FINAL TECHNICAL REPORT
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Project Title: **REMOVAL OF PYRITE AND TRACE ELEMENTS FROM
WASTE COAL BY DISSOLVED-CO₂ FLOTATION AND
CHELATING AGENTS**

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ABSTRACT

The overall objective of this project was to use ultrafine bubbles generated by dissolved CO₂ to recover useable fuel, and reject pyrite and other minerals from a waste coal in flotation. In addition, a chelating agent was used to remove trace metals from the froth products.

Illinois No. 6 waste coal obtained from a refuse thickener of a coal cleaning circuit was used as the feed in flotation. The as-received waste coal had a top size of 2400 microns. The waste coal was ground to -75 microns (-200 mesh) and -44 microns (-325 mesh). The as-received and the ground waste coal samples were subjected to flotation.

Dissolved-CO₂ flotation tests were performed mainly in a 3-inch diameter by 8 feet high packed column under various test conditions. Some tests were also performed in a 2-inch diameter microbubble column for comparison. The flotation performance of the waste coal in the microbubble column was higher than that for the packed column. The packing in the packed column hindered the coal flotation. The separation efficiency of the ground coal was less than that for the as-received coal.

Flotation of the waste coal was also performed in the packed column using coarser bubbles generated by dispersed CO₂ and air. The separation efficiency of the ground waste coal of 44 microns top size was higher than that for dissolved-CO₂ flotation.

Additives were used to modify the waste coal surfaces. Triton-X 100, a nonionic surfactant and EDTA, a chelating agent, increased the separation efficiency of the waste coal.

Most of the trace metals in coal were reduced in different degrees by flotation. Triton X-100 or EDTA enhanced removal of chromium, nickel, and selenium. Applying EDTA to the froth products further removed lead significantly.

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EXECUTIVE SUMMARY

The overall objective of this project was to recover useable fuel from coal wastes using dissolved- CO_2 technology. Ultrafine bubbles were generated by first dissolving CO_2 in water under pressure and then releasing the pressure during operation.

Illinois No. 6 waste coal obtained from Kerr-McGee Coal Company located at Galatia, Illinois was used as the feed for the flotation tests. The waste coal was the underflow from a refuse thickener of a coal cleaning circuit. The coal waste was characterized using ASTM coal analyses. The coal waste had an ash content of 48.99% (dry basis). The pH of the coal waste slurry was 7.7. The ash was also analyzed.

The particle size distribution of the as-received waste coal was determined by wet screening and by Leeds and Northrup Microtrac analyzers. The particle size distribution was a bimodal distribution. The top size was 2400 microns and the mass mean diameter was 84.02 microns. The waste coal was ground to a top size of 75 microns (200 mesh) and of 44 microns (325 mesh).

The as-received and the ground waste coal samples were subjected to flotation. The dissolved- CO_2 flotation tests were performed in both a 3-inch diameter packed column and a 2-inch diameter microbubble column. The columns were modified by connecting a pressurized tank to the flotation columns. The pressurized water containing dissolved CO_2 was supplied by the tank to the columns. Flotation tests were performed at various conditions. Both columns were operated under similar conditions. Each column was not operated at its optimum conditions.

Kerosene was used as a collector and methyl isobutyl carbinol (MIBC) was used as a frother. Nonionic surfactants (Triton X-100, X-45, N-101, and N-42), flocculants (Betz 3367L and 3395), and ethylenediamine tetraacetate (EDTA), a chelating agent, were added to modify the coal surface.

The froth and tail samples were collected after about five column volumes of liquid has passed through the columns. The samples were analyzed for Btu, pyritic sulfur, and ash. The Btu recovery, pyrite rejection, ash rejection, and separation efficiency (which equals the Btu recovery plus pyrite rejection minus 100) were determined.

