-25205
	Calc Feed		14.1					

A.F.=Airfoam; PS=pyritic sulfur; OS=organic sulfur; TS=total sulfur;
K=Kerosene

Conditions: 2-liter Denver cell, 1075 rpm, Air flow rate=8 scfh;

Note: Pyritic sulfur and organic sulfur data are missing where there was not enough sample available.

by methanol, tetrahydrofuran (THF), THF and water, and acetone. The dry solids were washed with solvent (6:1 w/w % solvent to dry solids), agitated at high speed agitation in a blender for two minutes, then filtered.

It is interesting to note that washing of the ES product by methanol or acetone tended to concentrate the ash and decrease the Btu value relative to the individual ES product. On the other hand the THF and THF/H₂O-washed ES product had slightly higher Btu values and lower ash values than did the unwashed ES product. One possible explanation is that THF is absorbed more into the coal matrix, whereas methanol actually dissolves some of the "organic" oil; this hypothesis was partly supported by a decrease in organic sulfur for the methanol-washed ES product in comparison with the unwashed ES product (.61% vs .90%). Table 9(B) indicates the results of ultrasonically treating a methanol-extracted ES product; the ash, total sulfur, and Btu values are roughly the same as those for the untreated methanol-washed sample.

TABLE 11. Oil agglomeration of methanol-washed ES product

	Sample number	%					Btu
		Wt	Ash	PS	OS	TS	
IITRI feed coal (6/10)	C-25094	---	8.6	2.47	1.40	3.86	13100
IITRI ES product (6/10)	C-25043	---	12.2	2.03	0.90	2.94	12622
MeOH washed, 15% kerosene							
Conc 1	C-25077	97.4	11.4	1.65	0.86	2.51	---
Tails	C-25078	2.6	30.2				---
Calc feed			11.9				

PS=pyritic sulfur; OS=organic sulfur; TS=total sulfur

Conditions: 15% (wt%) kerosene added to 10% ES solids product; agitation at high speed in a Waring blender for 5 minutes. Product screened at +100 mesh.

TABLE 12. AF separation of ES product at pH 10.5

	Sample number	%					Btu
		Wt	Ash	PS	OS	TS	
Conc	C-25598	56.3	12.60	1.14	1.16	2.31	12699
Tails	C-25599	43.7	12.70	1.09	1.32	2.60	12473
Feed (calculated)			12.64	1.12	1.23	2.44	12600

PS=pyritic sulfur; OS=organic sulfur; TS=total sulfur

Conditions: 2-liter Denver cell; 1075 rpm, 1% solids, 5 lbs active Airfoam/t ds

AF separation on organic solvent washed ES products (6/10/86 sample). Several AF runs were made on ES product that had been washed with methanol and combinations of methanol and THF. Results are shown in table 10. In general, some ash beneficiation was noted in each case for the concentrate, as compared with the tail fraction. The AF separation of methanol-washed ES product appears to be significant for TS and ash while having a fair yield (68.5%) for combined concentrations 1 and 2.

Further efforts to separate the ES product physically

Oil agglomeration of methanol-washed ES product (6/10/86) sample. We attempted to determine if another comparable fine coal cleaning approach could be successful in utilizing the ES product after methanol extraction. A conventional oil agglomeration laboratory procedure was used on the extracted 6/10/86 ES product. The specific conditions and results are shown in table 11. Although the yield is rather high (~97%), it appears that some beneficiation occurred (1.65% pyritic sulfur in concentrate versus 2.03% in ES product).

Changes in pH. Attempts to physically separate the ES product by AF included attempts at flotation at both low (pH=3.0) and high (pH=10.5) pH levels. With low pH, significant amounts of H₂S were evolved from the slurry; this release of H₂S would be environmentally unacceptable at a commercial level, and would preclude the subsequent AF step. Results in table 12 indicate no beneficiation at high pH.

TABLE 13. Flocculation separation of ES product with and without dispersant

With dispersant						
	Sample number	%				Btu
		Wt	Ash	TS	PS	
(+200m) product	C-25379	73.3	11.50	2.61	1.27	12989
(-200m) refuse	C-25378	26.7	12.10	2.86	1.66	12864
Feed (calc)	---	---	11.66	2.68	1.37	12956

Solids-2.0%, 6.0 lbs/ton Nalco Anionic Polyacrylamide; 1000 ppm, SHMP*

Without dispersant						
	Sample number	%				Btu
		Wt	Ash	TS	PS	
(+200m) product	C-25376	49.1	12.20	2.72	1.58	12772
(-200m) refuse	C-25377	50.9	12.20	2.74	1.57	12780

Solids: 2.0%; 3.0 lbs/t Nalco Anionic Polyacrylamide

PS=pyritic sulfur; TS=total sulfur

Conditions: Slurry agitated at 1000 rpm, flocculant added with agitation for 20 seconds followed by immediate decantation onto a 200 mesh screen.

*SHMP=Sodium hexametaphosphate

TABLE 14. Reverse flotation of ES product

Sample number	%					Btu	
	Wt	Ash	PS	OS	TS		
Feed (calc)	100.0		1.04	1.37	2.42		
Conc-1	C-25520	38.97	11.20	0.87	1.22	2.10	13104
Conc-2	C-25521	43.14	12.90	0.88	1.73	2.61	12794
Composite (conc)		100.00	12.09	0.88	1.49	2.37	12941
Tails	C-25525	17.89		1.80	0.85	2.65	

OS=organic sulfur; PS=pyritic sulfur; TS=total sulfur

Dosage: Conc 1: 2.9 lbs/t Armak Cationic Surfactant; Conc 2: 1.0 lbs/t Armak cationic surfactant plus 2.9 lbs/t pyrite depressant

Conditions: 1.0 wt% solids; 1075 rpm, 8 scfh, 2-liter Denver cell

Flocculation and reverse flotation procedures. Flocculation (with and without dispersants) and reverse flotation separation procedures were also used to explore alternate separation methodologies. Flocculation using long-chain polymers essentially agglomerates the macerals while leaving the minerals in suspension. We thought that reverse flotation, using cationic surfactants, might cause the clays and other minerals to float while the clean coal product remained in the tailings. Tables 13 and 14 summarize the results, which indicate no evidence for separation.

Other supporting experimentation

AF separation of IITRI feed coal (KY11). In an attempt to determine the possible beneficiation of the KY11 feed coal with AF (no ES treatment), a series of Perl Mill attrition grinds (grind times: 5, 10, and 20 min) of the feed coal were prepared, and AF procedures were run, varying the

TABLE 15. Comparison of AF yields on IIRI feed coal (KY11) with varying perl mill grind and reagent dosages

%	5 minutes		10 minutes		20 minutes	
	(Dosage lbs active/tds)		(Dosage lbs active/tds)		(Dosage lbs active/tds)	
	2.0	3.0	2.0	3.0	2.0	3.0
Feed ash (calc)	9.6	9.7	10.0	9.9	10.5	10.5
Ash product	5.9	7.5	5.4	6.7	5.1	6.1
Pyritic sulfur feed (calc)	2.30	2.18	2.50	2.38	2.70	2.67
Pyritic sulfur product	1.34	1.62	1.22	1.55	0.93	1.27
Btu recovery	72.3	94.5	38.2	93.5	19.5	89.1
Ash rejection	57.3	29.1	80.5	39.7	91.0	51.0
Pyrite rejection	59.6	32.0	82.6	41.6	93.6	60.2

Flotation conditions: pulp density: 3.5 to 4.5% solids: 4-liter Denver cell; 1075 rpm, 8 scfh
 Reagent: Airfoam; particle size (average): 5 minutes, 24.1 mm; 10 minutes, 14.2 mm; 20 minutes, 12.1 mm

dosages (2.0 and 3.0 active Airfoam/tds). Specific conditions and results are shown in table 15. Results indicate the effect of increased grind time (smaller particle-size distribution) and recoveries obtained for equivalent dosages. At 2.0 lbs active Airfoam/tds there is a perceptible decrease in Btu recovery with increased grind time, as would be expected. At 3.0 lbs active Airfoam/tds, the 5- and 10-minute grinds appear to be slightly overdosed, which is reflected by the relatively low ash and pyrite rejection values and the high Btu recovery. The 20-minute grind is roughly at its point of dosage/recovery optimization at 3.0 lbs active Airfoam/tds. Further dosage optimization work on the 5- and 10-minute grinds would allow comparison of ash and pyrite rejection values for equivalent Btu recovery with variation in grind times.

