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PHYSICAL DESULFURIZATION OF IOWA COAL BY FLOTATION

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PREFACE

This report was prepared as an account of work sponsored by the Iowa Coal Project and conducted in the Energy and Mineral Resources Research Institute at Iowa State University. Financial support for the research was provided by an appropriation for the Iowa Legislature in June 1974.

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ABSTRACT

An experimental investigation was carried out to develop a flotation technique for the efficient beneficiation of Iowa coal fines that could be applied on a pilot plant scale at the Iowa State University coal preparation plant.

Flotation techniques found to be effective on Appalachian coals were studied to determine their effectiveness on Iowa coals. A single-stage flotation technique using metal salts was studied at different pH values. The effects of metal salt concentrations and different frother agents were also examined.

Flotation techniques that performed well on appalachian coals were found to be less effective on Iowa coals. The metal salts tested behaved more as coal activators than as pyrite depressants. The frothers examined exhibited collector-like properties. A single-stage flotation technique using 10^{-4}M concentration of metal salts and MIBC as the frother was found to effectively beneficiate Iowa coal fines.

I. Introduction

In 1974, the Iowa Legislature established the Iowa Coal Research Project to provide basic information and to do research which might lead to the redevelopment of Iowa's coal mining industry as an internal energy source. One phase of this project is concerned with coal cleaning or beneficiation. Most Iowa coals contain between 3 and 8% total sulfur, which must be reduced to meet state and federal emission control standards. Although the organic sulfur cannot be removed by mechanical means, the liberated pyritic sulfur can usually be removed quite effectively.

Coal particles larger than those which would pass through a 48 mesh screen can be cleaned efficiently by gravity separation methods; however, coal particles smaller than 48 mesh do not respond well to this technique due to their colloidal properties.

Because there is concern about waste material polluting lakes, rivers, and the landscape and because fossil fuel reserves are dwindling, efforts are being made to recover and clean fine coals. One technique used to clean fine coals is froth flotation or simply flotation.

Flotation is a physical process used for the separation of different particles in an aqueous medium which does not rely on gravity separation. Instead the separation is accomplished by creating a froth or bubble mass which selectively floats certain particles from a water slurry. The usefulness of such a process is based on the principle that certain particles will adhere to the froth while other particles will remain in the liquid phase of the system.

The mechanism of particle to bubble attachment is generally believed to be based on the solid-liquid, solid-gas, and liquid-gas interfacial tensions and the associated contact angle which determines whether wetting or nonwetting of a surface occurs. If the contact angle between the solid and liquid is approximately zero, the liquid will spread over the solid wetting it. This type of solid is said to be hydrophylic. When the contact angle is approximately 90°, the liquid does not wet the surface but instead beads-up on the surface. This type of surface can better adhere to air and is said to be hydrophobic. The charge of the particles is generally neglected when considering particle to bubble attachment (1). Schulman (18,19), however, believes that the mechanism of bubble attachment is based on the electrostatic and molecular interactions between the bubble and particle. Traditionally then, flotation is thought of in terms of whether or not the particles are hydrophobic or hydrophylic and in creating a system in which both types of particles coexist, resulting in separation of the different particles. In coal flotation this amounts to insuring that coal is in a hydrophobic state and that pyrite and other ash forming minerals are in a hydrophylic state or vice versa.

Creating such particle conditions may require the use of certain chemical reagents. A frother is usually required to produce a stable froth to which the hydophobic particles are attached. The frother is often a long-chained hydrocarbon molecule with an attached polar group, such as methyl amyl alcohol (MIBC) or pine oil. It is because of the polar group that some investigators believe the frother, in addition to creating a froth, acts as a collector and in effect controls the selectivity of the entire flotation process through electrostatic interactions with the particles (7,19,20).

Collectors or promoters are reagents which enhance the floatability of the particles to be floated by selectively adsorbing on these particles. Depressants are reagents that reduce the floatability of other particles which are not to be floated by selectively adsorbing on those particles. Depressants can also be used to inhibt collector adsorption on these particles. Depending on the pH of the flotation slurry some collectors can act as depressants or vice versa (16). Consequently the slurry pH is very important and is usually controlled by the addition of an acid or base prior to adding other reagents.

Flotation was originally applied to the separation and recovery of minerals from their ores, and it is still widely used in that field (6,9,22). The application of flotation to coal beneficiation is a relatively new area because fine coal benefication was not considered to be of much importance.

The literature contains little on the application of flotation to coal beneficiation. Prior to 1930 very few reports on coal flotation were published. However, during the 1930's, the U.S. Bureau of Mines began investigating the use of flotation to remove sulfur and ash from Appalachian coals. Yancey and Taylor (21) tested various mineral flotation reagents and frothers over a wide range of pH values. They also investigated the flotation of oxidized pyrite. Their findings indicated that the oxidation products of pyrite are powerful pyrite depressants in the pH range of 4.5 to 6.9. Further, that a nuetral or slightly acidic or basic environment is best for coal flotation. Also that ferrous and ferric salts can act as pyrite depressants. They also found that many of the reagents commonly used in mineral flotation are not effective in coal flotation. Most of the research conducted on coal flotation for several decades was under the direction of the U.S. Bureau of Mines. Areas studied included evaluation of commercial flotation cells used in cleaning coal and the use of kerosene in coal flotation (8), and the correlation of washability and flotation data by means of a timed release analysis technique (5).

During the last decade a new wave of coal flotation research has begun. The first study of the electrokinetic properties of coal as they relate to flotation and flocculation was conducted by Campbell and Sun (4). This research was aimed directly at developing a theory of coal flotation. Baker and Miller (2) continued the early work of Yancey and Taylor with the investigation of various hydrolyzed metal ions as pyrite depressants. The most recent development by the Bureau of Mines is a two-stage flotation process which uses a reverse flotation technique in the second stage (15).

Over the past two years a study on coal flotation was conducted under the auspices of the coal beneficiation division of the Iowa Coal Research Project. The object of this study was to develop a flotation technique for the efficient beneficiation of Iowa coal fines which could be applied on a pilot plant scale at the Iowa State University coal preparation plant. This report covers the experimental work conducted and describes the results obtained.

II. Materials and Equipment Used

Initially coal samples from the Star, Lovilia, and ICO Mines in southeast Iowa were tested. These samples were used for evaluating the Bureau of Mines two-stage flotation process and a single stage process using hydrolyzed metal ions as pyrite depressants. The ash and sulfur contents of the samples are presented in Table 1. The coal was prepared for flotation by crushing with a Raymond Lab Mill. The size distribution of the crushed coal is presented in Table 2.

Table 1. Analysis of Iowa Coals

Coal Mine	Ash, wt.%	Total Sulfur, wt.%	Pryitic Sulfur, wt.%
Star (R.O.M.)	36.35	8.88	6.62
Star (Channel)	14.95	5.33	
Lovilia	11.63	3.20	2.04
ICO	14.06	2.40	

Table 2. Typical size distribution of crushed Iowa coals.

Size, Tyler Mesh	Weight % Passing	Weight % Retained
48	100.0	0.0
60	98.0	2.0
100	91.6	8.4
200	50.3	49.7
325	17.8	82.2

When the I.S.U. Demonstration Mine No. 1 became operational, attention turned to applying flotation to beneficiating the natural fines from this mine. Natural fines are coal fines created by mining and handling operations. All subsequent flotation tests used natural coal fines from the I.S.U. Mine. These fines contained between 6.80 and 8.80% total sulfur, between 18.0 and 32.0% ash and between 4.5 and 6.5% pyritic sulfur. A typical size distribution is presented in Table 3.