The separation efficiency of the as-received waste coal in the 3-inch diameter packed column as compared to that for the 2-inch diameter microbubble column was 34.1% versus 49.2%. The waste coal had better separation by dissolved CO_2 in the microbubble column than in the packed column. The packing in

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the packed column appeared to hinder the flotation of the waste coal when fine bubbles were used.

The separation efficiency of the fine ground waste coal with 75 microns top size and the as-received waste coal in the packed column was 20.2% and 34.1%, respectively. The separation efficiency of 44 microns top size and the as-received coal in the microbubble column was 38.4% and 49.2%, respectively. The separation efficiency for the fine ground waste coal was less than the as-received waste coal in both columns.

Flotation tests were also performed in the 3-inch diameter packed column by bubbles generated by dispersing CO₂ and air. The separation efficiency of the ground waste coal with a top size of 44 microns in the packed column was 71.2% and 71.9% for dispersed CO₂ and air flotation, respectively. It appeared that the froth was more stable and froth height was increased when CO₂ was used as compared to when air was used.

When Triton X-100 and EDTA were used to modify the coal surface, the flotation efficiencies of the waste coals had an increase of 1.5% to 12 %.

Flotation reduced most of the trace metals in coal. The reduction of arsenic, cadmium, chromium, nickel, lead, and selenium by dispersed-CO₂ flotation was approximately 45%, 58%, 40%, 50%, 54%, 10%, respectively.

Addition of EDTA and Triton X-100 in flotation enhanced removal of chromium, nickel, and selenium. Applying EDTA to the froth products further removed lead significantly.

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OBJECTIVES

The objectives of the project were to 1) use ultrafine bubbles generated by dissolved- CO_2 to separate pyrite and mineral matter from coal, 2) modify the coal surface to increase the separation of coal, and 3) apply a chelating agent on the froth products to further reduce trace metals in coal. The specific goals were to:

- develop chemical packages to enhance the separation of coal from pyrite and other mineral matter from Illinois No.6 waste coal;
- develop the optimum operational conditions for dissolved- CO_2 technology on Illinois No. 6 waste coal;
- determine the Btu recovery, pyrite rejection, ash rejection, and separation efficiency of the flotation on Illinois No. 6 waste coal;
- reduce trace metals in clean coal products by treating the coals with a chelating agent.

INTRODUCTION AND BACKGROUND

The coal wastes generated from coal mining operations and coal cleaning processes contain fine and ultrafine coals. Recovery of the fine/ultrafine coal from the coal wastes reduces the loss of useable fuels and the environmental impact.

Because of more stringent regulations on sulfur emissions from coal-fired boilers, it became necessary to remove pyrite from coal prior to coal combustion. Grinding the coal finer can liberate more pyrite which is then more accessible for rejection in coal cleaning. Advanced flotation technologies were used to separate the fine ground coal ^[1-7].

In physical cleaning of coal by flotation, the key controlling variables are the particle size of the feed, the coal surface property, and the operating conditions. In addition, the compatibility of the bubble size with the particle size is important. A large difference in size between the coal particles and the bubbles can result in poor separation.

In this project, ultrafine bubbles were used to recover fine/ultrafine coal from Illinois No. 6 waste coal. The fine bubbles were generated by first dissolving CO_2 in water under pressure prior to flotation and then releasing the pressure of the water during flotation. Based on observation, the majority of the bubble sizes in dissolved- CO_2 flotation were approximately 100 to 200 microns in diameter ^[8]. The fine

bubbles have the advantage of large surface area per unit volume of gas and may have the potential to recover fine coal.

The rationale of using CO_2 , instead of air, in flotation was the higher solubility of CO_2 in water than air. In addition, it was reported that CO_2 was more beneficial to coal flotation than air^[9,10]. Adsorption of CO_2 on coal surface retards the oxidation of pyrite resulting in favorable conditions for pyrite rejection^[9,10].

