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Control of Pyrite Surface Chemistry in Physical Coal Cleaning

by

G. H. Luttrell, R. H. Yoon and Z. S. Ou

Virginia Center for Coal and Minerals Processing
Department of Mining and Minerals Engineering
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0258

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Program Officer

Robert Dolence
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

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ABSTRACT

The successful separation of pyrite from coal by flotation is dependent to a large extent upon the selectivity of the process, and the use of a pyrite depressant is one of the most important and cost-effective techniques for achieving this.

This report evaluates the effects of three factors on the floatability of pyrite. These are 1) the superficial oxidation of pyrite, 2) the contamination of pyrite surfaces by carbonaceous matter, and 3) pulp redox potentials. XPS (x-ray photoelectron spectroscopy) and IR spectrometry have been used to identify surface reaction products. Microflotation, laboratory-scale conventional flotation and microbubble column flotation were used to quantify the effects of these factors.

It was found that low (reducing) pulp potentials are effective depressants of pyrite (more so for fresh, unoxidized samples than for oxidized samples), whilst at the same time do not materially affect coal flotation.

INTRODUCTION

The primary objective of this research is to generate fundamental information on the surface properties of coal pyrite as they relate to advanced physical coal cleaning (APCC) processes. This goal is being met by: (1) investigating the mechanisms responsible for the inefficient rejection of coal pyrite and (2) developing schemes for improving the rejection of coal pyrite based on information gathered from part (1).

Flotation is an important method for the removal of pyrite from coal because pyrite is typically only liberated at flotation sizes and because flotation is often used to recover marketable coal from fines and/or refuse streams [1]. Unfortunately, little success has been achieved so far because the coal-pyrite flotation separation is insufficiently selective.

Many different reagents have been studied as pyrite depressants in coal flotation, including pH modifiers, oxidizing or reducing agents, natural and synthetic organic polymers, dyes and some chelation compounds [2,3,4,5,6]. Hydrolyzed metal ions have also been proposed as pyrite depressants [7]. Many of these reagents show good selectivity with some coals, although flotation performance is often determined by the dosage rate of a particular depressant, since pyrite depressants are often also good coal depressants at similar or higher dosages [5]. Therefore, great care must be taken when any pyrite depressant is used in coal flotation.

Other strategies proposed to improve sulfur removal include reverse flotation using sulphydryl collectors to float pyrite while depressing the coal with organic polymers [8,9], and the "Grab and Run" technique, which uses starvation reagent addition rates under gentle, strictly controlled operating conditions in rougher flotation to yield a low-sulfur clean coal. The rest of the recoverable coal is typically recovered to a scavenger coal concentrate under more intense operating conditions and further desulfurized, either by reverse flotation or by pyrite depression [1]. However, these approaches are not effective for all coals and the performance varies from coal to coal [10].

It is well known that pyrite particles often appear in the froth product for reasons other than mechanical entrapment and coal-pyrite locking. Free coal pyrite often possesses some floatability as a result of contamination by carbonaceous matter [4] and/or superficial oxidation to form elemental sulfur and metal-polysulfides, which are inherently hydrophobic [11,12,13]. Therefore, it is logical to conclude that the control of the oxidation-reduction potential of the slurry might prevent surface oxidation and/or remove surface oxidation products so that pyrite flotation could be reduced.

The objective of the work this quarter was to evaluate the effects of superficial oxidation and/or coal contamination of pyrite surfaces on the flotation of the pyrite and to investigate the conditions of pyrite depression in coal flotation through the control of pulp oxidation-reduction potentials.

EXPERIMENTAL MATERIALS AND PROCEDURES

Large chunks of coal pyrite from a Chungking coal mine (Sichuan Province, Peoples Republic of China) and from the Pittsburgh No. 8 seam were used as the pure pyrite for this study. A coal-contaminated pyrite sample assaying 69.59% ash, 40.55% sulfur and 1.74% fixed carbon and consisting of specimens 10 mm and larger was also selected from the Chungking coal pyrite and stored. These samples were ground in an iron mortar with an iron pestle to 100x150 mesh shortly before testwork to minimize the influence of surface oxidation.

The coal samples used for the study were a high-sulfur coal from the same Chungking coal mine, a sample of Illinois No.2 and a sample of Upper Freeport coal. The Chungking coal is difficult to de-ash and de-sulfurize, and SEM examination shows that the ash-forming minerals and pyrite are finely disseminated in the coal matrix (Fig. 1). The analyses of these samples are given in Table 1.

Table 1. Analyses of Coal Samples Used in the Study.

Coal Sample	% Ash	% S_{Total}	% S_{Pyrite}	% Fixed Carbon	% Volatile Matter
Chungking Coal	32.74	3.63	2.91	49.77	17.49
Illinois No. 2	6.90	2.84	1.63	53.30	39.80
Upper Freeport	17.65	2.25	1.80	-	-