Table 3. Typical size distribution of I.S.U. Demonstration Mine No. 1 natural fines

Size, Tyler Mesh	Weight % Passing	Weight % Retained
48	100.0	0.0
60	96.5	3.5
100	72.0	23.0
200	45.3	54.7
325	5.6	94.4

The natural fines were obtained from the mine samples collected for washability and statistical studies of the I.S.U. mine. All chemical analyses were conducted either by the Ames Laboratory analytical services group or by the Warner Laboratories of Cresson, Pennsylvania, in accordance with ASTM methods.

All flotation experiments were conducted using a Denver D-1 subaeration laboratory scale flotation cell, with the standard open impeller and diffuser and 2400 ml. stainless steel tank.

The pH of the slurry was measured with a Beckman Model G pH meter. A calomel reference electrode with ceramic junction and a silver-silver perchlorate glass pH electrode were used.

All reagents with the exception of the frothers, were prepared as 1.0% aqueous stock solutions. The frothers were used in a concentrated form as supplied by the manufacturers. When the pH was modified with hydrochloric acid (HCl), this too was applied in concentrated form.

Iowa State University tap water was used in all flotation experiments.

III. Experimental Methods & Results

In order to evaluate the flotation process for beneficiating Iowa coals, a program of experimentation was implemented. This program consisted of 1.) attempting to apply techniques proven satisfactory on Appalachian coals to Iowa coals, and 2.) attempting to obtained a set of optimum initial operating conditions to be applied to pilot plant scale processing. The effectiveness of the bench scale tests was evaluated in terms of the following quantities:

$$\text{Yield (\%)} = \frac{\text{weight of dry product}}{\text{weight of dry feed}} \times 100$$

$$\text{Ash Removal (\%)} = \frac{\text{\% ash in feed} - \text{\% ash in product}}{\text{\% ash in feed}} \times 100$$

$$\text{Sulfur Removal (\%)} = \frac{\text{\% sulfur in feed} - \text{\% sulfur in product}}{\text{\% sulfur in feed}} \times 100$$

Evaluation of the Bureau of Mines Two-Stage Process

The first attempt to beneficiate Iowa coal was to apply the recently developed Bureau of Mines two-stage process (15). Experiments were conducted using the following procedure:

1. 200 g of coal was placed in the flotation cell and 1150 ml. of tap water was added.
2. The slurry was conditioned for 5 min. to insure a uniform mixture and the frother was added.
3. The impeller speed was set at 2000 rpm and air was applied at 0.3 to 0.4 cu.ft./min. The slurry was then floated until clean which took 8-10 min.
4. The tailings from the first stage were filtered, dried and analyzed.

5. The first stage product was then put back in the cell. Tap water was added to the pulp to bring it to the 1150 ml. level. This pulp was then conditioned for 5 min.
6. A coal depressant (Aerodepressant 633), a pyrite collector (potassium amyl xanthate), and the frother were added.
7. The impeller speed was set at 2000 rpm and air was applied at 0.3-0.4 cu.ft./min. as in the first stage. The second stage was floated until a clean froth appeared.
8. The second stage concentrate and tails were filtered and dried.

The results are summarized in Table 4, and show that the two stage process reduced the total sulfur content 9-14% depending on the coal tested.

In the second stage of the process the concentrate should contain the refuse while the tailings contain the clean coal. This never was accomplished using Iowa coal. Large amounts of clean coal were always floated in the second stage. Xanthates are known to be powerful collectors of both coal and pyrite (4). It is quite possible that the Aero depressant 633 could not counteract the collecting ability of the xanthate, resulting in second stage flotation of coal. It does appear that some of the pyrite was floated; however, not all of it was. The pH may have been such that the xanthate was acting both as a collector and depressant on the pyrite and as a collector on the coal (16).

Evaluation of a Single-Stage Flotation Process

Because the Bureau of Mines two-stage process did not appear to effectively beneficiate Iowa coals, a more basic single-stage flotation technique which uses metal salts to increase coal and pyrite separation was investigated. This technique has also met with success on Appalachian coals.

Table 4. Two-stage flotation tests on Iowa coals

Coal	Treatment	Product	Total Sulfur %	Sulfur Removal %
Star	1st Stage: 1.1 wt. % MIBC	Clean Coal	8.07	9.1
	2nd Stage: 1.1 wt. % MIBC	Reject 2	18.20	
	0.025 wt. % Xanthate	Reject 1	10.7	
	0.035 wt. % Aero 633			
Star	1st Stage: 0.4 wt. % Pine Oil	Clean Coal	7.79	12.2
	2nd Stage: 0.4 wt. % Pine Oil	Reject 2	8.51	
	0.025 wt. % Xanthate	Reject 1	11.60	
	0.035 wt. % Aero 633			
Lovilia	1st Stage: 1.1 wt. % MIBC	Clean Coal	3.46	[---][a]
	2nd Stage: 1.1 wt. % MIBC	Reject 2	2.55	
	0.05 wt. % Xanthate	Reject 1	6.16	
	0.70 wt. % Aero 633			
Lovilia	1st Stage: 0.4 wt. % Pine Oil	Clean Coal	2.75	14.0
	2nd Stage: 0.4 wt. % Pine Oil	Reject 2	2.70	
	0.05 wt. % Xanthate	Reject 1	8.66	
	0.070 wt. % Aero 633			
ICO	1st Stage: 1.1 wt. % MIBC	Clean Coal	2.09	12.9
	2nd Stage: 1.1 wt. % MIBC	Reject 2	2.29	
	0.025 wt. % Xanthate	Reject 1	6.64	
	0.035 wt. % Aero 633			

[a] The clean coal contained more total sulfur than the raw coal.

Research by Baker and Miller (2) has shown that ferric chloride ($FeCl_3$) is effective in increasing ash and pyrite removal. During this series of experiments the metal salt was applied in concentrations of 1.3×10^{-4} and 2.6×10^{-4}M. The experiments were conducted in the following manner:

1. 200 g of coal was placed in the cell and 1150 ml. of tap water was added.
2. This slurry was agitated at 1000 rpm for 5-10 min. to insure a uniform mixture.
3. The metal salt and frother were added and allowed to condition for 5 min. at an impeller speed of 900 rpm.
4. Air was applied at 0.3-0.4 cu.ft./min. and the impeller speed increased to 2000 rpm.
5. The slurry was floated until a clean froth was produced.

The results are summarized in Table 5, and show that the single stage process using a metal salt reduced the sulfur content 11-18% and the ash content 19-34%. These results are somewhat better than the results obtained with the two-stage process. The single-stage process is less complicated and would probably be more applicable to Iowa coals on a production basis.

Effect of Metal Salt Conditioning Time

During the initial experimentation with $FeCl_3$ as an aid to pyrite removal, the slurry or pulp was allowed to condition 5 min. after $FeCl_3$ was added but before air was introduced. It was thought that this conditioning time could be an important factor in the flotation process. It was also thought that higher concentrations of $FeCl_3$ could produce beter pyrite removal. To test these theories a series of experiments was conducted using the procedure previously described with the exception that $FeCl_3$ was applied in concentrations of

Table 5. Single-stage flotation test on Iowa coals

Coal	Treatment	Product, %			Removal, %	
		Yield	Ash	Total Sulfur	Ash	Total Sulfur
Lovilia	1.1 wt. % MIBC	93.1	8.25	2.72	20.0	16.0
Lovilia	1.1 wt. % MIBC 1.3×10^{-4}M $FeCl_3$	92.9	8.00	2.65	22.4	18.2
Lovilia	1.1 wt. % Pine Oil 2.6×10^{-4}M $FeCl_3$	96.5	7.08	2.63	33.7	18.5
Star (Channel)	1.1 wt. % MIBC 2.6×10^{-4}M $FeCl_3$	91.5	12.06	4.76	19.3	11.0
Star (Channel)	1.1 wt. % Pine Oil 2.6×10^{-4}M $FeCl_3$	95.1	11.61	4.37	22.3	18.0

2.6×10^{-4}M, 1.25×10^{-3}M and 2.5×10^{-3}M, and the slurry was allowed to condition at 900 rpm for 5, 10 and 20 min. in all tests. 1.0 wt.% MIBC was used.