These results indicate the practical limits of AF performance on the washed KY11 feed coal (without ES). The AF process can further reduce the ash and pyrite contents in the washed coal by 50% and 60% respectively while retaining almost 90% of the heat content.

Comparison of thermogravimetric analyses of feed coal and ES product
 Thermogravimetry (TG) was used to investigate the devolatilization behavior of the feed coals and ES products. In these experiments, 5 to 10 mg of a sample was heated in argon (100 cc/min) to 700°C. The thermal curves for one feed coal and one ES product are shown in figures 1 and 2. Distinct differences were observed between the devolatilization behavior of the feed and ES products from the KY11 coal.

A 2.5% weight loss was observed in the untreated KY11 coal (fig. 1), between 50°C and 150°C and was attributed to the moisture content. A major devolatilization stage (during this stage liquid and gaseous hydrocarbons are released) began at 350°C, peaked at 440°C, and ended at 520°C. The corresponding weight loss in this stage was 25%. The shoulder peak observed at 530°C represents breakdown of pyrite in the coal. The total weight loss at 700°C was 30 percent.

Examination of the thermal curve for the KY11 ES product (fig. 2) revealed that devolatilization occurred in two stages. During the first slower stage, which continued to 350°C, a weight loss of nearly 10% was observed. The second stage began at 350°C and ended at 600°C. The weight loss was 19%. For the ES product, the pyrite peak at 530°C was absent during the devolatilization stage. The origin of the peak between 650°C and 750°C is not known.

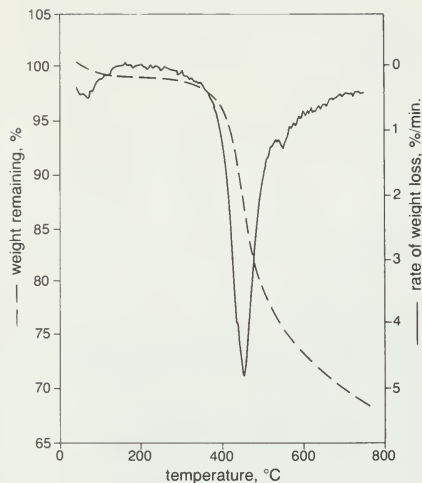


Figure 1. TG Analysis of ES feed coal (KY 11).

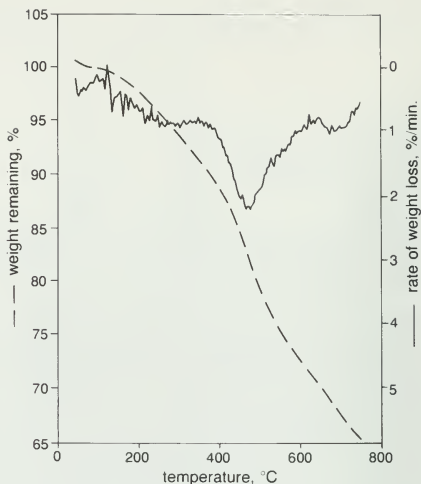


Figure 2. TG Analysis of ES product (KY 11).

A comparison of the thermal curves indicated that during the major devolatilization stage the release of volatile matter from the ES product occurred at a much lower rate than that observed for the feed coal. Also, the temperature corresponding to the maximum rate of weight loss was shifted by 40°C (i.e., 480°C). For the ES product the weight loss observed below 350°C could be due to evaporation of the in-situ oil that had been adsorbed on maceral and mineral particles. This possibility leads us to believe that the oily coating considered responsible for poor AF performance is due to sorption of evolved oils from the ES treatment. While the values for total volatile matter in both feed (41.4%) and ES product (40.2%) are essentially equivalent, the nature of both feed and product has changed because of the higher temperature and pressure conditions during ES.

Fisher Assays were also performed on the IITRI KY11 feed coal and ES product to compare oil yields and to observe the initial temperature at which tars start to volatilize. The oil yields were similar (35.5 and 34.4 gal/U.S. ton) for the feed coal and ES product, respectively. However, the ES product yielded tars at 257°C while the feed coal did not produce tars until 350°C. Total weight loss for the feed coal was 32.8% as compared with 25.9% for the ES product; this difference was caused by the higher moisture of the feed coal (11.2% as compared to 7.4%) and its greater amount of noncondensable gases (9.0% vs 6.3%).

Chemical analyses of methanol extract of ES product. In order to better understand the chemical nature of the organic compounds that are evolved during the ES process and subsequently re-adsorbed into the shattered

particles, we performed an overnight room temperature methanol extraction (6 parts methanol and 1 part KY11 ES product) and analyzed the resulting extract by gel permeation chromatography, gas chromatography, and IR spectroscopy.

An aliquot (100 mL) of the sample extract was centrifuged and the supernatant was decanted and concentrated to approximately 10 mL by heating it to 50°C under a stream of dry nitrogen gas. Acetone was added and the solution was again concentrated. The latter process was repeated three times to remove the last traces of methanol and water.

Approximately 30 mg of the extract was dissolved in THF. One gram of silica gel was added and the THF was evaporated by a stream of dry nitrogen gas. The sample-coated silica gel was placed on top of a silica gel chromatography column. The column was then eluted in sequence with 30 mL hexane (fraction 1); 30 mL of 1:1, hexane: benzene (fraction 2); and 30 mL of 1:1 benzene: methanol (fraction 3). The following fractions were obtained: (1) aliphatics -7%, (2) aromatics -3%, and (3) polar -90%.

When the aliphatic fraction (1) was analyzed by gas chromatography, the n-paraffins from C₁₄ through C₂₉ were detected. C₁₅ and C₁₆ were the most dominant, and pristane and phytane were also identified.

The aromatic fraction (2) was not analyzed further. It probably consists mostly of low-molecular-weight (up to 3 rings) compounds.

The polar fraction (3) was analyzed by infrared spectroscopy. The spectrum showed peaks for hydroxyl (phenols), carboxylic, carbonyl, and possibly nitrogen-containing functional groups. Also, aliphatic, aromatic, and unsaturated peaks were in evidence. The molecular weight (MW) range is thought to be mixed (both high and low MW species involved).

In conclusion, this sample is not very different from other samples of volatile products obtained from heated coal. These results confirm the presence of organic compounds that apparently coat these particles of ES product and inhibit significant separation.

Biochemical desulfurization of ES product. An IITRI explosively shattered Kentucky (No. 11) coal was collected by filtration and air dried. In separate containers the explosively shattered coal and a 200-mesh Illinois (Herrin No. 6) coal (2.3% pyritic sulfur), both at a 5% pulp density, were added to TMS medium (per liter: (NH₄)₂SO₄, 1.6 g; KH₂PO₄, 0.4 g; MgSO₄·7H₂O, 0.16 g). The pH was adjusted to 2.5 with HCl, and the medium was autoclaved at 121°C for 20 minutes. A 1% inoculum of Thiobacillus ferrooxidans ATCC 23270, grown on TMS amended with 0.5% pyrite, was added. The cultures were incubated at 30°C on a gyratory shaker at 150 rpm. Uninoculated control cultures were included with experiments being run in duplicate. Periodically, aliquots were removed from the incubator and centrifuged at 10,000 x g for 30 minutes. Sulfate concentration in the supernatant was determined turbidimetrically. During 28 days of incubation there was no measurable sulfate production from the explosively shattered coal. In the same time interval, approximately 90% of the pyritic sulfur in the 200-mesh Illinois (Herrin No. 6) coal (the control sample) was released as

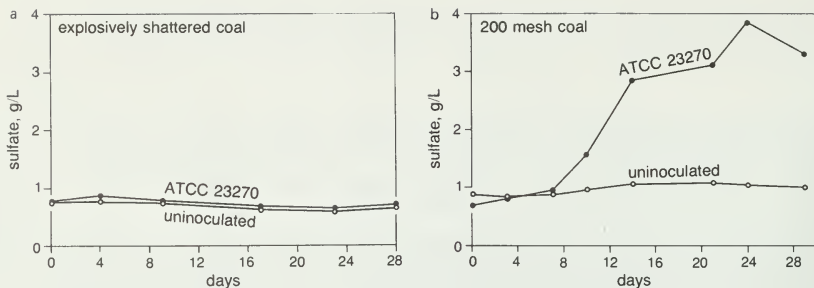


Figure 3. Microbial treatment of ES product and coal.

sulfate. These results, shown in figure 3, essentially indicate that the ES product cannot be desulfurized using microorganisms. A possible reason is that the ES particles are coated with organics; this inhibits penetration, which the microbial process requires.