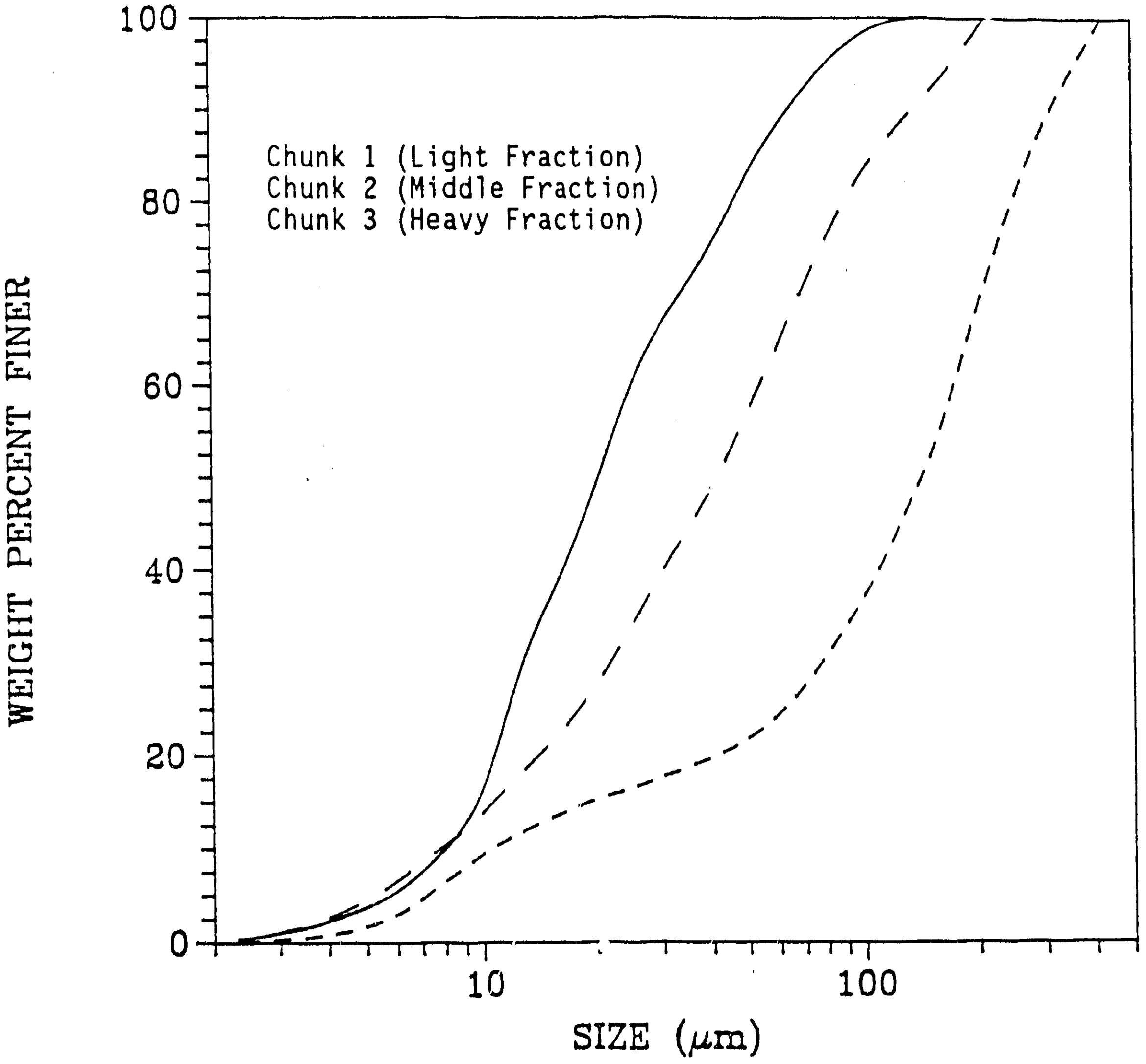


Figure 1: Pyrite size distribution for Chungking coal.

Chemical reagent grade pyrogallic acid ($C_6H_3(OH)_3$, from Fisher Scientific) was used as the pyrite depressant. This is a stable, active organic reductant that acts to reduce the potential of the flotation pulp. Pulp pH was adjusted by adding KOH or HCl.

The floatabilities of the different 100x150 mesh coal pyrite samples were determined for various reagent/pH conditions using the 120 ml microflotation cell shown in Figure 2. For tests on fresh, unoxidized coal pyrite, about 0.9 gram of sample was deslimed and conditioned in 100 ml of solution containing the depressant at desired concentration and pH for 5 minutes and then was floated with 0.5 ml/l of MIBC (99% purity, purchased from Aldrich Chemicals) for 2 minutes using pure nitrogen at a flow rate of 40 cm^3/min. Because the fresh, unoxidized coal pyrite samples floated poorly, 0.1 ml/l of kerosene was also used to enhance their floatability. For the tests on pre-oxidized coal pyrite, the samples were deslimed, conditioned in double distilled water for 15 minutes at the desired pH, and then transferred to the cell and floated with 0.5 ml/l of MIBC for 2 minutes. For the microflotation tests on oxidized clean coal, 65x100 material was soaked in a 0.3% H_2O_2 solution at room temperature for 7 days, filtered and dried at 60°C and then stored in a bottle for subsequent use.

Bench-scale, conventional flotation testwork with the Chungking coal sample was conducted in a Denver mechanical flotation cell. The coal was pulverized by stage crushing in hammer mills to 100% minus 32 mesh (0.5 mm). In each test, 250 grams of coal was pre-conditioned in 5 liters of tap water for 10 minutes, followed by 5 minute conditioning with depressant and 1 minute conditioning with 100 μl of DowFroth MF150. Five froth products were collected, at 0.5, 1, 2, 4, and 8 minutes from the beginning of froth overflow, to generate grade-recovery curves.