The results are presented in Table 6 and Figure 1. Increased conditioning time produced a decrease in total sulfur removal. It appears that the best results would be produced when the slurry is not conditioned after the salts are added. Of the $FeCl_3$ concentrations used, 1.25×10^{3}M produced the best results.

Effect of pH

A series of tests was conducted to determine the effect of pH on flotation using different metal salts. Ferric chloride ($FeCl_3$), aluminum chloride ($AlCl_3$), and chromium chloride ($CrCl_3$) were tested. 50 ml. of 1% metal salt solution per batch was used. The pH was modified by adding sodium hydroxide (NaOH) or HCl prior to other reagent addition. The pH was determined at this point. In all tests 1.0 wt.% MIBC was used.

Table 6. Single-stage flotation tests with different conditioning times

Treatment		Product, %			Removal, %	
$FeCl_3$ Concentration, M	Conditioning Time, min.	Yield	Ash	Total Sulfur	Ash	Total Sulfur
2.6×10^{-4}	5	66.0	21.4	7.46	32.7	20.2
2.6×10^{-4}	10	54.0	20.44	8.00	35.7	14.4
1.25×10^{-3}	5	63.0	21.31	7.06	36.1	24.3
1.25×10^{-3}	10	60.0	20.30	7.19	36.1	23.1
1.25×10^{-3}	20	62.0	20.74	7.52	34.8	19.5
2.50×10^{-3}	5	66.5	19.58	7.03	38.4	24.8
2.50×10^{-3}	10	50.0	19.48	7.41	38.7	20.8
2.50×10^{-3}	20	62.0	21.45	7.58	32.5	18.9

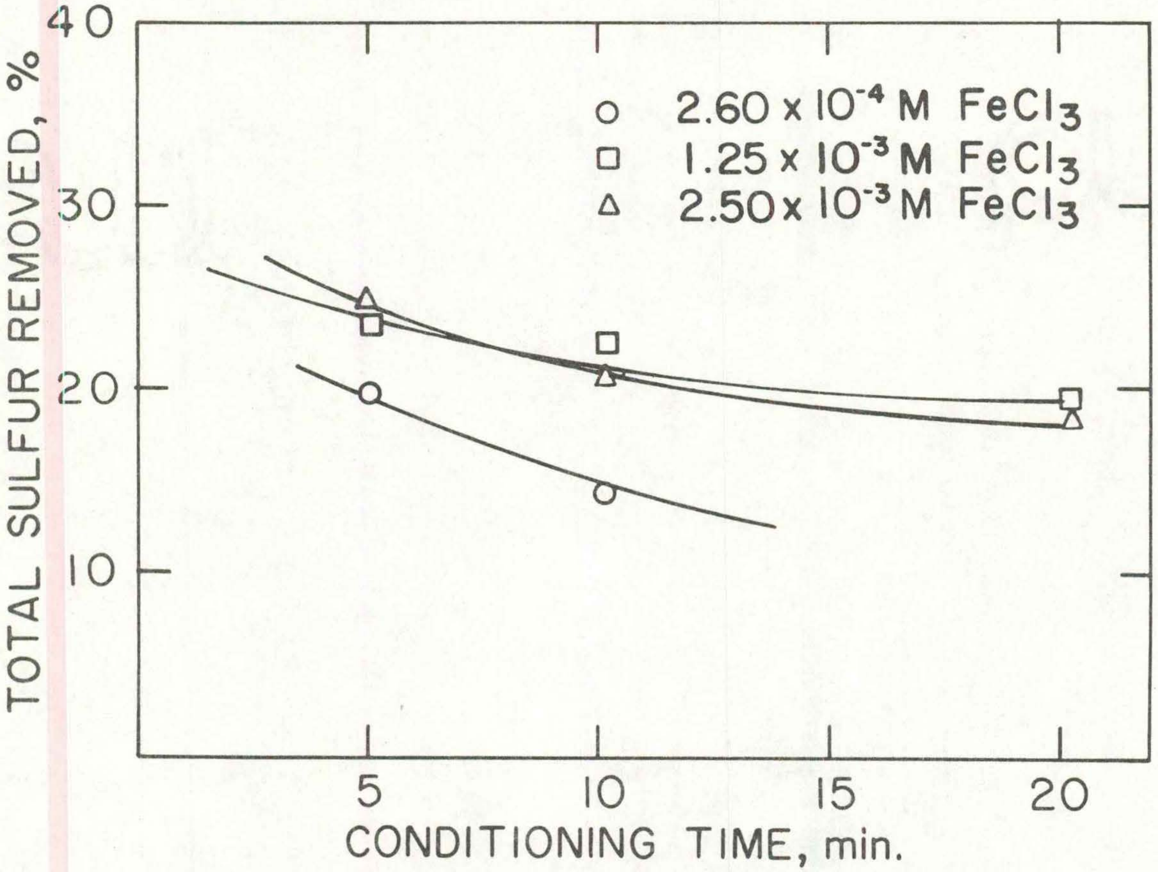

Figure 1. Effect of conditioning time and $FeCl_3$ on total sulfur removal.

The single-stage flotation procedure was used with the exception that 115.0 g. of natural I.S.U. coal fines was mixed with 2300 ml. of tap water. The pulp density was changed to more closely resemble the design pulp density proposed for flotation operation in the I.S.U. coal preparation plant. Also the slurry was not conditioned after the metal salts were added.

The results of this series of tests are presented in Table 7 and Figures 2-4. The ash and sulfur removal appear to be very pH dependent. With $FeCl_3$ and $CrCl_3$ the best results were produced at pH values of less than 2, while with $AlCl_3$ the best results were in the pH range of 5-6. $FeCl_3$ and $CrCl_3$ produced essentially similar results in the pH range of 3-7.

Effect of Different Salts

When the I.S.U. coal preparation plant became operational in May, 1976, research efforts shifted to determining a set of optimum flotation conditions to be used in the pilot plant scale flotation cells.

A single-stage technique using a frother and a metal salt as the only reagents was selected. The pH of the -48 mesh material from the beneficiation plant which would eventually be processed by flotation, was measured on various days during July, 1976, and found to have an average value of 5.5. All further flotation testing was conducted at this pH value.

Research by Miller and Baker (2) on using metal salts in flotation has shown that pyrite may be depressed by the adsorption of the highly charged hydrolysis products of the salts. While metal chlorides were actually tested, the hydrolysis products of metal nitrates were reported. The hydrolysis products of the metal nitrates are believed to be different from the metal chloride hydrolysis products due to the penetrating chloride ion (10-14,20). This difference may have an effect on ash and sulfur removal, when these salts are used in coal flotation.