Microbial conditioning for physical desulfurization. A large (800 ml) batch culture of explosively shattered coal in TMS was prepared as described as above. In this case, a 10% inoculum was used. The culture was incubated at ambient temperature on a gyratory shaker at 150 rpm. The ES material was submitted for AF treatment after microbial treatment for 20 days. A control run (no microbial treatments) was also made. These results are shown in table 16. We concluded that no beneficiation occurred as a result of microbial treatment.

Petrographic characterization. The purpose of petrographic examination was to evaluate the degree of comminution of the explosively shattered samples in comparison to that of mill-ground samples, and to note any problems or unusual sample characteristics that would affect potential cleaning behavior.

Microscopic specimens (pellets of the first two samples and smear mounts of the last five) were made with some difficulty because the samples tended to clump in the bottle and during mixing with epoxy. We used a low-viscosity epoxy to minimize this problem. The pellets and smears were well mixed and the epoxy set without pressure. After polishing, the samples were examined at 320x to 500x magnification under oil on a Leitz Orthoplan optical microscope.

Kentucky feed samples. The first ES samples we examined were from continuous runs with the Kentucky coal feed, numbered C-24540 (3/27/86) and C-24637 (4/15/86). These samples were examined at 320x magnification.

Both samples had characteristics with which we were unfamiliar. The mean particle size of the ES samples was clearly smaller than that of the 5-minute mill-ground sample. The ES particles all had some angular faces; many were blade-shaped, arcuate, and/or pointed. The vitrinite in the ES

TABLE 16. AF separation of microbially treated ES sample (1L6)

Control (no treatment)					
%					
	Sample number	Wt	Ash	Total sulfur	Btu
Feed	C-25811		9.25	2.53	12513
Conc-1	C-25799	52.7	8.48	2.42	11750
Conc-2	C-25800	13.3	8.36	2.50	12194
Tails	C-25801	34.0	11.75	2.56	9880
Microbial treatment					
Conc-1	C-25802	70.2	9.99	2.00	12507
Conc-2	C-25803	14.4	8.51	1.72	12546
Tails	C-25804	15.4	8.95	1.70	12366

Conditions: 4-liter Denver cell, 1075 rpm, 8 scfm, 5.4 lbs/ton Airfoam for microbial run, 10.1 lbs/ton Airfoam for control.

TABLE 17. Characteristics of initial continuous ES samples

	C-24540	C-24637
Mean estimated particle size	6- to 8- μ m diameter	15- to 20- μ m diameter
Common characteristics of particles	Generally <100 μ m; particles have holes and gashes	Generally <80 μ m; particles with cracks, crevices inside them
Inertinite characteristics	Uncommon over 25- μ m; 1- to 80- μ m range	Uncommon over 25- μ m; 1- to 80- μ m range
Degree of clumping	Prominent	Prominent
Size of clumps	200 to 800 μ m long; particles <4 μ m common in centers	200 to 500 μ m long; small particles common in centers
Pyrite	Nearly complete liberation	Nearly complete liberation

samples was mottled or granular and generally had less reflectance than the macerals in the mill-ground sample, but also some areas of higher reflectance. Some vitrinite was also pocked with small vacuoles; variation in texture made it difficult to distinguish particles on the polished surface from those seen through thin epoxy. The inertinites were less affected by the ES process. The more brittle and porous fusinite particles were moderately well broken up, but the semi-fusinite particles seemed unaffected unless they were also porous before ES.

Differences in the samples (see table 17) were largely a matter of degree. Typical views of a loose clump and the inside of a larger clump are seen in figure 4. While we originally felt that some of the clumps seen were formed immediately after shattering, later work indicates this is not the case. We now believe that the distinction between clumps with

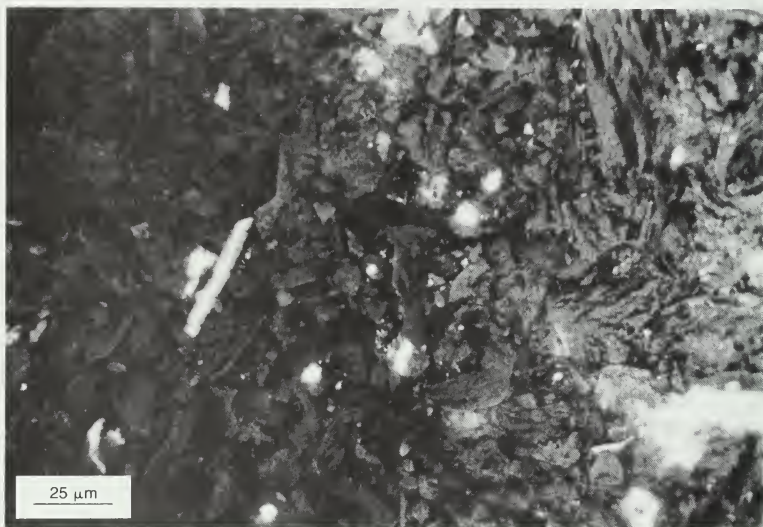
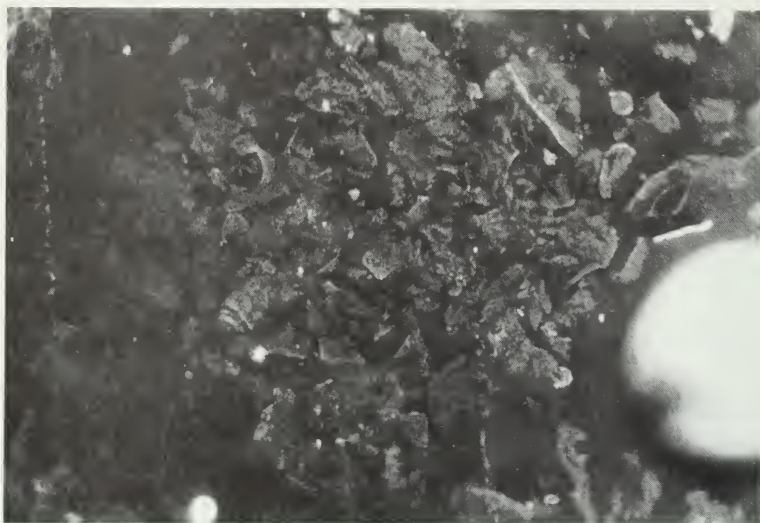


Figure 4. Views of an early ES sample (C24637) (600x); (a) loose clump with some pyrite; (b) inside of larger clump showing tight packing.

tight, unepoxied centers and those with loose, epoxied centers is related to the degree of mixing with epoxy. The pyrite was liberated and distributed widely throughout the sample; thus, most of the pyrite was found in clumps because most of the particles as a whole are found in the clumps. For comparison, the feed coal is illustrated at a similar magnification in figures 5a and 7a.

Our preliminary petrographic findings are:

- The coal particles were shattered in both samples; the mineral matter was not as finely comminuted as the macerals were.
- Clumping of the particles was a real problem, because it bound liberated minerals to maceral particles, inhibiting their separation.
- Pyrite liberation was excellent; only a few remaining pyrite grains had attached to macerals.
- The largest remaining vitrinite-dominated particles have multiple subparallel fracture/delamination planes that could be easily exploited should further size reduction be required.

To evaluate possible ways to reduce the clumping of the ES product, a set of small-batch ES runs was made with KY11 coal feed. Reactor and receiver charges were varied to evaluate whether clumping could be lowered, but temperature and pressure could not be closely controlled. The samples were received as slurries. Two control slurries were added to the set, one an ES product from the continuous ES apparatus and the other a mill-ground sample. These seven samples were freeze-dried to remove water, which was thought to contribute to clumping during sample preparation. Experimental conditions and qualitative petrographic evaluations of the samples are found in table 18.

Sample P2308 represents a base-level run with a water trap; dilute NaOH was added to sample P2309 in the trap; methanol and water was used in the trap for sample P2310; P2311 had methanol in the ES charge and methanol in the trap; and P2312 had a clay-water slurry as a trap. We observed differences in the petrographic analyses and attempted to interpret them.

Our first observation of significance was that the degree of comminution varied substantially (compare figures 5a, 5b, and 7d). Because significant comminution was found only in the first batch sample (P2308), no comparison of the effects of water, methanol, and NaOH in the receiver could be made. However, sample P2308 could be compared with the two controls, P2313 and P2314, for tendency to clump. Of the three, the continuous run ES product (P2313) showed a moderate tendency to clump, while the small ES batch product (P2308) and mill-ground control showed very low tendencies to clump (see fig. 6a). Although this is encouraging, the reasons for these behaviors are not completely clear. If it is advantageous to keep the temperature below 900°F (see following discussion) and the pressure high, then it is unclear why comminution was not also greater for P2309.