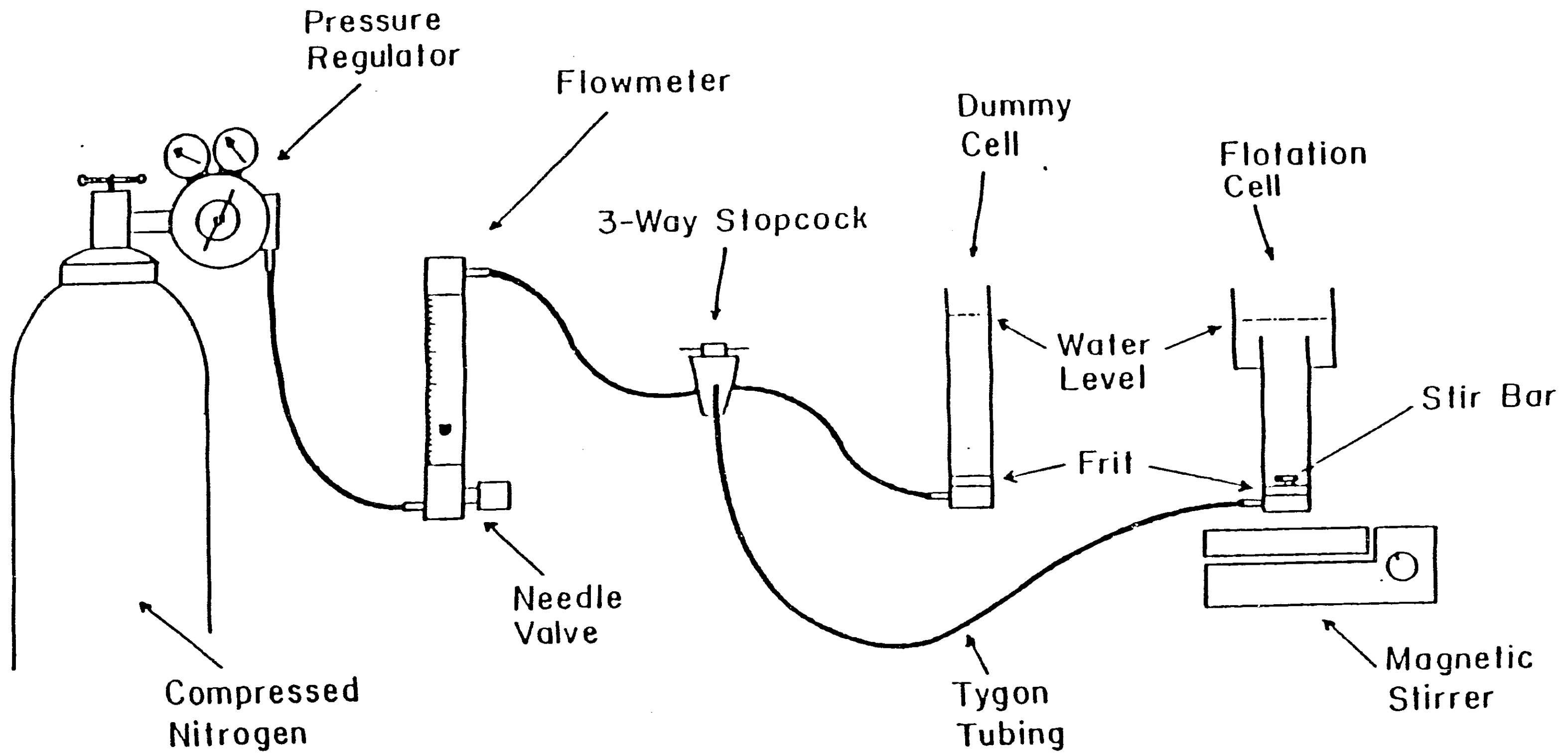


Figure 2: Schematic diagram of the micro-flotation apparatus.

For better sulfur rejection, samples of the 3 coals were further ground in a stirred ball-mill for 5 minutes to a nominal -200 mesh and then floated in a 2 in. diameter microbubble flotation column. The following procedure was used in all tests: 1200 grams of feed coal was pulped in a conditioning tank with 22.8 liters of tap water (equivalent to 5% solids). When required, Kerosene (1 lb/ton of solid) was added to the tank and conditioned for 5 minutes. The pH and Eh of the pulp were recorded at this time, and then the column was started and adjusted. Froth product and tailing were collected for assay after the column had reached steady state (about 15 minutes after the final adjustment). Following this, depressant was added to the conditioning tank, changes in pH and Eh of the pulp were recorded, the system was brought to steady state, and further froth product and tailing samples were collected.

To investigate the mechanism of depression, unoxidized and depressant treated pyrite surfaces were examined by x-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

The dependence of the floatability of Chungking coal pyrite on conditioning time in distilled water is illustrated in Figure 3. This shows that the fresh, unoxidized coal pyrite surface is basically hydrophilic, but that flotation recovery increases sharply with increasing conditioning time in the first 20 minutes and then slowly approaches a maximum value. Again, this is evidence that hydrophobicity of coal pyrite surfaces can be induced by initial superficial oxidation. The hydrophilicity of unoxidized coal pyrite surfaces can be seen in Figs. 4 (c) and 5 (c), which show the floatability of freshly ground Pittsburgh No.8 and Chungking pyrite *vs.* pulp pH in the presence or

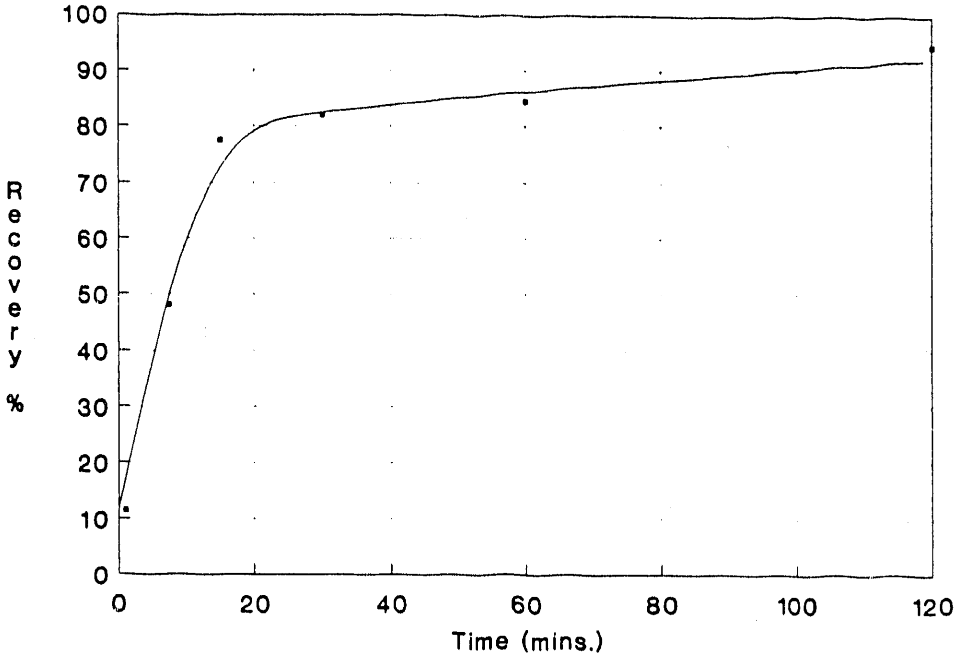
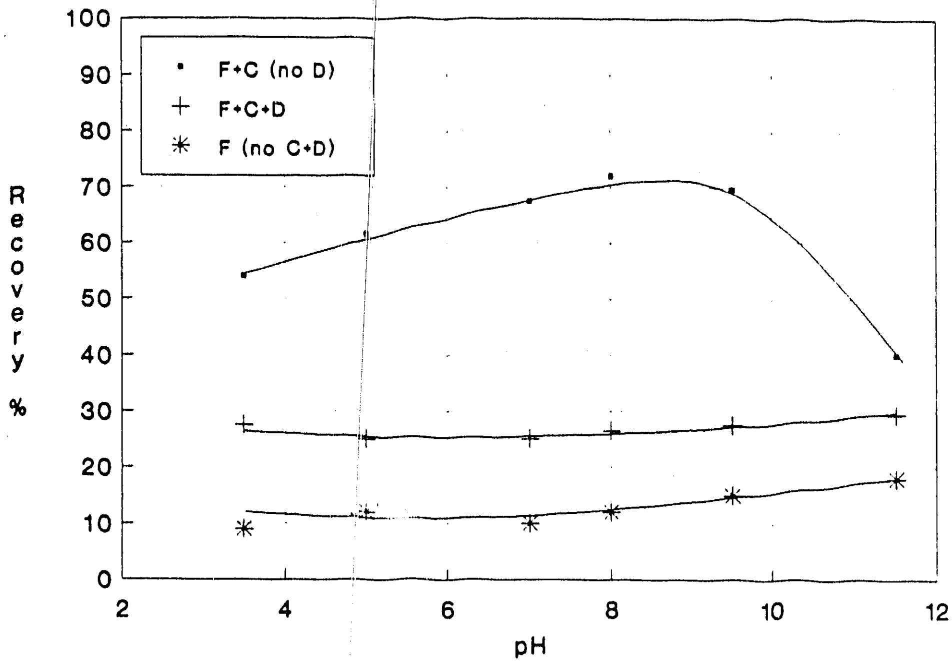