Table 7. Single-stage flotation test of I.S.U. natural coal fines at different pH at constant metal salt concentration

$FeCl_3$						$CrCl_3$						$AlCl_3$					
	Product, %			Removal, %			Product, %			Removal, %			Product, %			Removal, %	
pH	Yield	Ash	Total Sulfur	Ash	Total Sulfur	pH	Yield	Ash	Total Sulfur	Ash	Total Sulfur	pH	Yield	Ash	Total Sulfur	Ash	Total Sulfur
0.7	85.7	10.79	6.12	33.9	27.1	0.9	80.0	15.32	6.58	34.7	23.9	0.5	86.8	14.85	5.58	38.4	18.1
0.9	87.0	10.85	5.87	33.5	30.0	1.1	78.0	14.10	5.85	39.9	32.4	1.4	95.9	11.15	5.99	39.9	12.0
1.0	78.8	10.74	5.91	34.2	29.6	1.6	81.2	11.48	6.18	25.8	26.0	2.4	92.6	10.5	5.84	43.4	14.0
1.8	85.8	10.82	5.96	30.4	27.5	2.2	81.9	11.93	6.31	22.9	24.4	2.9	87.9	15.32	5.79	36.5	15.0
2.0	87.5	11.58	6.29	25.5	23.5	3.0	76.9	10.87	5.72	29.7	31.5	3.8	92.9	11.89	6.13	35.9	9.7
2.9	82.9	10.25	5.87	34.0	28.6	4.75	74.4	10.79	5.87	29.8	29.7	4.3	84.0	14.85	5.79	38.4	15.0
5.9	84.9	11.84	6.15	23.8	25.2	5.2	84.1	11.71	6.44	24.3	22.9	4.8	84.8	15.53	5.56	35.6	18.4
7.5	88.3	11.55	6.55	25.7	20.3	6.7	75.6	10.88	5.87	29.7	29.7	5.5	81.8	15.31	5.27	36.5	22.6
						9.2	90.7	14.82	5.36	22.3	22.9	6.6	85.2	15.27	5.76	36.7	15.4
						11.0	82.1	14.38	5.61	24.6	19.3	8.8	90.8	14.02	6.04	25.5	12.5
												9.3	88.7	14.18	6.15	24.6	10.9
												10.1	87.9	13.34	5.66	29.0	17.3

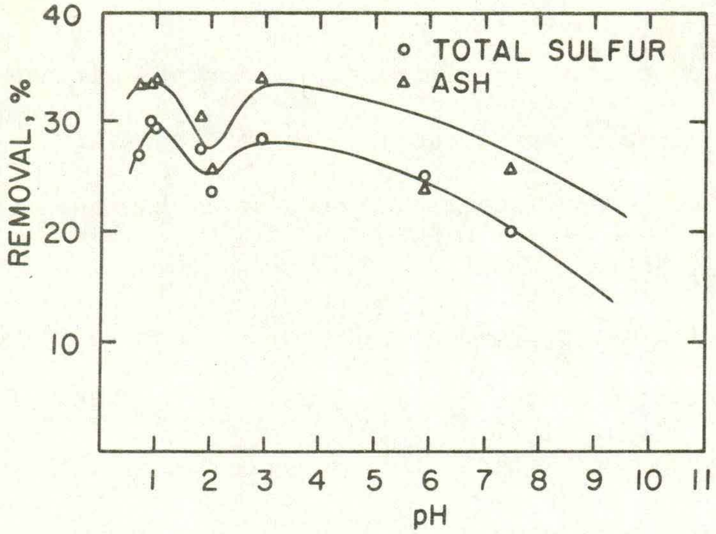

Figure 2. Effect of pH on ash and total sulfur removal at constant $FeCl_3$ concentration.

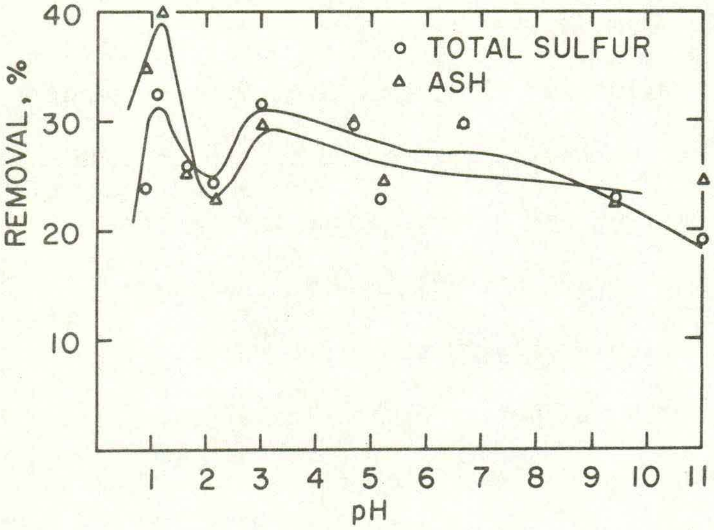

Figure 3. Effect of pH on ash and total sulfur removal at constant $CrCl_3$ concentration.

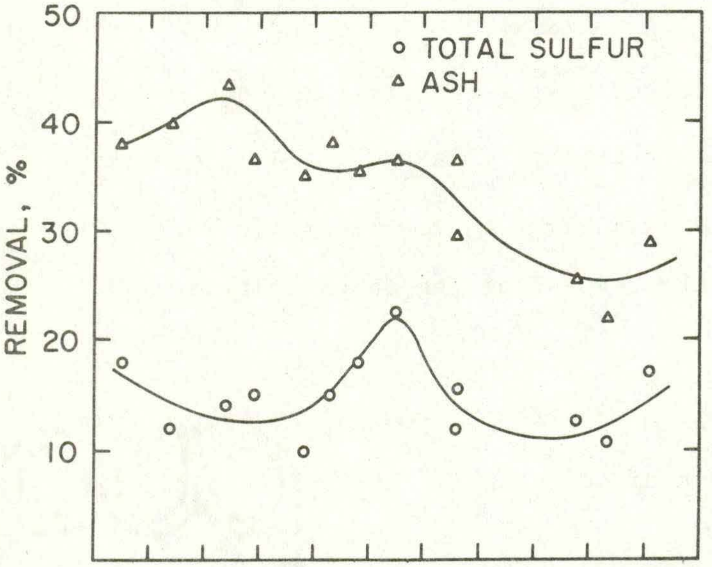

Figure 4. Effect of pH on ash and total sulfur removal at constant $AlCl_3$ concentration.

A series of experiments was conducted using $AlCl_3$, $FeCl_3$, aluminum nitrate ($Al(NO_3)_3$) and ferric nitrate ($Fe(NO_3)_3$) to compare the effects of the metal chlorides and nitrates. The use of $CrCl_3$ was discontinued because it has been identified as a carcinogenic substance (17).

Aged solutions of some metal salts may polymerize and produce more positively charged hydrolysis cations (11-14). The more highly charged cations may adsorb more readily on the pyrite surface producing better sulfur removal. Hence, a series of experiments was also conducted with a solution of $FeCl_3$ that had been prepared 9 months prior to testing to compare the effects of an aged solution with a fresh solution on ash and sulfur removal.

The effect of metal salt concentration was also reexamined in this series of tests. In the case of $FeCl_3$, the concentration was varied from 0 to 1.25×10^{-3}M or from 0 to 50 ml. of a 1.0% solution per batch. Since the best ash and sulfur removal was obtained when the dosage of $FeCl_3$ was in the range of 0 to 10 ml. per batch, this dosage was also used with the other salts. In all of the tests 0.5 wt.% MIBC was used as the frother. The results of this series of testing are presented in Table 8 and Figures 5-9. Slightly better results were produced when $Fe(NO_3)_3$ was used than when $FeCl_3$ was used. Approximately equal results were produced with $AlCl_3$ and $Al(NO_3)_3$.

The aluminum salts generally produced better results than the freshly prepared solutions of iron salts. With both the fresh $FeCl_3$ and aged $FeCl_3$ solutions, a slight decrease in sulfur occurred, followed by an increase and then decrease or leveling off of the removal as the concentration was increased.

With the aged $FeCl_3$ solution this trend was shifted to the left. This shift may have been due to the presence of more highly charged cations from hydrolysis in the aged solution.