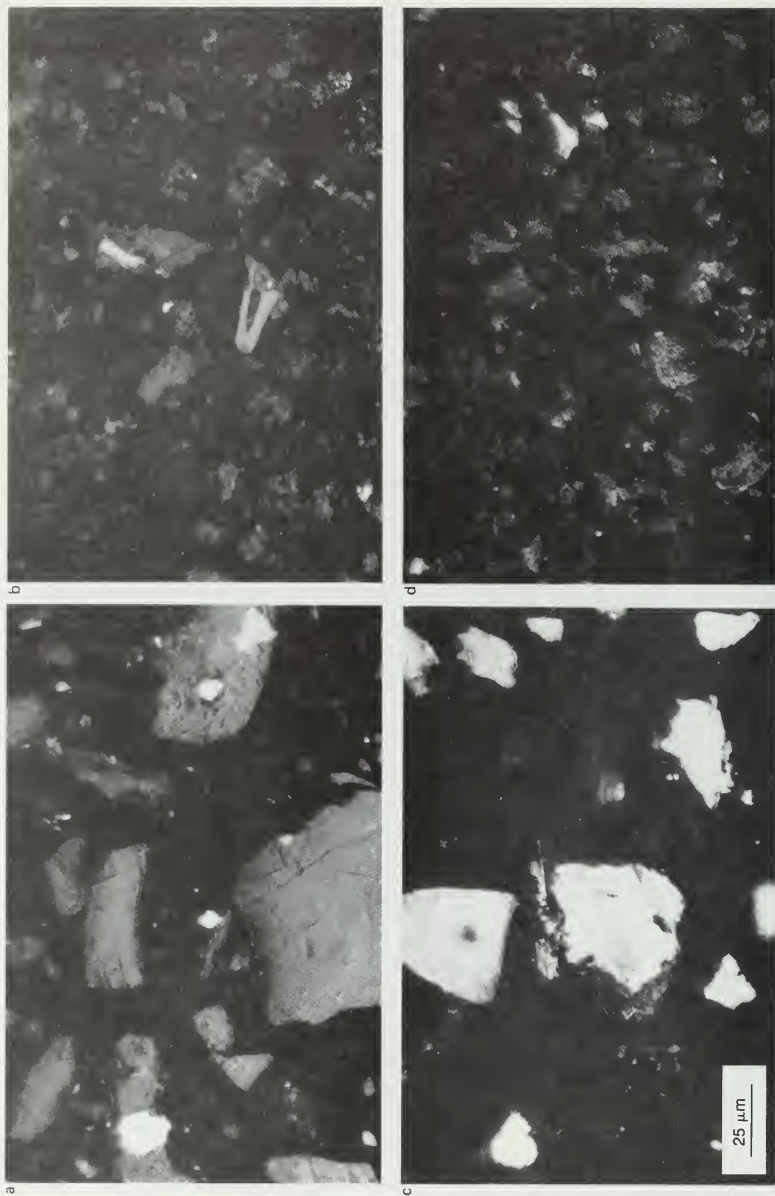


Figure 5. Views showing effectiveness of ES comminution (570x): (a) typical coal particles in the Kentucky feed coal (-80m); (b) view of batch ES product from Kentucky feed samples (P2308); (c) typical coal particles in the Illinois feed coal (-80m) (C25716); (d) typical view of continuous ES product from Kentucky feed sample (P2313).

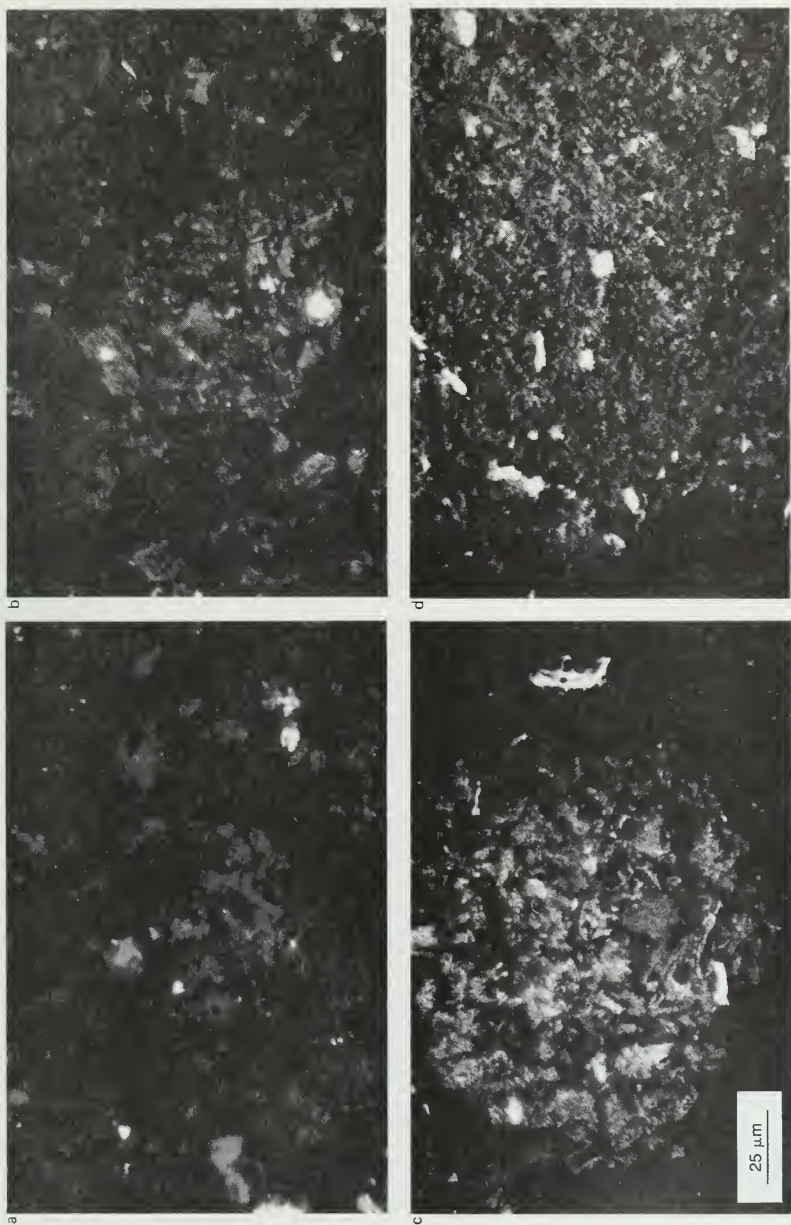


Figure 6. Views showing various degrees of clumping (570x): (a) loose cluster of small particles (P2308); (b) typical field with loose cluster including two pyrite grains (P2313); (c) cluster typical to cycloned ES products (C25719); (d) interior of tightly packed clump in ES product (C25717).