Figure 3: Dependence of the floatability of Chungking pyrite on the time of conditioning in distilled water.

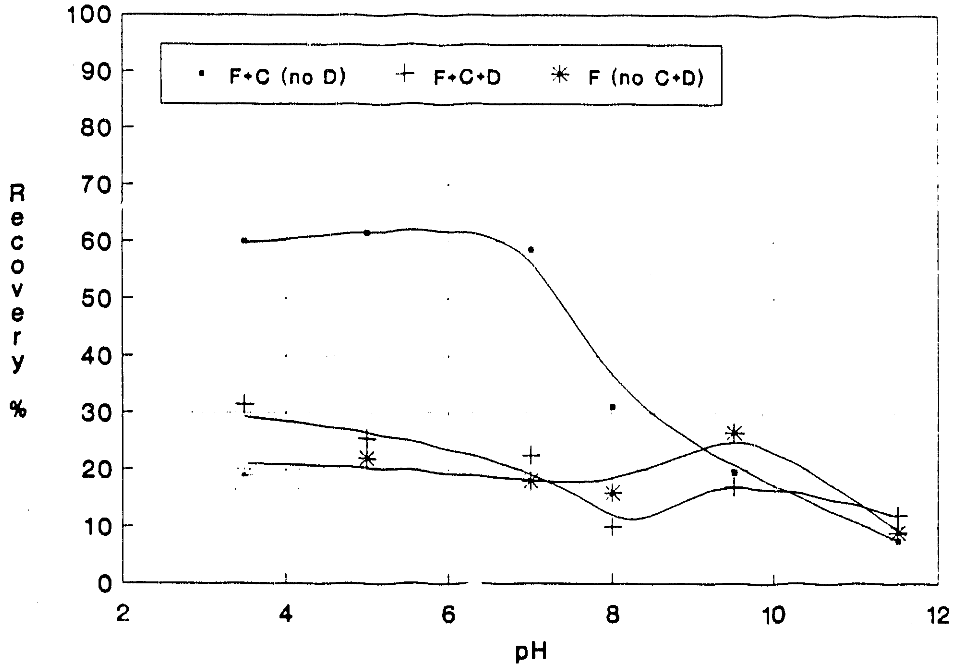


F+C (no D):
0.5 ml/l MIBC
0.1 ml/l Kerosene
No $C_6H_3(OH)_3$

F+C+D:
0.5 ml/l MIBC
0.1 ml/l Kerosene
$1x10^{-3}M\ C_6H_3(OH)_3$

F (no C+D):
0.5 ml/l MIBC
No Kerosene
No $C_6H_3(OH)_3$

Figure 4: Floatability of freshly ground Pittsburgh No. 8 pyrite *vs*. pulp pH.



F+C (no D):
0.5 ml/l MIBC
0.1 ml/l Kerosene
No $C_6H_3(OH)_3$

F+C+D:
0.5 ml/l MIBC
0.1 ml/l Kerosene
$1x10^{-4}M\ C_6H_3(OH)_3$

F (no C+D):
0.5 ml/l MIBC
No Kerosene
No $C_6H_3(OH)3$

Figure 5: Floatability of freshly ground Chungking pyrite *vs*. pulp pH.

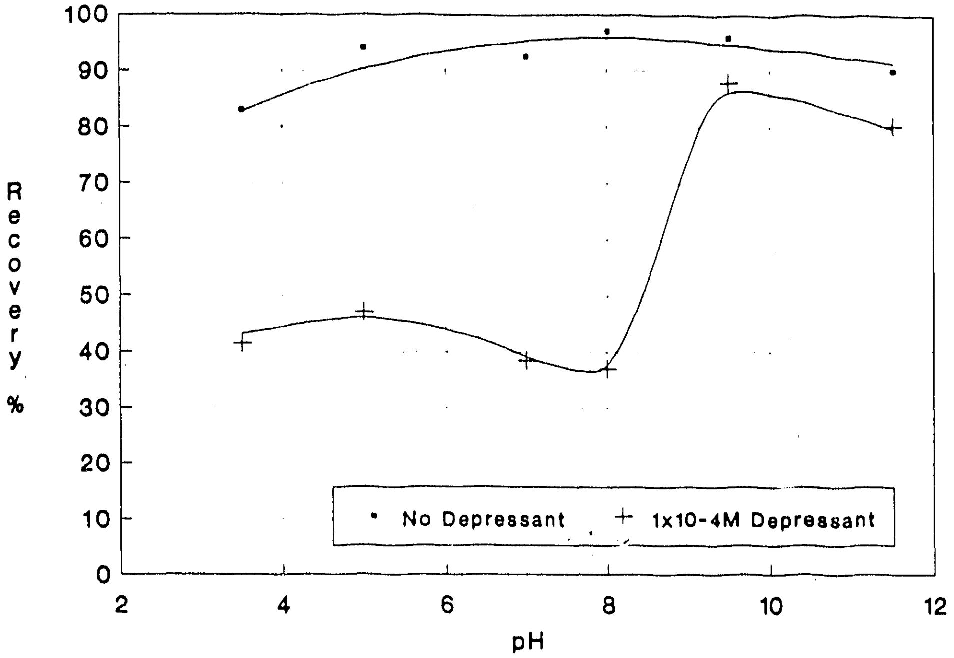


Figure 6: Floatability of coal-contaminated Chunking pyrite with 0.5 ml/l of MIBC and 0.1 ml/l of kerosene *vs.* pulp pH in the absence or presence of depressant.