Table 8. Single-stage flotation tests on I.S.U. natural fines with different metal salts at constant pH

Treatment		Product, %			Removal, %	
Metal Salt	Concentration, ml.[a]	Yield	Ash	Total Sulfur	Ash	Total Sulfur
$FeCl_3$	0.0	84.7	24.14	5.57	24.6	15.6
	0.5	87.1	24.12	5.69	24.7	13.8
	1.0	87.3	23.30	5.66	27.3	14.2
	5.0	85.5	24.12	5.50	24.7	16.7
	10.0	87.5	24.91	5.73	22.2	13.2
Aged $FeCl_3$	0.0	81.9	13.01	5.37	29.0	20.4
	0.5	86.0	13.75	5.45	24.4	16.8
	1.0	79.1	12.63	5.08	33.8	24.7
	5.0	82.4	73.33	5.34	27.3	20.9
	10.0	88.3	13.36	5.51	27.1	18.4
$Fe(NO_3)_3$	0.0	84.7	24.14	5.57	24.6	15.6
	0.5	84.9	22.46	5.45	29.9	17.4
	1.0	82.1	23.13	5.68	27.8	13.9
	5.0	83.0	23.71	5.46	25.9	17.3
	10.0	85.9	23.84	5.48	25.6	16.9
$AlCl_3$	0.0	88.3	23.36	5.87	24.1	8.9
	0.5	88.5	23.54	5.35	23.5	16.9
	1.0	82.8	23.24	5.40	24.5	16.2
	5.0	85.7	22.32	5.43	27.5	15.7
	10.0	86.2	22.10	5.47	28.2	15.1
$Al(NO_3)_3$	0.0	85.1	23.32	5.77	26.1	11.9
	0.5	84.0	22.96	5.30	27.2	17.1
	1.0	84.0	22.54	5.51	28.5	15.9
	5.0	84.3	22.69	5.55	28.1	15.3
	10.0	85.2	22.18	5.29	29.6	17.2

[a] Metal salts applied as 1.0% stock solutions.

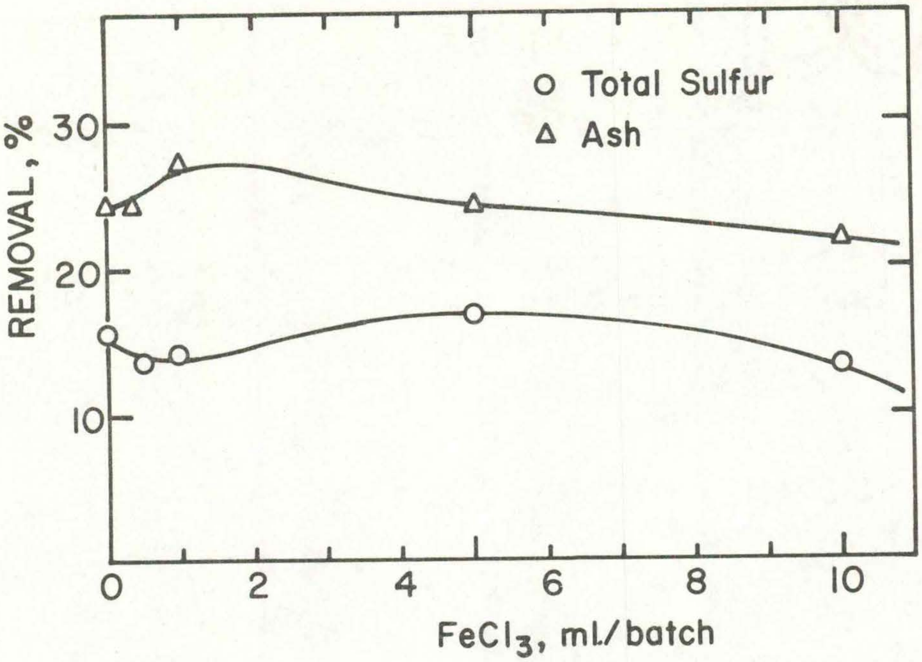

Figure 5. Effect of fresh FeCl$_3$ on ash and total sulfur removal at constant pH.

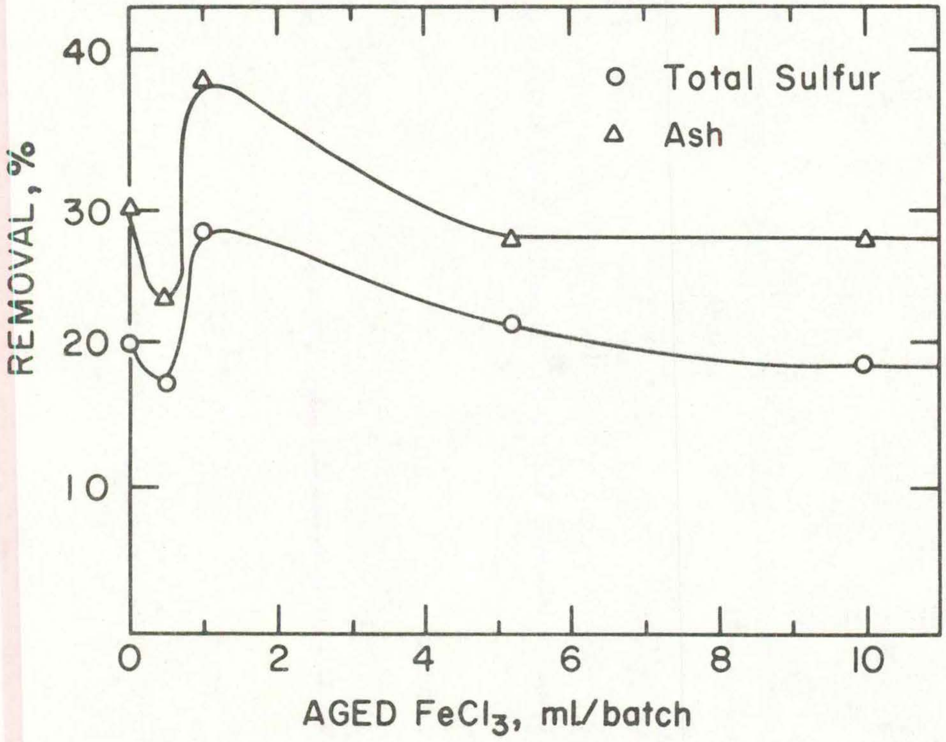

Figure 6. Effect of aged FeCl$_3$ on ash and total sulfur removal at constant pH.

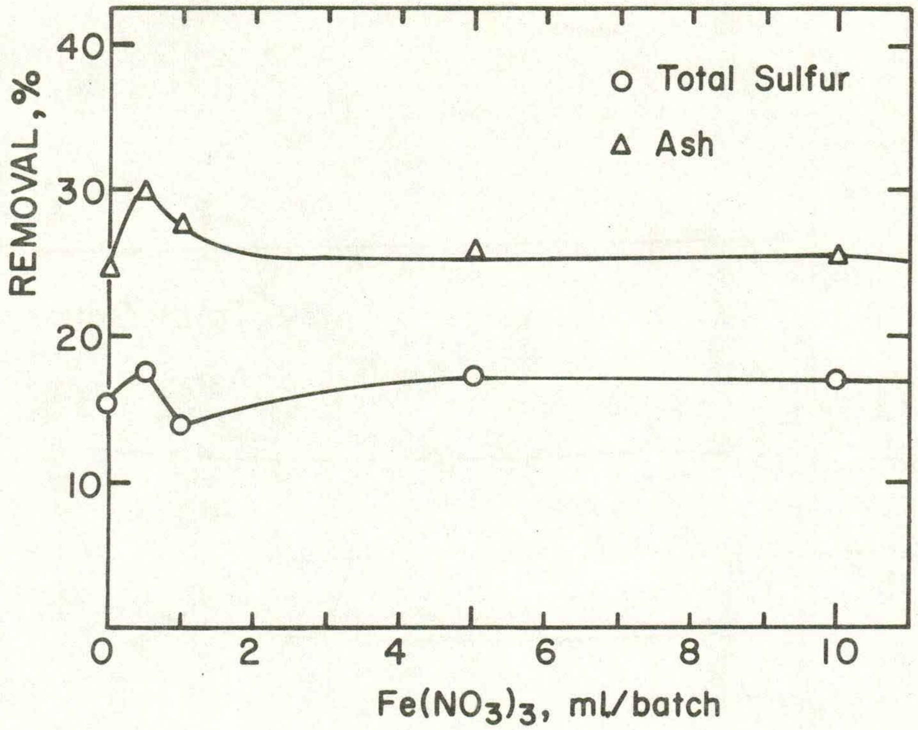

Figure 7. Effect of $Fe(NO_3)_3$ on ash and total sulfur removal at constant pH.