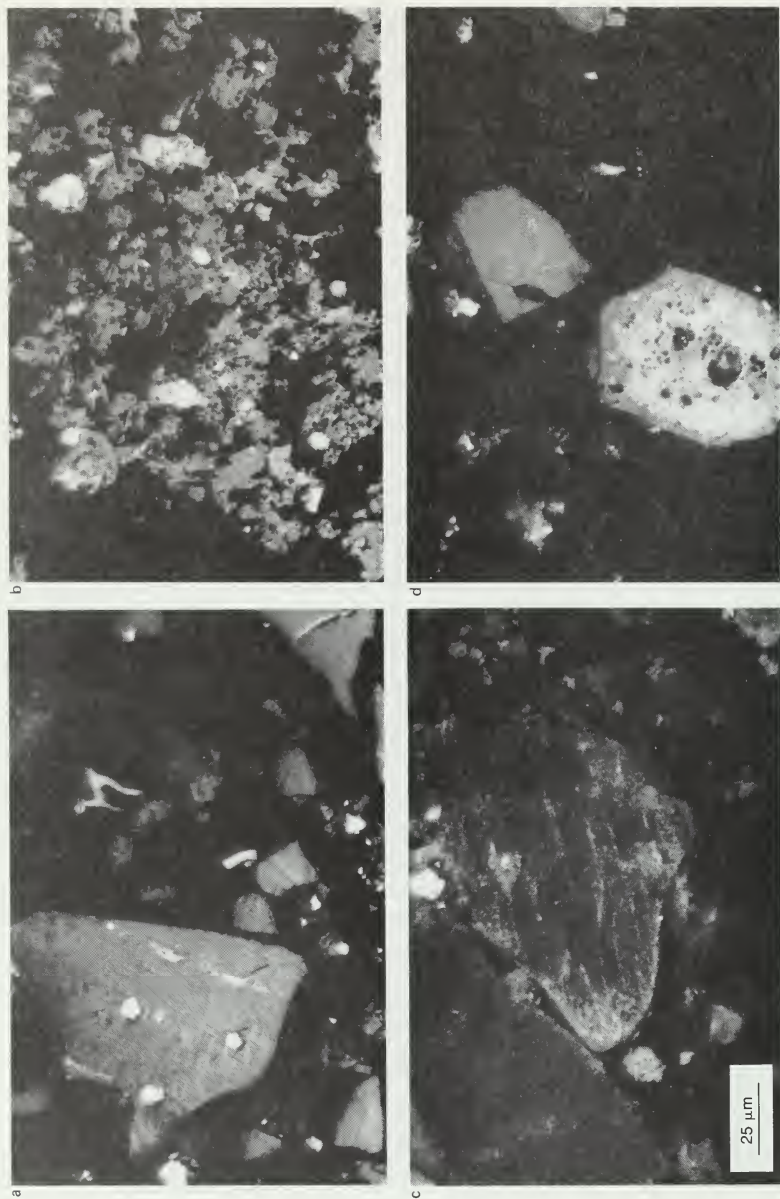


Figure 7. Views showing vitrinite alteration: (a) typical view of feed sample with both free and enclosed pyrite (C24386); (b) "popcorn" or loose cluster of several partly comminuted particles (P2309); (c) two "pillows" showing granular texture and linear zones of high reflectance (P2310); (d) two unshattered particles, one with many internal vacuoles (P2310).

TABLE 18. Experimental and petrographic data for ES batch sample preparation (KY11 Coal)

Sample no.	Reactor charge	Receiver charge	Temp. (°F)	Pressure (psi)	Degree of comminution	Tendency to clump	Notes
P2308	2 g coal 3 cc H ₂ O	10 cc H ₂ O	890	8400	Good; most particles under 15 μm apparent diam.	Very low	Inertinite particles dominate larger fraction of particles
P2309	2 g coal 3 cc H ₂ O	10 cc NaOH soln pH 10.3	880	9400	Poor; most particles over 30 μm apparent diam.	Moderate	Incomplete comminution; some alteration; "popcorn" particle common
P2310 P2310	2 g coal 3 cc H ₂ O	10 cc 50/50 mix MeOH and H ₂ O	930	7700	Very poor; most particles over 30 μm apparent diam.	Uncertain	Vitrinite alteration at maximum; "pillows" common
P2311	2 g coal 3 cc 50/50 mix MeOH and H ₂ O	10 cc 50/50 mix MeOH and H ₂ O	900	6500	Very poor; most particles over 30 μm apparent diam.	Uncertain	Some vitrinite alteration; some "popcorn" present
P2312 P2312	2 g coal 3 cc H ₂ O	10 cc H ₂ O and and 2 g Na- Montmorill- inite	910	5900	Poor*	Uncertain	Clay dominates sample after swelling
(control) Kentucky ES product P2313	---	---	---	---	Very good; most particles under 10 μm apparent diam.	Moderate	Inertinite particles dominate larger fraction of particles
(control) Ground Illinois coal P2314	n.a.	n.a.	n.a.	n.a.	Fair; most particles are under 30 μm apparent diam.	Very low	Vitrinite particles dominate larger fraction of particles

* Sample could not be separated from clays; sample evaluated at lower magnification than others.

We concluded that freeze-drying reduced the tendency of all the ES samples to clump. For the small-batch ES sample P2308, clumping was reduced to a level comparable to that of a mill-ground sample. Because the continuous run ES sample P2313 still showed a moderate tendency to clump (see fig. 6b) we concluded that: (1) clumping remains a significant problem, and (2) this problem may be more significant in samples from the continuous run. However, storing the continuous ES sample as a slurry for several months before the experiment may also have contributed to the clumping problem.

No pattern of sample variation was found to be related to reactor and receiver charges, and we did not discover why comminution was effective only in sample P2308. With the exception of P2309, comminution was poor with low-pressure conditions, but these samples subjected to low-pressure conditions (table 18) also were subjected to higher temperatures, and the higher temperatures may have produced significant changes in the samples. A possible explanation for the differences in comminution between P2308 and P2309, which reached similar maximum temperatures and high pressures, may be a break in the temperature/pressure rate curves. A break in the curve occurred for P2309, but not for P2308. If premature gas generation occurred at that point, this could explain why comminution may have occurred at the end of the test. The large vacuoles (up to 40-μm diam) in many of the unexploded particles in P2309 offer some visual support for this hypothesis.

Alteration of vitrinite was noticed in all of the ES samples, but most notably in the samples taken to 900°F and above. Three of the four samples in which comminution was poor or very poor (P2309, P2310, P2311) could be evaluated for alteration of the original particles. Two types of unusual particles were noted in these samples. The first type, called "popcorn," consists of large, partly disaggregated, vitrinite-dominated particles that tend to interlock with other particles (see fig. 7b). These generally have small vacuoles and although appearing nearly shattered, still hold together. This type was found in all three samples. The second type of particle is called "pillow" because of the rounded shape (fig. 7c); these particles are highly altered vitrinite with a granular, high-reflectance surface. They appear to have become enlarged and/or coalesced into aggregates in the 150- to 200- μ m range. Some particles showed clear evidence of devolatilization and carbonization (evidenced by increased reflectance) along linear interfaces within those particles (see fig. 7c, center). Although this was not investigated in detail, the different behaviors of some vitrinite particles probably reflect the characteristics of subpopulations of vitrinite, such as pseudovitrinite. Subenvironments within the reactor vessel at the moment of explosion may also affect the range of particular types produced.

We planned to do reflectance measurements in oil of the -80M feed (C-25386) and the test 2 sample (P2308); particles seen in continuous run samples are too small for vitrinite reflectance evaluation. Only the larger remaining particles could have been measured in batch test 2, but these were found to be inhomogeneous in reflectance. Further, that subpopulation of particles was probably biased toward higher reflectance vitrinites and semifusinite particles, so results would have been questionable for this reason as well.

Other particles in these samples appear to be vitrinite-dominated particles containing medium to large vacuoles. There are also small populations of shattered particles in these samples, presumably generated from the smaller-sized particles in the feed.

The correlation between samples with higher levels of vitrinite alteration and maximum temperature in table 18 suggests a causal relationship. Minimization of this alteration will maintain Btu levels and may also reduce levels of organic by-products produced during explosive shattering, provided that shattering can be induced at lower temperatures. Since effective shattering has been carried out at as low as 765°F, this finding suggests that 900°F should not be exceeded in future tests.

Illinois feed samples. The last set of samples examined came primarily from the Illinois sample of Herrin No. 6 Coal. It was expedient not to freeze-dry these samples; most came to us already air-dried to some degree. Identical sample preparation was followed to allow comparisons between samples.

The purpose of these runs was to see if the Illinois (IL6) sample was generally similar in characteristics to the Kentucky (KY11) sample, the principal coal used in this work. The IL6 coal will probably be used for all future efforts. We also wanted to see if adding a dispersant to the ES product affected its clumping tendency and if substituting the ITRI

TABLE 19. Petrographic data for IL6 ES feed samples, air dried

Sample No.	Degree of comminution	Particle-size range; (est. mean diam.)	Tendency to clump	Notes
C-25716 Feed to ES	screened to -80M	1 to 150 μ m -30 μ m	None	Less than 50% pyrite still enclosed; rounded particles common
C-25717 ES product	High	1 to 90 μ m under 10 μ m	High; many clumps 1 to 3 mm diameter	Semi-fusinite common in larger size fraction
C-25718 ES product with dispersant	High	1 to 90 μ m under 10 μ m	High; many clumps 1 to 2 1/2 mm diameter	Semi-fusinite common in larger size fraction
C-25719 ES product cycloned	High	1 to 90 μ m under 10 μ m	High; many clumps 1/2 to 1 1/2 mm diam.	Semi-fusinite common in larger size fraction
P2315* ES product MeOH-washed	Very high	1 to 60 μ m -8 μ m	Moderate; most are .2 to .6 mm diameter	Semi-fusinite common in larger size fraction

*Sample produced from Kentucky feed

cyclone dry trap (for the dilute NaOH solution trap) affected the clumping observed by petrography. Finally, we wanted to observe if washing the ES product in methanol eliminated clumping.