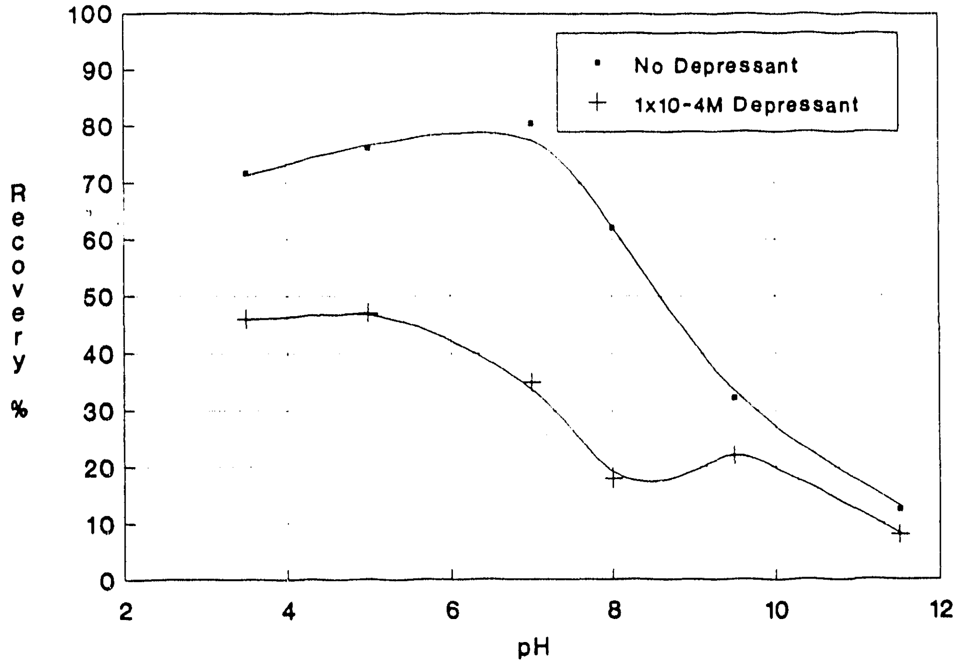


Figure 7: Floatability of superficially oxidized Chungking pyrite with 0.5 ml/l of MIBC (no kerosene) *vs.* pulp pH in the absence or presence of depressant.

absence of depressant. These figures also demonstrate that the kerosene-enhanced flotation of Pittsburgh No. 8 and Chungking pyrite can be depressed efficiently with $C_6H_3(OH)_3$. However, if the pyrite surface is oxidized, depression of pyrite by $C_6H_3(OH)_3$ is less efficient, as shown in Fig. 7, which illustrates the floatability of superficially oxidized Chungking coal pyrite *vs.* pulp pH in the presence or absence of $C_6H_3(OH)_3$. This may be because the elemental sulfur and/or polysulfides formed during surface oxidation cannot be totally removed by adding reducing agent, especially in acidic solutions where elemental sulfur is thermodynamically stable [14]. Figures 7, 8 and 9 show the influence of depressant concentration and redox potential on the flotation of pure pyrite, coal-contaminated pyrite, and oxidized coal. The flotation of pyrite is generally sensitive to changes in redox potential, although depression of coal-contaminated pyrite requires lower potentials, *i.e.*, higher concentrations of depressant. However, the flotation of oxidized coal is not affected by the changes in redox potential, and it floats almost completely, even at very high concentrations of depressant.

Table 2: Relative Integrated Intensity of Different Elements in the Surface Layer of Pyrite

Sample	S	C	O	Fe $2p_{3/2}$	Fe 3p
Fresh FeS_2	1	0.13	0.20	0.50	0.35
FeS_2, 15 min. in $1\times10^{-3}MC_6H_3(OH)_3$	1	0.52	0.23	0.38	0.32
Fes_2, 30 min in H_2O then 15 min in $1\times10^{-3}MC_6H_3(OH)_3$	1	0.44	0.34	0.47	0.37

Results of the XPS analysis are shown in Fig. 11 and Table 2. These show no substantial change in the iron to sulfur ratio on the three pyrite

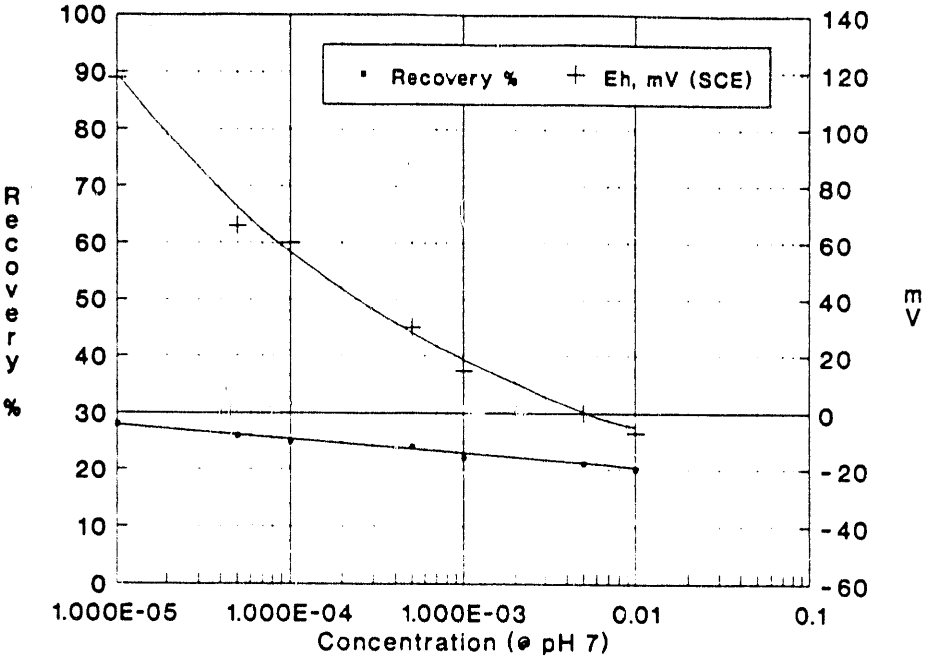


Figure 8: Floatability of a pure Chungking pyrite *vs.* $C_6H_3(OH)_3$ concentration and solution Eh (SCE).