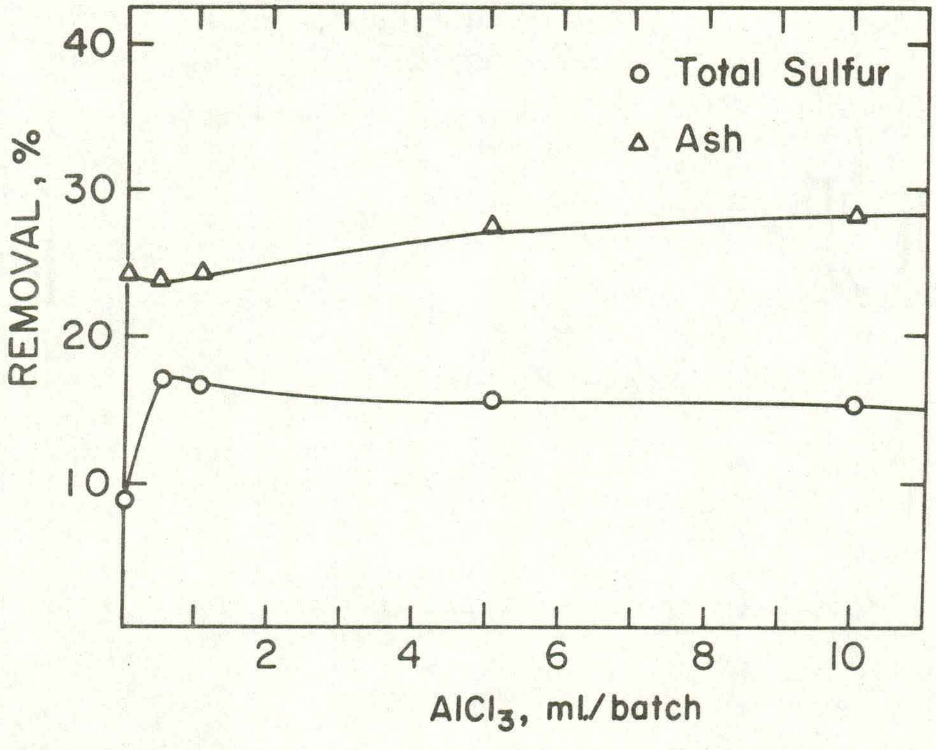

Figure 8. Effect of $AlCl_3$ on ash and total sulfur removal at constant pH.

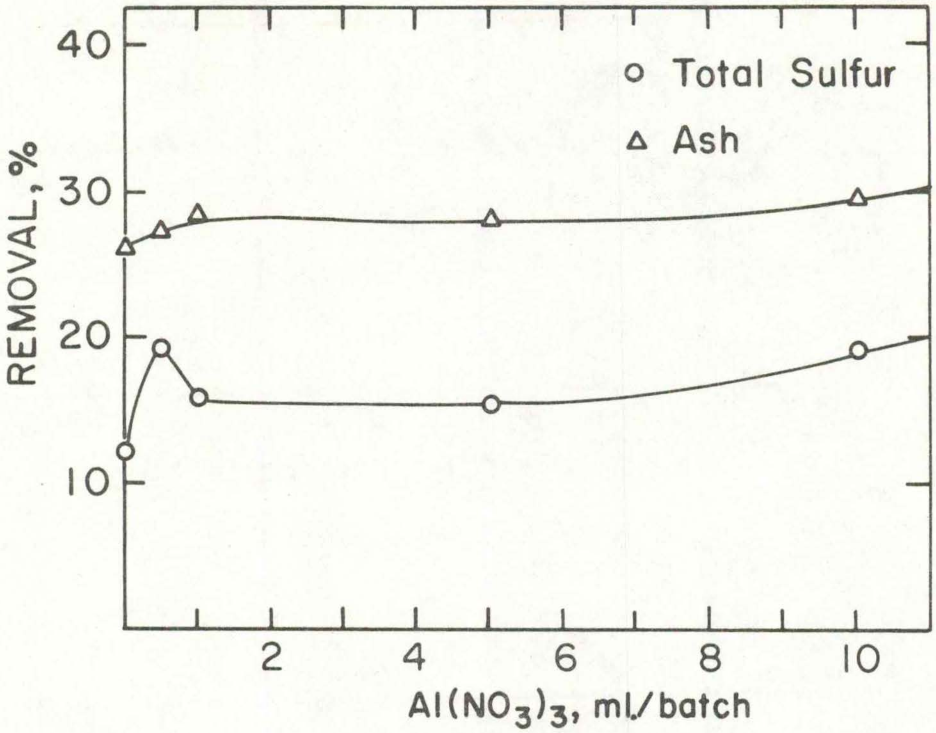

Figure 9. Effect of $Al(NO_3)_3$ on ash and total sulfur removal at constant pH.

The ash and sulfur removal characteristics of the system may be due to the creation of partial monolayers of hydrolysis cations on the coal and pyrite as a function of salt concentration, and the interaction of frother and monolayer as explained by Gaudin (7) and Schulman (18,19). The observed behavior does indicate, however, that the metal salts were acting as collectors or activators rather than as depressants. The role of the metal salt and its interaction with the frother, is quite complex and any speculation would best be left until further research is conducted on the adsorption characteristics of the metal ions and frother.

Effect of Different Frothing Agents

In prior testing either MIBC or pine oil was used as a frother because of their accepted use in coal flotation. To determine which frothing agent was most effective on Iowa coals, the following six widely used frothers were tested:

American Cyanamid - Aerofroth 65
Dow Chemical - Dowfroth 250 & 1012
Union Carbide - UCON 200
Hercules - Yarmor F Pine Oil
Eastman Organics - MIBC

Testing was conducted at a fixed metal salt concentration and pH. In all tests 1.0 ml. of aged $FeCl_3$ solution per batch or $1.6 \times 10^{-5}M$ $FeCl_3$ was used. The metal salt was used to obtain some indication of the maximum coal-gangue separation that could be expected. The pH was adjusted to 5.5 with HCl or NaOH. The results of the frother experiments are presented in Table 9 and Figures 10-15. MIBC produced the best ash and sulfur removal of the frothers tested. All the frothers exhibited some collecting ability as evidenced by a decrease in ash and sulfur removal with increasing concentration. From these results it appears that the type and concentration of frother can control the effectiveness of the flotation process.

Table 9. Single-stage flotation tests on I.S.U. natural fines with different frothers

Treatment		Product, %			Removal, %	
Frother	Concentration, ml.[a]	Yield	Ash	Total Sulfur	Ash	Total Sulfur
Aerofroth 65	1.0	92.8	16.86	7.17	14.3	5.7
	0.5	91.6	15.25	6.91	22.5	9.1
	0.25	87.4	14.11	6.75	28.3	11.2
Dowfroth 250	1.0	91.7	15.65	6.98	20.4	8.2
	0.5	87.5	15.25	6.81	22.5	10.4
	0.25	87.0	13.43	6.43	31.7	15.4
Dowfroth 1012	1.0	90.3	18.08	7.85	22.9	11.5
	0.5	82.5	16.04	7.34	31.6	17.2
	0.25	79.0	15.65	6.82	33.3	23.1
UCON 200	1.0	91.7	16.47	7.07	16.3	6.8
	0.5	91.6	16.04	7.07	18.5	6.8
	0.25	86.8	14.12	6.68	28.2	12.1
Yarmor F Pine Oil	1.0	87.0	16.35	5.99	32.6	19.2
	0.5	78.0	15.50	5.78	36.1	22.0
	0.25	75.3	16.40	5.51	32.4	25.6
MIBC	1.0	77.4	16.30	5.66	32.8	23.6
	0.5	74.9	16.85	5.40	30.5	27.1
	0.25	73.0	17.21	5.35	29.1	27.8

[a] Amount of concentrated frother used per batch.