Petrographic data for these samples are found in table 19. Clumping was a problem in all shattered samples, and was mitigated somewhat only in the methanol-washed sample (P2315). Comminution was comparable to that of the Kentucky sample. Both coals behaved similarly in terms of physical breakage; there was no indication of any significant differences in behavior during ES related to differences in the two feeds. Attempts to reduce clumping by quick cycloning or addition of dispersant were ineffective.

The comparison of this sample set with the freeze-dried samples suggests that significant differences in clumping behavior may be disguised during preparation of the air-dried samples. These samples tended to be only partly dried and clumped easily. Future evaluation of clumping should take advantage of freeze-drying in removing remaining moisture so that differences due to experimental variables can be examined.

CONCLUSIONS AND RECOMMENDATIONS

The main objective of this project--to use the ES and AF process sequentially to achieve a coal product with low total sulfur and ash contents but high Btu Recovery--was unsuccessful. Although we made extensive efforts to understand the limitations of this approach we reached only some tentative conclusions. The ES process resulted in fairly complete comminution, but it also generated organic devolatilization products that coated the finely divided macerals and minerals, making both particle types highly hydrophobic. Hence, physical separations based on differences in hydrophobic/hydrophilic surface properties were minimal and ineffective. The ES product must be treated or chemically altered in order to accommodate further physical beneficiation. Although ES comminution is

effective, by-product coatings generated during ES tend to reaggregate fine particles, preventing cleaning based on physical differences.

Attempts to alter the surface characteristics of the ES product prior to AF have also failed. The use of dispersants, change of pH, ultrasonic treatment, use of electrolytes, and microbial treatment produced no noticeable beneficial effect. Extraction of the ES product with organic solvents prior to AF was the only tactic that resulted in some beneficiation; however, yield of combustibles was low.

Several other fine-coal cleaning techniques used with the ES product (oil agglomeration, flocculation, and reverse flotation techniques) were also unsuccessful.

Because organic solvent extraction of the ES product caused some beneficiation, further effort was made to understand the nature of the evolved compounds. Comparison of thermal gravimetric analyses (TGA) results for feed coal and explosive shattered product revealed significant differences, confirming that some volatilization had occurred during ES and that the nature of the volatile matter in the ES product was different from that of the feed coal. The minor weight loss of the ES product observed during TGA below 350°C was interpreted as evaporation of adsorbed oils from the ES product. Results of gas chromatography and IR analyses of the organic extract of the ES product revealed mostly mixed molecular weight polar components, thought to be compounds typical of products obtained upon heating coal. Some evidence of substantially altered vitrinite was seen in samples heated at and above 900°F; we suggest that future ES runs should be restricted to temperatures below 900°F, if possible, to avoid this damage. Throughout the project, indications of possible procedural difficulties with the "forms-of-sulfur" analyses of the ES product occurred. The oil coating on the particles probably inhibits complete extraction by HCl and HNO₃ acids in accordance with ASTM procedure D-2292. Ash and total sulfur values were not affected; however, accurate estimation of organic sulfur content is somewhat questionable, because organic sulfur content is determined by calculating the difference between total sulfur and other forms of sulfur. We are currently working on determining sulfidic (S⁼) and elemental (S⁰) forms in these materials.

Future studies that could improve our understanding of problems encountered with this approach--and possibly lead to solutions--include further efforts to:

- Optimize organic solvent washing of ES product. Some beneficiation was observed when methanol was used to extract the ES product prior to AF separation. This approach may not be economically viable at commercial scale, but investigation of the best conditions for achieving efficient AF beneficiation would be of interest.

- Reduce hydrocarbon by-products. Additional study is needed to minimize the net release of hydrocarbon by-products during ES. Testing ES at lower temperature ranges in which vitrinite alteration is minimized would probably be beneficial in this regard, as would exploitation of natural coal porosity by the ES process. Pretreating the coal with a surfactant and/or selecting a more porous feed coal could possibly produce effective shattering at lower temperatures.

the feed coal appears to have a bearing on the effectiveness of comminution, narrowing the feed particle-size range could improve qualitative assessments about comminution and changes in particle properties in future tests.

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APPENDIX A. THE EXPLOSIVE SHATTERING (ES) PROCESS

The explosive shattering process is a physiochemical coal-cleaning process that offers promise for the complete liberation of pyrite from coal macerals and the simultaneous liberation of a substantial portion of the organically bound sulfur in coal. In this process, based on selective comminution of the coal particles, the size of the organic fraction is reduced, but the mineral matter remains in a relatively unground, liberated state. The process takes advantage of the dissimilar properties of the basic components of coal. Coal is a heterogeneous mixture of mineral particles bonded together by carbonaceous cement. The mineral portion is composed largely of relatively nonporous crystalline materials, whereas the hydrocarbon constituent is mostly amorphous and porous. The explosive shattering process impregnates the pores of the coal with a fluid compressed and heated to supercritical conditions. A sudden release of the restraining pressure allows the rapid adiabatic expansion of the fluid, which in turn creates large internal stresses within the maceral particles. Stresses in excess of the tensile strength of the coal cause explosive failure that literally shatters the material to micron-size particles. Since the mineral constituents of the coal are relatively nonporous, they remain largely unaffected by the process. The shattering results in a bimodal particle-size distribution in the product: coarse, well-liberated mineral particles and fine, mostly clean hydrocarbon particles.

The forces responsible for size reduction in the explosive shattering process depend on the energy available for evaporation of the water within the pore spaces. This energy, in turn, depends on the volume of supercritical water present in the pore spaces, the enthalpy of the supercritical water after expansion, and the total fraction of water in the pore spaces that is converted to steam. All of these factors can be included in a term called net enthalpy available for shattering, which is defined as:

$$NE = (H_{SW} - H_{LW}) F_{WS}$$

where

NE	is net enthalpy available for shattering, expressed per unit volume
H_{SW}	is the enthalpy (per unit volume) of supercritical water at temperature and pressure before expansion
H_{LW}	is the enthalpy of liquid water or normal boiling point expressed per unit volume
F_{WS}	is the fraction of total water converted to steam during expansion

Increasing the net enthalpy of water present in the pore spaces will increase the energy available for comminution and decrease the average size of the product. Average particle size of shattered coal decreases logarithmically with increase in the net enthalpy of water prior to expansion.

The particle-size distribution of the shattered product is usually determined on the feed material (including hydrocarbons and ash), using a Leeds and Northrup Microtrac instrument. The mineral fraction of selected samples was separated from the bulk material by low-temperature ashing to determine its size distribution. Size-distribution data obtained on the feed sample and mineral portion are shown in figure A-1 and A-2, respectively, for feed and shattered coal. The particle size of the product was reduced from about 60 microns (feed material) to about 3 microns, whereas the average size of mineral particles in both feed and shattered product remained about the same. These data show that the shattering produces selective comminution of the organic material present in coal.

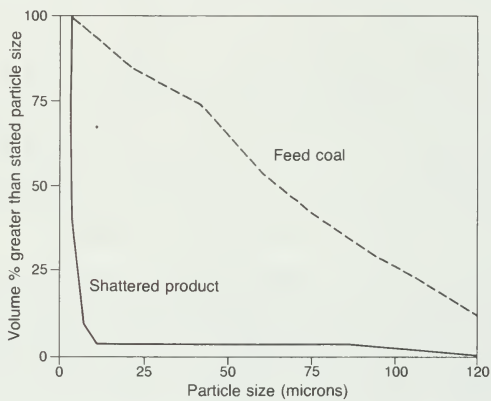


Figure A-1. Size distribution of feed and product for Illinois coal (IL6).

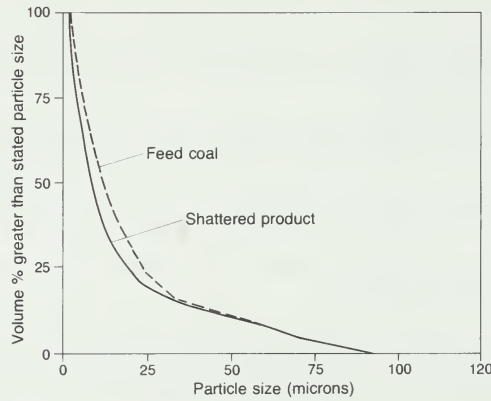


Figure A-2. Mineral particle-size distribution in feed and explosively shattered Illinois coal (IL6).