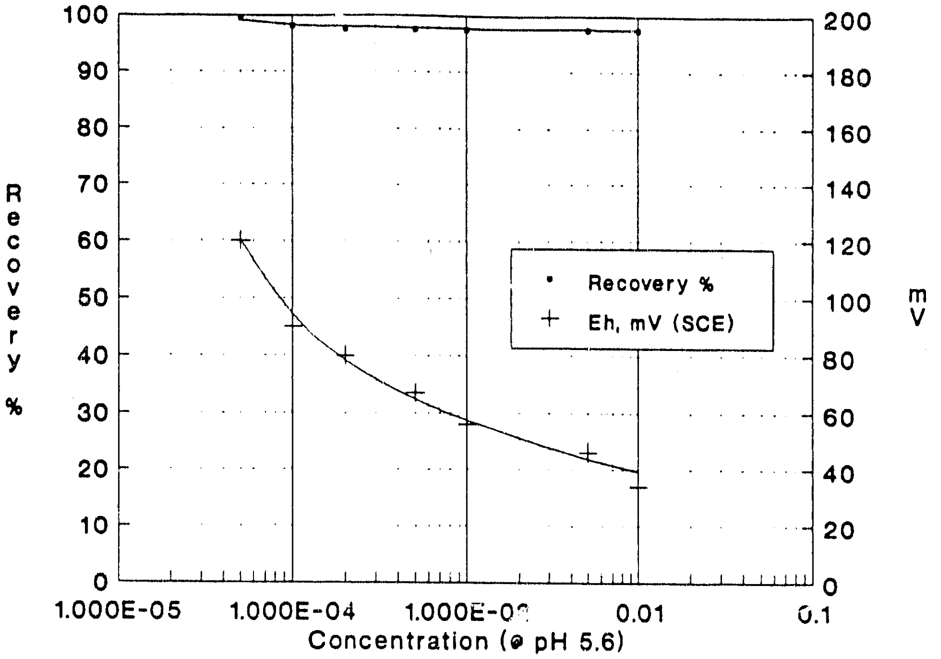


Figure 9: Floatability of an oxidized Chungking coal *vs.* $C_6H_3(OH)_3$ concentration and solution Eh (SCE).

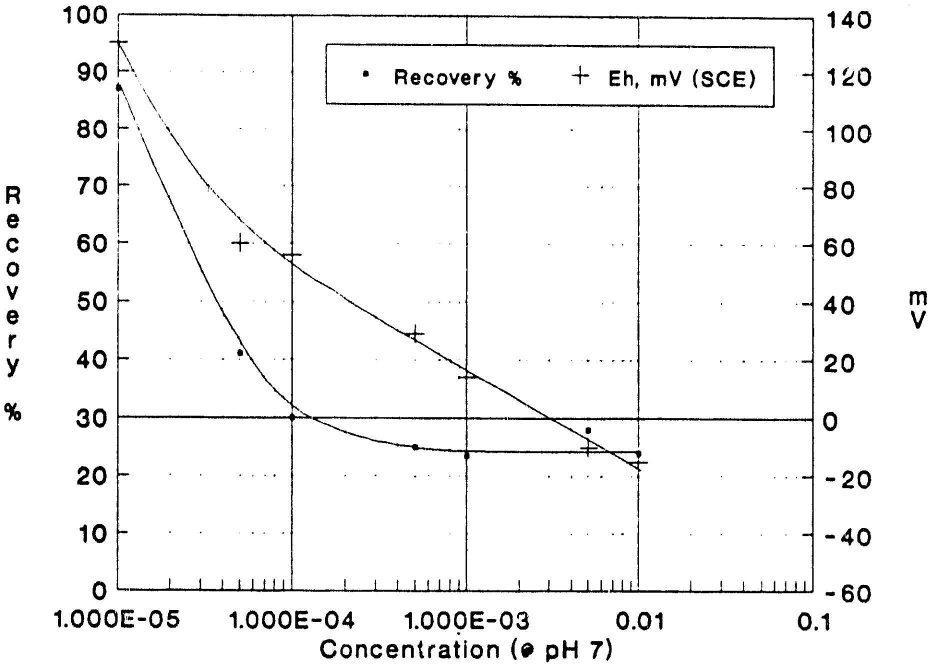
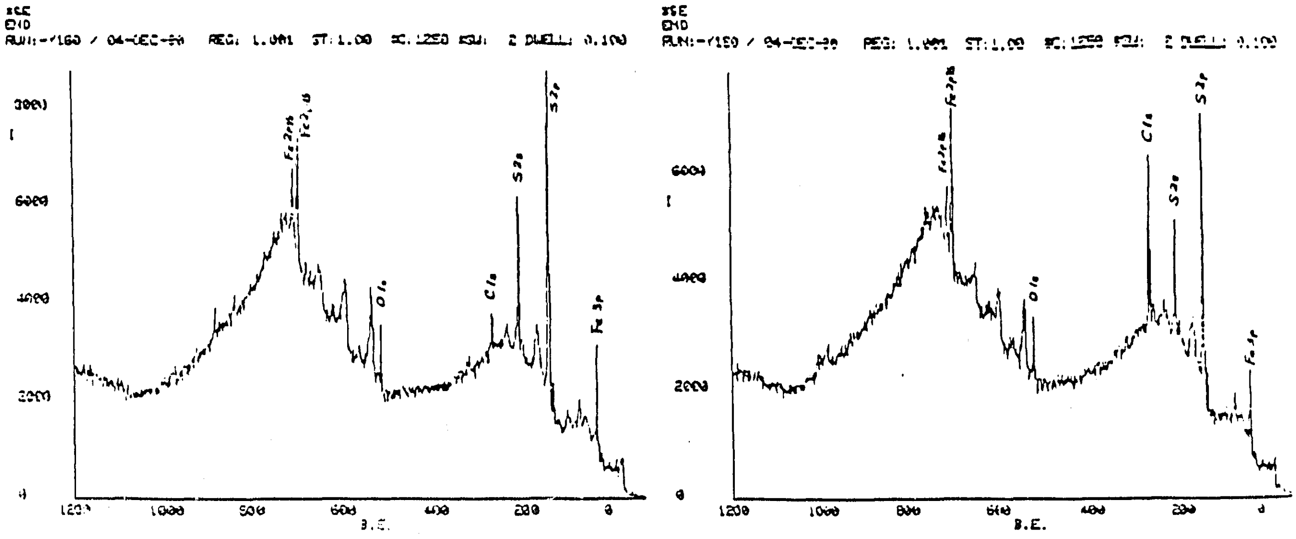
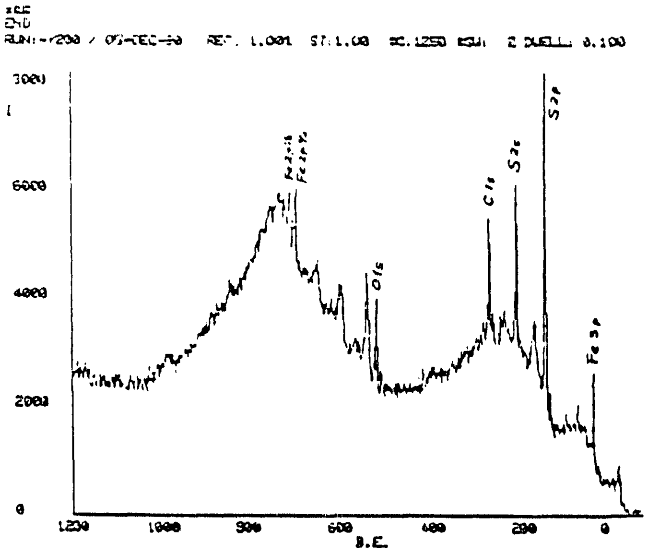