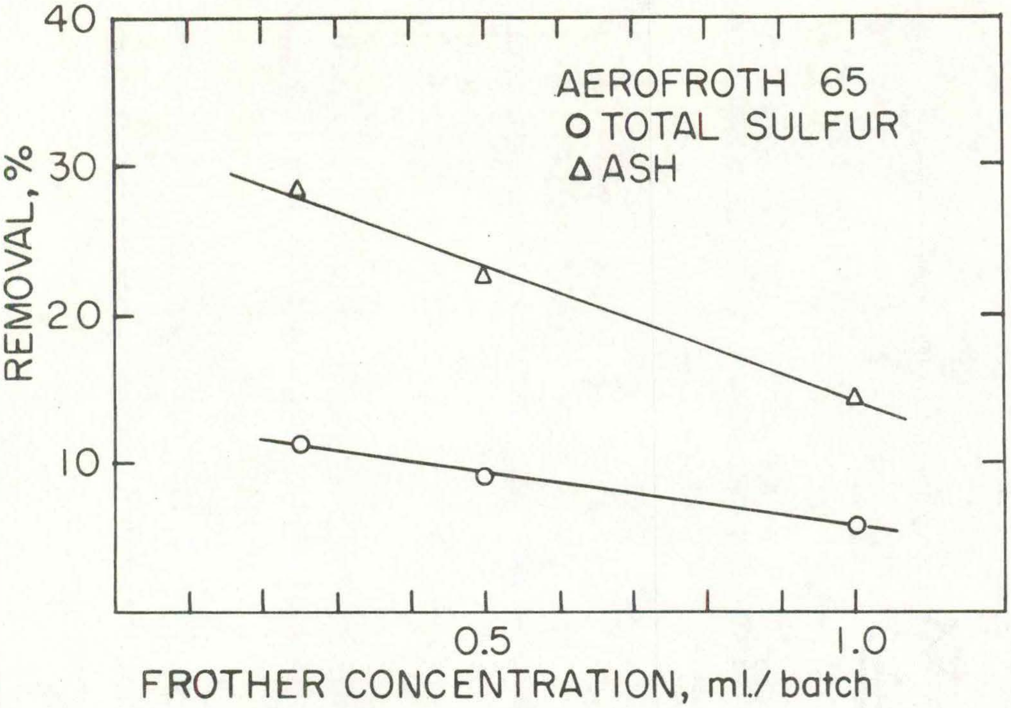

Figure 10. Effect of Aerofroth 65 frother on ash and total sulfur removal.

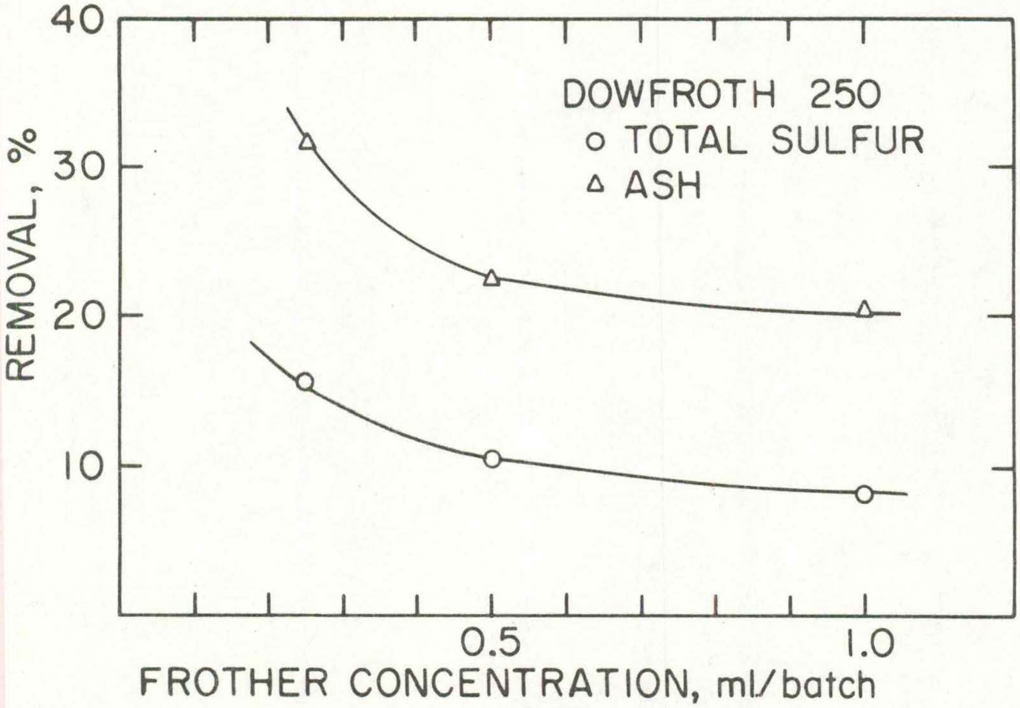

Figure 11. Effect of Dowfroth 250 frother on ash and total sulfur removal.

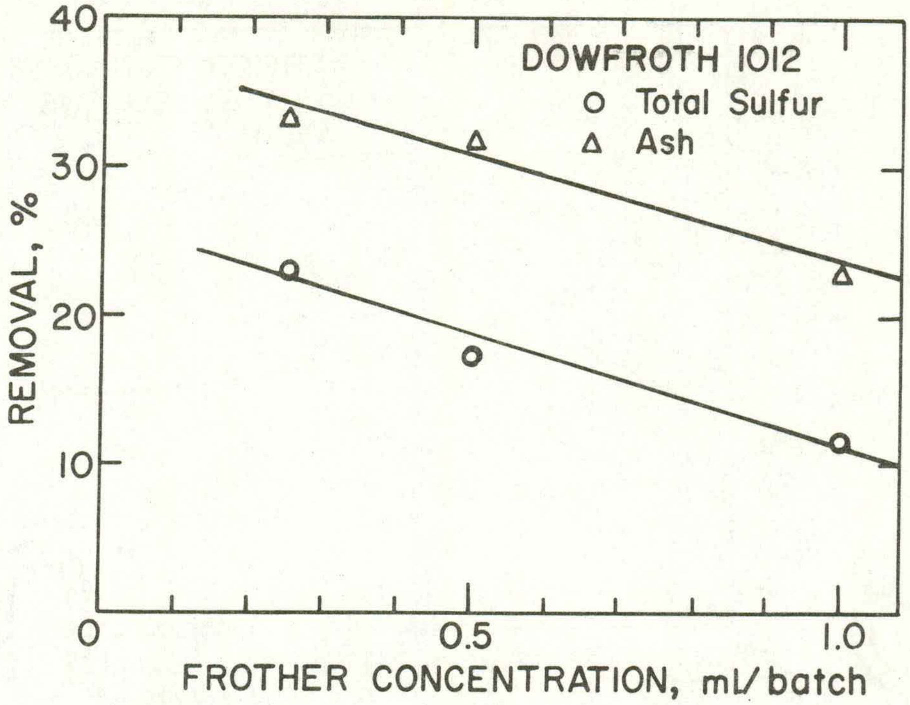

Figure 12. Effect of Dowfroth 1012 frother on ash and total sulfur removal.