APPENDIX B. ISGS AGGREGATE FLOTATION (AF) PROCESS

During the past four years The Illinois State Geological Survey (ISGS), in conjunction with researchers at Northwestern University (NU) and Southern Illinois University (SIU), has been developing an ultrafine (-400 mesh) advanced physical coal-cleaning process. The AF process, which utilizes conventional froth flotation equipment and ultrafine grinding technology to liberate pyrite and mineral matter from coal, has been shown to be quite effective. Restrictions in achieving effective separation of ash and pyrite from ultrafine coal have been overcome by utilizing "chemically selective" reagents. By taking advantage of differences between the surface chemistry of coal, mineral matter, and pyrite and applying principles based on coal surface properties/reagent composition to solve the problem of inefficient separations, extremely positive results have been attained.

A feature of the AF Process is a selective aggregation (aggregation encompasses selective agglomeration or selective coalescence as well as flocculation) of fine coal particles that have been made more hydrophobic by relatively low concentrations of proprietary collectors. As in conventional froth flotation, air bubbles are used. They give buoyancy to the aggregated coal, and provide a physical means for separating clean coal from ash-forming mineral particles (including pyrite). An advantage of this means of separation is that it can be carried out in conventional flotation cells. Additionally, the size of the bubbles, which must be small for fine coal, is controlled predominantly by the choice of the foaming surfactant, the collector, and the degree of agitation rather than by mechanical equipment design alone. The AF Process has advantages generally ascribed to froth flotation and oil agglomeration processes but not the major disadvantages of each (limited applicability to fine coal and high chemical costs, respectively).

The typical AF run includes the preparation of a desirable size of feed coal (such as 80% -400 mesh) by such techniques as rod milling or stirred-ball milling. A suitable pulp density ranging from 3.5% to 4.5% solids is obtained; the feed is then placed into a sub-aeration cell, and the impeller speed is set to 1075 rpm. The slurry is agitated so that it is thoroughly mixed, and after a time a known quantity of selective reagent is added and mixed for 2 minutes. Air is then introduced into the cell, and a coal-laden froth is produced; the froth is hand scraped from the top of the cell into collection receivers. The solids and liquids from the froth concentrates and tailings are separated by filtration, dried, and weighed.

- The AF process can achieve more than 80% Btu recovery while rejecting more than 70% of the pyritic sulfur and ash in run-of-mine coal.
- An additional 40% to 50% reduction in ash and pyrite can be obtained for pre-washed coals while maintaining more than 80% Btu recovery.
- The AF process produced a coal-water slurry at <1% ash and sulfur on an Appalachian coal, the Cedar Grove (VA) Seam Coal.

- Conventional or nonconventional froth flotation equipment can be used in the AF process. The unique character of microbubbles required to improve recovery and selectivity of ultrafine coal is controlled by specific, proprietary reagents.

- The AF process has achieved as great or greater ash and pyrite rejection than have conventional processes such as calcium flotation, froth flotation, and oil agglomeration.

- Results obtained from scale-up trials in continuous-flow units (30, 250, and 1000 lbs/hr), have been comparable to results obtained on a laboratory batch scale.

- AF has recovered salable product from waste streams and gob. Preliminary results on both feeds show high Btu recovery (80%) with reasonable ash rejection. A pre-cleaning step, such as tabling, may be required for processing gob.

- AF removes toxic trace elements and chlorine more effectively than does conventional froth flotation.

- Petrographic methods are useful in assessing the size and association of pyrite grains in feed and processed coal samples.

- X-ray diffraction has been used to determine the relative ease of removal of sulfur and ash-forming minerals in feeds, concentrates, and tailings from the AF process. The general order for ease of removal is calcite > pyrite > quartz > kaolinite > marcasite > illite > mixed layered, illite/smectite.

The technical objective of AF research is to develop an efficient and economical process to reduce pyritic sulfur and ash from difficult-to-clean Illinois Basin bituminous coals. Examination of other coals, including Appalachian Basin coals, has indicated that the process would be equally applicable to such coals.

The Illinois coal industry is struggling to compete in local, national, and international markets with coal that is lower in sulfur. Competition with western U.S. coal producers is intense and will continue to increase with implementation of pending proposed legislation requiring less SO₂ emissions. Since most Illinois Basin coals contain from 2% to 5% total sulfur (roughly equal amounts of pyritic and organic forms of sulfur), physical and chemical methods that remove both forms of sulfur must often be used to achieve compliance coals. Currently accepted practice is to remove SO₂ produced from combustion by means of flue gas desulfurization, which is capital intensive, is costly to operate, and generates wastes that are difficult to dispose of.

Desulfurization methods aimed at removing the organic forms of sulfur are generally expensive, since they involve the use of chemicals, heat, and pressure. Commercial methods used for limited removal of coarser pyritic sulfur are fairly cost effective but can be relatively inefficient. For instance, gravity based methods often remove coarse pyrite (+6 mesh) but leave the finely disseminated mineral matter trapped within the coarse clean-coal fraction. Even the present methods available for fine-sized

coal that are based on surface properties tend to be limited with regard to either cost or the efficiency of separation.

Although processing by froth flotation of 28x0 mesh feed in domestic coal preparation plants has become more prevalent as mining has become increasingly mechanized, flotation has been primarily used for recovering fines (28x100 mesh) and for reducing the ash-forming minerals in the fines. Recovery of this fraction has become an economical and environmentally sound procedure for recovery of marketable product representing up to 20% of the plant feed. Unfortunately, traditional flotation of feed of this size does not significantly reduce the pyritic sulfur or associated mineral particles in Illinois coals.

One method for unlocking enclosed pyrite is extensive comminution to ultrafine sizes (<400 mesh), but this procedure yields a coal product that can be difficult to separate from mineral matter on either a wet or dry basis. The numerous wet processes for separation of ultrafine coal from mineral matter include oil agglomeration, selective flocculation, coal-pyrite flotation, and dry processes such as high gradient magnetic separation. All have been reported to be successful at reducing pyritic sulfur in coal. Nevertheless, because of extensive retrofits and unproven at full-scale process testing, a number of researchers feel that some form of the froth flotation process will ultimately be the preferred method for removing pyrite and ash from ultrafine coal. Currently there are obstacles preventing its immediate implementation.

A significant problem in floating ultrafine coal is the decreased flotation rate and resulting loss of recovery in comparison to that in fine coal. In a flotation process, the coal particle must first collide with a rising air bubble, and then surface interactions cause the particle to adhere to the air bubble as it rises to the collection zone. The probability that a particle and bubble will collide is adversely affected by smaller coal particle size, lower mass to size ratio, surface charges on the particles, and stream lines around the bubble. A decrease in recovery at ultrafine sizes is due in part to a reduced probability of bubble/particle collision.

Additionally, reagent selectivity, which is based on hydrophobic/hydrophilic interactions between the flotation reagent and the coal surface in an aqueous environment, can significantly influence the overall effectiveness of coal flotation processes. Adhesion of particles to bubbles is affected not only by these interactions but by the natural hydrophobicity of the coal particle, induction time, balance between bubble growth and coalescence, and surface tension. The flotation of ultrafine coal can therefore be significantly affected by many process parameters.

Attempts to control the rate of flotation of ultrafine coal by using microbubbles have been reported (Yoon, 1984). Introduction of externally generated microbubbles into a column of ultrafine coal improved recovery and product quality over that of conventional subaeration cells. However, considering the widely differing frother dosages used for comparison with the control, the actual effectiveness of the experiment is debatable.

The concept of microbubble flotation, nonetheless, does attempt to take advantage of the differences in particle and bubble diameter dependencies; a mathematical relationship has been defined by Jameson et al. (1977), and Yoon (1984) regarding rate of flotation and bubble/particle size. Yet as coal particles become smaller, not only will the specific surface area increase significantly, but surface charges and chemical interactions with the reagent will become increasingly important in controlling the process. Microbubbles, in and of themselves, may not completely control effective flotation of ultrafine coal.

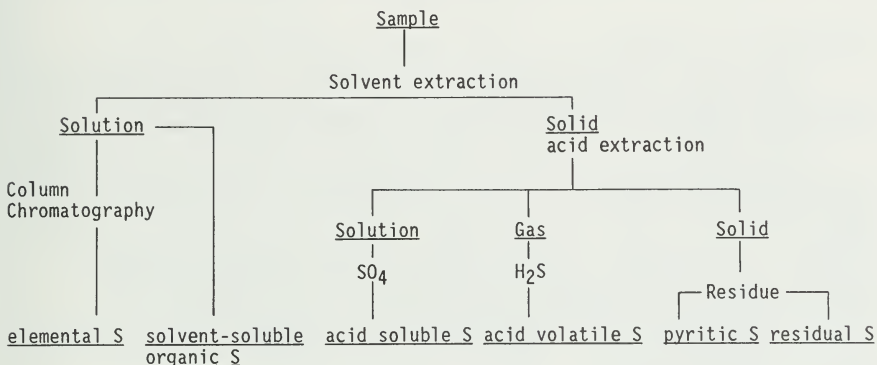
The ISGS Aggregate Flotation process attempts to incorporate both generation of fine bubbles and chemically controlled interactions in the flotation of ultrafine coal. The bubbles are generated in situ and their size is controlled by a surfactant. The surfactant can be combined with either an alcohol and/or an oily collector, such as kerosene; this helps increase the specific surface area of the alcohol reagent and collector by emulsification and enhances the bond attachment of the apolar agent to the fine-coal particle. With enhanced stability of collector attachment, the adhesive bond (chemisorption) between the coal particles and the air bubbles is strengthened, resulting in improved recoveries. With the preferential adsorption of the charged surfactants onto the coal surfaces, both ash and pyrite rejection are subsequently improved.