Figure 10: Floatability of coal-contaminated Chungking pyrite *vs.* $C_6H_3(OH)_3$ concentration and solution Eh (SCE).



1. Fresh FeS_2

2. FeS_2 (15 minutes in $1x10^{-4}M$ $C_6H_3(OH)_3$ solution)



3. FeS_2 (30 minutes in H_2O and then
15 minutes in $1x10^{-4}M$ $C_6H_3(OH)_3$ solution)

Figure 11: XPS Spectra of the different pyrite samples.

surfaces, indicating that all three are in a reduced state. However, a significant increase in carbon content is observed on both the unoxidized and oxidized $C_6H_3(OH)_3$ treated surfaces, with more $C_6H_3(OH)_3$ adsorbing onto the unoxidized surfaces. Since $C_6H_3(OH)_3$ is a metal-complexing agent, the adsorption might be due to the formation of iron complexes on the surfaces, which are hydrophilic and result in pyrite depression. If this is true, then lower adsorption of $C_6H_3(OH)_3$ onto the oxidized/$C_6H_3(OH)_3$ treated surface, i.e., fewer iron complexes formed on the surface, may be the cause of the less efficient depression of oxidized pyrite. However, the reasons for the lower iron complex formation on the oxidized surface are still unknown. The observed increase in oxygen content on the oxidized pyrite surface may be due to the adsorption of oxygen from solution and the formation of oxidation products of pyrite on the surface, possibly competing with the iron complex adsorption. Thus, the XPS results suggest that coal pyrite may be depressed by two mechanisms when $C_6H_3(OH)_3$ is used as a depressant: (1) by preventing elemental sulfur and/or polysulfide formation, and (2) by iron-complex formation on the surface.

The flotation behavior of pyrite contaminated with carbonaceous matter is shown in Fig. 6. This figure shows that the contaminated pyrite floats much more readily than does clean pyrite (Fig. 5), even though the fixed carbon content is only 1.74%. This is further confirmed by the results given in Figs. 8 and 10.

The results of desulfurization tests on the Chungking coal using the bench-scale Denver flotation cell are presented in Table 3 and Figure 12. For the purposes of comparison of test results under different conditions, a combined efficiency, E, is introduced. E is defined as $R_c.S_{rej}/10^4$, where R_c is the percent recovery of combustibles, and S_{rej} is the percent total sulfur rejection. The data display only modest sulfur rejection when using $C_6H_3(OH)_3$ as a depressant. This may be due to inadequate pyrite liberation at the feed size used (-32 mesh); pyrite surface contamination by carbonaceous matter; and/or the superficial oxidation of the pyrite (10 minute conditioning for coal wetting before adding depressant). In addition, mechanical entrapment of free pyrite particles in the froth, often associated with conventional flotation, would also contribute to the inefficient desulfurization. A slight decrease in pyrite recovery was observed when the depressant was used. This may be due to the depression of locked particles.