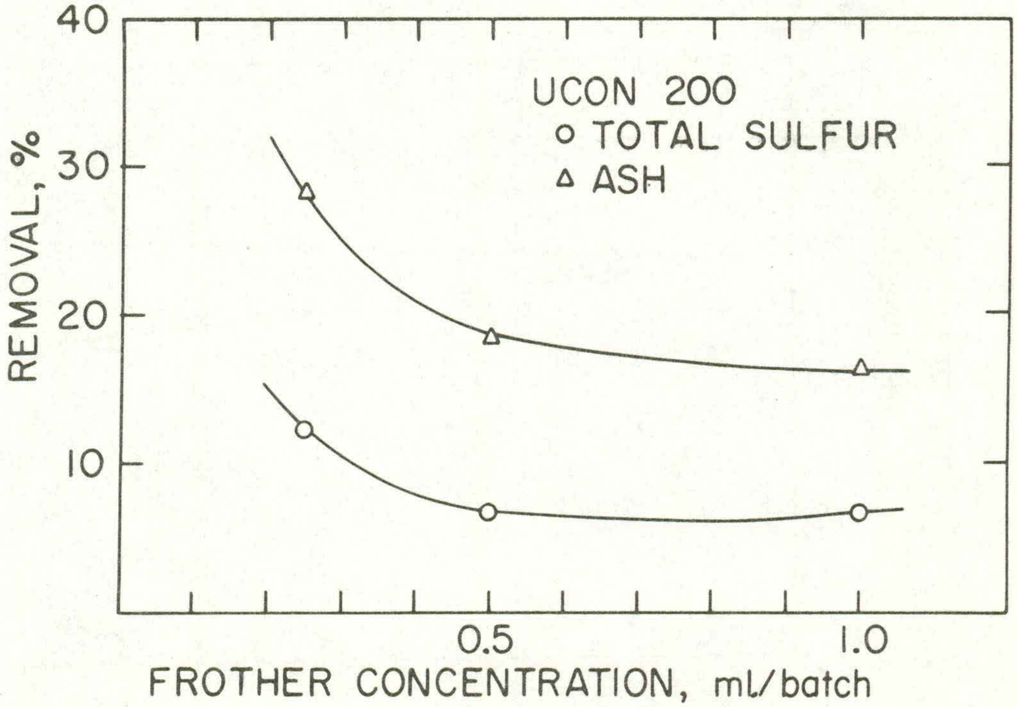

Figure 13. Effect of UCON 200 frother on ash and total sulfur removal.

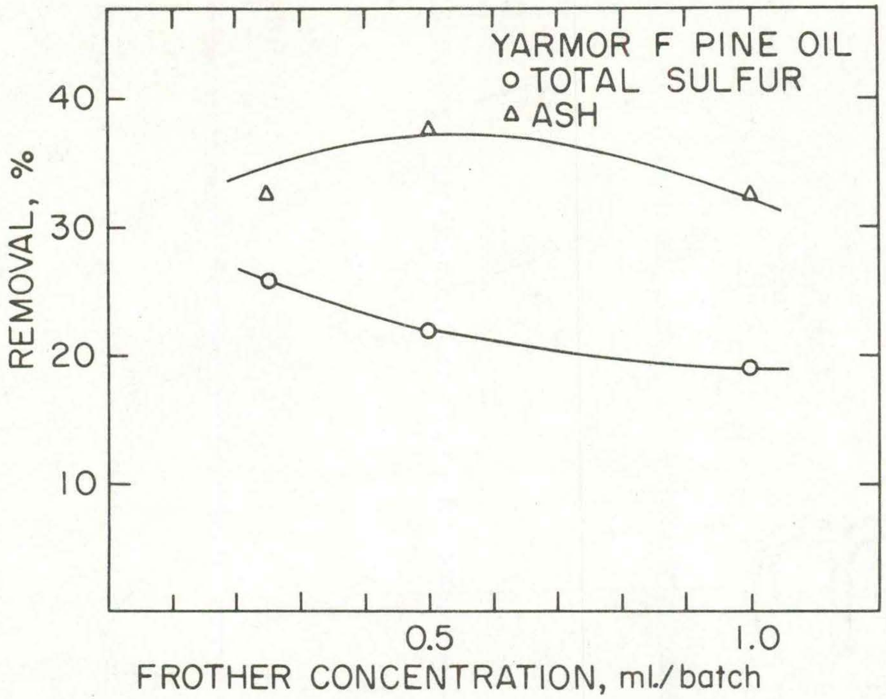

Figure 14. Effect of Yarmor F pine oil frother on ash and total sulfur removal.

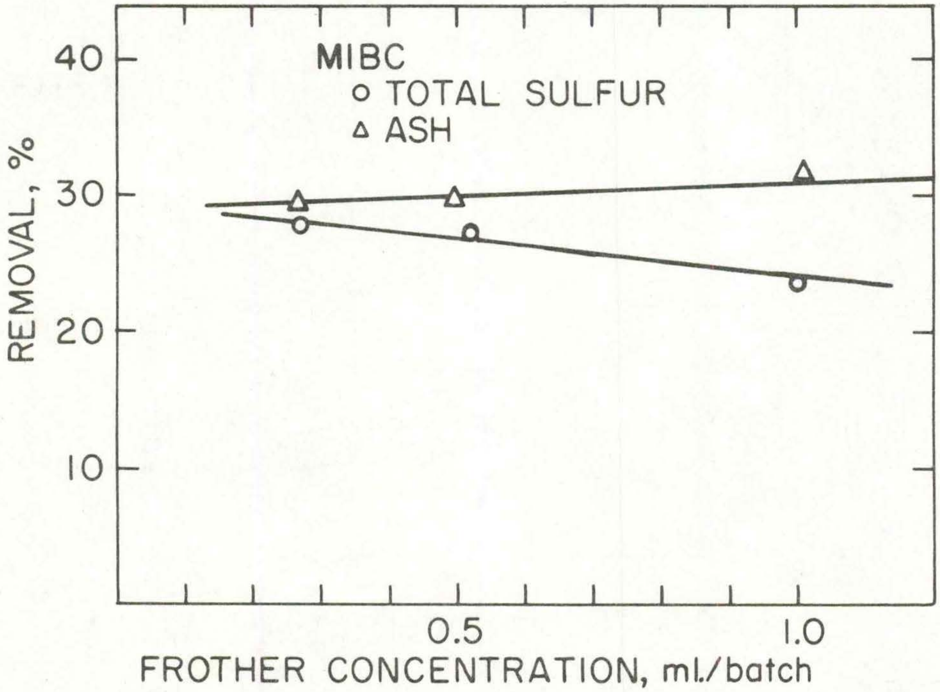

Figure 15. Effect of MIBC on ash and total sulfur removal.

IV. Conclusion

1. The Bureau of Mines two-stage flotation process was not found to function as described on Iowa coals.
2. A single-stage flotation technique using metal salts was found to be somewhat effective for cleaning Iowa coals.
3. A metal salt concentration of 10^{-5}M was found to be most effective in reducing the ash and sulfur content of the coal.
4. Conditioning of the coal slurry after adding $FeCl_3$ and prior to flotation was shown to decrease the ash and sulfur removal.
5. The hydrolysis products of $AlCl_3$, $Al(NO_3)_3$, $FeCl_3$, and $Fe(NO_3)_3$ were found to exhibit collector like properties in coal flotation.
6. Among six commercial frothers tested, MIBC produced the best ash and total sulfur removal. Little change was produced when a concentration of over 0.5 ml./batch was used. All of the frothers tested appeared to exhibit collector-like properties.

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