Results to date indicate substantial potential for physically beneficiating coal by grinding it until optimum mining matter liberation occurs, as indicated by petrographic analyses. The coal is then selectively floated with foaming surfactants, which promote the stabilization of smaller bubbles and the formation of coal-air aggregates. Very high Btu recoveries (80% to 90%) and excellent rejections of pyrite and ash (70% to 90%) have been obtained for most of the coals tested, utilizing presently available conventional froth flotation equipment. The initial economic evaluation is quite encouraging.

APPENDIX C. FORMS-OF-SULFUR CHARACTERIZATION

Determinations of elemental sulfur and acid volatile sulfides are not included in the analytical methods recommended by ASTM committee D-5 (procedure D-2492). Analytical procedures for these two sulfur forms are being developed by the ISGS Coal Analysis Laboratory for a CRSC-funded proposal titled "Forms of Sulfur: A fractionation scheme for coal pyrolysis products" (Project No. 1-5-90249). According to this proposal, total sulfur in coal and its high-temperature derivatives are fractionated into elemental sulfur, solvent-soluble organic sulfur, acid-soluble sulfur, pyritic sulfur, and residual sulfur.

This flow sheet shows the unified fractionation scheme.



The forms of sulfur of special interest to this project are elemental and acid volatile (sulfidic).

Elemental sulfur

Coal or char samples are solvent extracted by a micro-Soxhlet extraction technique. Either methylene chloride or cyclohexane is used in this procedure. The later solvent is preferable because of its lack of absorption spectra in the region of 200 to 350 nm.

When added to cyclohexane, the elemental sulfur shows two broad absorption peaks at 233 and 256 nm. It is possible that the solvent extracts from coal, after being passed through a clean-up chromatographic column, can be used for quantitative determination of elemental sulfur by using second derivative analyses of the UV absorption peaks; this procedure is being investigated. Meanwhile, the following procedure is used. A coal or char sample is weighed into a 10x50-mm soxhlet thimble having a maximum loading capacity between 1 and 2 grams. The sample is extracted for 72 hours in a micro-Soxhlet extraction unit using approximately 30 ml of cyclohexane (B.P. 81°C). The extract is then diluted to volume (25 ml) using the same

solvent. An aliquot is taken for chromatography. The chromatographic column is made in a 15x250-mm column packed with a 100-mm bed of activated Florisil (60 to 100 mesh activated at 540°C for 1 hr and 130°C for 3 hrs). The clear eluate is evaporated to dryness using a rotary evaporator. Five ml of 0.2% NaCN in 95% acetone/5% water solution is added to the flask. The solution is mixed and allowed to stand covered for 2 minutes. Five ml of 0.1% FeCl₃ in acetone is added to the mixture. The absorbance of the solution is determined by spectrophotometry at 465 nm. Beer's law is observed beyond 50 ug elemental sulfur/ml. The color is stable for at least 2 hours if the solution is kept covered and stored in darkness. In most cases, the elemental sulfur concentrations obtained for samples of coal following explosive shattering are quite low, ranging from less than 1 µg/g to 204 µg/g. This seems to indicate that oxidation of pyrite to elemental sulfur is minimal. However, if elemental sulfur were produced by ES, it might be lost in the heating process and deposited in the vessels or exit gas lines.

Acid-volatile sulfides

The residue remaining in the extraction thimble is vacuum dried and stored in an inert-atmosphere desiccator until ready to be analyzed. The following procedure is used for the explosive shattered samples.

The thimble is dropped into a boiling flask connected to a distillation column through which a constant flow of nitrogen gas is maintained. An aliquot of dilute phosphoric acid (2 M) is added to the sample via a side-arm, pressure-equalized delivery funnel. The H₂S released from the sample is absorbed in a solution of 2 M NaOH containing an ascorbic acid-EDTA mixture. The resulting sulfide is then titrated with a lead perchlorate solution employing a sulfide-sensitive specific ion electrode as the indicator. The end point is observed at -765 mv. When sulfide concentration is low the response of the electrode is not rapid enough to overcome possible oxidation by air.

The procedures for determining the elemental sulfur and acid volatile sulfides used in this investigation are parts of the ongoing method development for the unified sulfur fractionation scheme for feed coal and its pyrolyzed derivatives. This scheme requires that a coal sample be carried throughout the entire fractionation procedure; hence, the coal or char sample is weighted into the cellulose soxhlet thimble and elemental sulfur is the first species determined. This initial solvent extraction has an advantage, because samples that normally are not wettable by water become wettable and can be treated with dilute acid used in the subsequent method for acid-volatile sulfide.

APPENDIX D. REMOVAL OF ORGANIC SULFUR THROUGH EXPLOSIVE SHATTERING PROCESS

The treatment of hydrocarbons such as coal with supercritical water liberates a significant portion of the organic sulfur and offers the possibility of producing fine-coal particles that are low in organic sulfur. Samples of shattered coal, processed from Illinois Herrin No. 6 coal during 1978, were analyzed to determine if the organic sulfur content of the coal macerals in the feed coal was decreased by explosive shattering. Sulfur-scavenging minerals (shown in table D-1) were added to the product to adsorb any released hydrogen sulfide and other sulfur-containing compounds and to prevent reabsorption of the sulfur compounds on the coal. All of the scavengers used in these studies were crushed from natural minerals to -60/+325 mesh and were added in amounts twice the stoichiometrically required quantities to react with all of the sulfur present in the coal. Table D-1 shows the results of the experiments.

The sulfur distribution reported in table D-1 was obtained by determining the total sulfur content of the coal after combustion in a bomb and subsequent precipitation of the sulfur as barium sulfate. The organic portion of the coal was removed by low-temperature ashing of the samples under an activated oxygen plasma, and the remaining mineral matter was analyzed to determine the inorganic sulfur content. It is possible that a small amount of oxidation of FeS or FeS₂ might have occurred during low-temperature ashing. The organic sulfur content was determined by difference.

TABLE D-1. Evaluation of sulfur scavenging mechanisms during explosive shattering of coal

Sample	Sulfur scavenger	Sulfur (%)			
		Organic	Inorganic	Total	Organic/ inorganic
Feed	---	1.19	1.81	2.99	0.66
Product	---	1.54*	1.31	2.85	1.18
Product	Fe ₂ O ₃	0.43	1.64	2.06	0.26
Product	ZnO	0.39	1.25	1.64	0.31
Product	Cu ₂ O	1.03	1.04	2.07	0.99
Product	CaO	0.23	1.97	2.20	0.12

*The increase in organic sulfur content of the product is probably due to reabsorption of sulfur compounds on coal particles.

TABLE D-2. Reduction in sulfur content of shattered samples

Analysis	Sulfur reduction from feed (%)			
	Dry sample from cyclone	Condensed with caustic	Wet sample with calcite	Wet sample with hematite
Total sulfur	32	33	41	36
Sulfate sulfur	81	91	90	100
Pyritic sulfur	32	35	37	22
Organic sulfur	18	16	35	37

Feed coal: KY11
Shattering conditions: 767°F and 5050 psi
Mean particle size: 12.3 microns

The addition of sulfur scavengers decreased the organic sulfur content of the shattered product by as much as 80%. Calcium oxide produced the best results.

Addition of sulfur scavengers was also investigated under the current explosive shattering program in experiments using the KY11 coal. Distribution of sulfur between organic and inorganic forms was determined using the standard ASTM procedure (D-2492). Results shown in table D-2 indicate that organic sulfur content of the product decreased by about 17% without the addition of sulfur scavengers and by about 36% after the addition of sulfur scavengers. Additional data shown in table 9 of the main part of this report also showed a 36% reduction in organic sulfur. We believe that shattering the coal to produce finer particles (2 to 3 microns) will liberate larger quantities of organic sulfur.