Table 3. Denver Flotation Results

No.	Ash %		S_t %		E^*	
	2 min	8 min	2 min	8 min	2 min	8 min
1	21.58	23.51	2.96	3.09	0.2880	0.2160
2	19.81	20.12	2.68	2.69	0.3579	0.3544
3	19.86	21.43	2.61	2.78	0.3551	0.2945

* E (Combined Efficiency)=$R_c \cdot (100-R_s)/10^4$

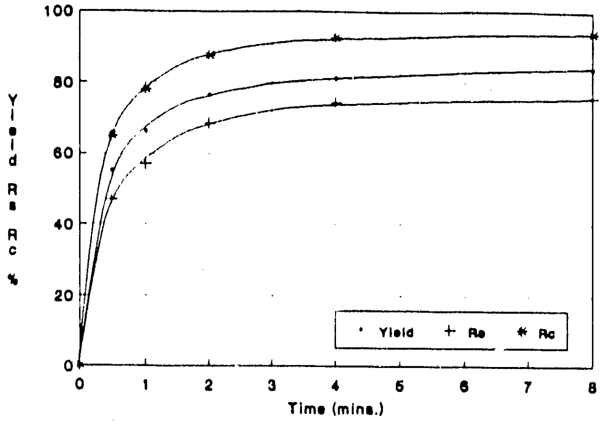
Test Conditions:
(1) 100 μl Frother, no Kerosene, no Depressant
(2) 100 μl Frother, no Kerosene, 5×10^{-4}M $C_6H_3(OH)_3$
(3) 100 μl Frother, no Kerosene, 1×10^{-4}M $C_6H_3(OH)_3$

The results of the column flotation tests on all 3 coal samples are presented in Table 4. The fact that the froth products from column flotation have much lower sulfur and ash contents for the Chungking coal demonstrates better liberation of pyrite and ash forming minerals in the feed, and/or reduced mechanical entrapment during flotation. Based on the combined efficiency, E, of each of the tests, sulfur removal is better for all tests except the second test on the Chungking coal, which has an E value slightly inferior to that obtained without depressant. This is may be due to improper operation of the column (giving too low a product yield). Again, a pronounced decrease in product ash is observed. The column test results clearly show the de-ashing effect of the depressant.

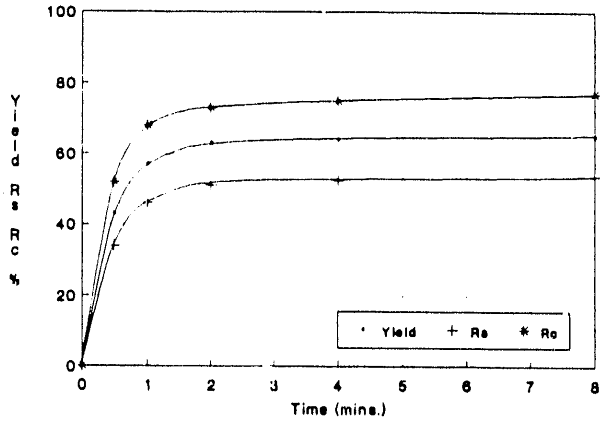
CONCLUSIONS

The following conclusions can be drawn from the data obtained in this study:

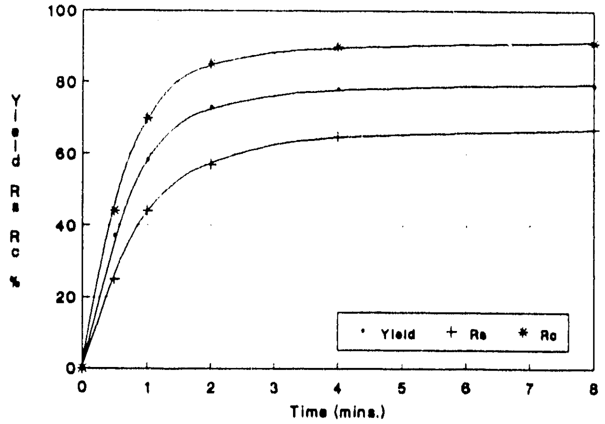
1. Incipient superficial oxidation and the surface contamination of pyrite by carbonaceous matter are the most important causes of the hydrophobicity of coal pyrite surfaces.
2. Coal pyrite flotation can be partially depressed through the use of reducing agents (or other means) to give a low oxidation-reduction potential and prevent elemental sulfur and polysulfide formation on the surface.
3. $C_6H_3(OH)_3$ depresses coal pyrite flotation but does not significantly effect the flotation of coal. The mechanism of depression may be (1) the reduction of the pulp potential, and (2) the formation of iron-metal complexes and their subsequent adsorption on the pyrite surface.
4. The depression of initially oxidized coal pyrite is less efficient. This is of practical importance, since the coals treated in most coal preparation plants are usually superficially oxidized to some degree.



(1) 100 μl Frother
No Kerosene
No Depressant



(2) 100 μl Frother
No Kerosene
5×10^{-4}M $C_6H_3(OH)_3$



(3) 100 μl Frother
No Kerosene
1×10^{-4}M $C_6H_3(OH)_3$

Figure 12: Flotation of Chungking coal using a laboratory Denver flotation cell in the absence and presence of depressant.

Table 4: Column Flotation Test Results

Coal Sample	Feed %			Froth %				Tailing %			R_c	S_{rej}	E	Test Conditions		
	Ash	S_t	S_p	Ash	S_t	S_p	Yield	Ash	S_t	Yield	%	%	*	C	D	WW
Illinois No. 2	6.53	2.77	1.63	3.08	1.92	0.65	38.57	8.68	3.31	61.43	39.98	73.27	0.2970	YES	NO	700
	6.52	2.72	1.63	2.87	1.80	0.53	46.19	9.73	3.52	53.81	48.04	69.43	0.3335	YES	YES	700
	5.63	2.94	1.63	3.06	1.96	0.69	70.67	14.89	5.32	29.33	73.29	58.89	0.3876	YES	YES	4(
Upper Freeport	17.65	2.25	1.80	8.66	1.44	0.94	74.19	43.39	4.58	25.81	82.29	52.52	0.4322	NO	NO	700
	17.65	2.24	1.80	8.05	1.32	0.82	71.18	41.36	4.50	28.82	74.48	58.05	0.4619	NO	YES	700
Chungking Coal	32.75	3.37	2.91	11.82	1.72	0.91	36.23	44.64	4.31	63.77	47.51	81.51	0.3873	NO	NO	700
	32.75	3.05	2.91	8.80	1.54	0.96	32.42	44.24	3.78	67.58	43.97	83.63	0.3677	NO	YES	700
	32.75	3.06	2.91	10.55	1.70	1.23	47.78	53.15	4.31	52.02	63.82	73.44	0.4887	NO	YES	400

R_c % recovery of combustibles to product
S_{rej} % total sulfur rejection
E Combined efficiency = $R_c \cdot S_{rej}/10^4$

Test Conditions:

C (Collector)	1.0 lb/ton where indicated
D (Depressant)	5×10^{-4}M where indicated
WW (Washwater)	ml/min as indicated

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