EXPERIMENTAL PROCEDURES

Waste Coal and Characterization

Illinois No.6 waste coal was obtained from Kerr-McGee Coal Corporation located at Galatia, Illinois. The sample was an underflow from a refuse thickener of a coal cleaning circuit.

A drum of the waste coal left from last year's ICCI project was used as the feed for the flotation tests in this project. The drum was tumbled for approximately 2 hours using a tumbler to redisperse the settled waste coal. Waste coal samples were taken immediately after tumbling for chemical analysis. The waste coal was characterized for proximate analysis, ultimate analysis, gross heating value, and sulfur form using ASTM methods. Chlorine was determined by oxygen bomb combustion and Volhard titration (ASTM D2361-91). The ash of the waste coal was also analyzed using inductively coupled plasma (ICP) spectroscopy.

The particle size distribution was determined by B&W's wet screening method and Leeds and Northrup Microtrac particle analyzers. Major trace metals in the waste coal were analyzed including: arsenic, chromium, cadmium, beryllium, lead, cobalt, nickel, selenium, and mercury. Mercury was determined using oxygen bomb combustion/cold vapor atomic absorption spectrophotometry (ASTM E-1184). Arsenic, beryllium, cadmium, lead, and cobalt, and selenium, were analyzed using electrothermal (graphite furnace) atomic absorption analysis (ASTM D 3684) with modified ASTM methods of E-886 and E-926 for sample preparation. Chromium and nickel were analyzed using inductively coupled plasma spectroscopy (ASTM D-1976) and the results were checked using atomic absorption spectroscopy.

The solids content of the waste coal was determined using a Computrac moisture analyzer. The pH of the slurry was measured using a pH meter.

Feed Preparation:

The waste coal had already been exposed to various chemicals during coal cleaning processes. Also, three types of flocculants were used in the thickening process. Leaching of the mineral matter and oxidation of the pyrite may result in changing the pH and increasing the dissolved mineral content in water. These may have some impact on the effectiveness of the chemicals used in the dissolved-CO₂ flotation process.

The waste coal feed samples were prepared at approximately 10% solids. Kerosene was added to the waste coal slurry as a collector to increase the hydrophobicity (water repelling) of coal surface. This enhanced the attachment of the bubbles on the coal surface. Methyl isobutyl carbinol (MIBC) was added to the slurry as a frother to increase the bubble generation.

Nonionic surfactants (Triton X-100, X-45, N-101, N-42), flocculants (3376L and 3395), and EDTA, a chelating agent were used to modify the surface of coal. Nonionic surfactants were obtained from Union Carbide. Flocculant 3367L and 3395 were obtained from Betz Industrial.

The as-received waste coal had a top size of 2400 microns was ground to a top size of 75 microns (200 mesh) and of 44 microns (325 mesh). The fine ground waste coal feeds were also prepared in a similar manner as for the as-received waste coal feed prior to flotation.

Dissolved-CO₂ Flotation:

The dissolved-CO₂ flotation tests were performed in a 3-inch diameter, 8-ft high packed column. The column was purchased from GL&V, Ontario in Ontario, Canada. The flotation column was modified by connecting a pressurized tank to the column for dissolved-CO₂ bubble generation. Figure 1 is a photograph of the test facility. This pressurized tank was used to dissolve CO₂ in water prior to and during flotation. Proper water level control was necessary for maintaining the fine size of the bubbles.

Prior to testing, the pressurized tank was purged with CO₂ at near one atmospheric pressure. The tank was then filled with water to a certain level. The gas pressure was increased until the tank pressure reached to 40 psig. Twenty minutes was allowed for CO₂ to be dissolved in water. A backpressure regulator at the bottom of the pressurized tank was opened to let the water flow from the pressurized tank to the bottom of the flotation column. Because of releasing of the pressure, the dissolved CO₂ was released from the water to form ultrafine bubbles. The feed slurry was then pumped to the column for separation.

Figure 1 - Photograph of Flotation Facilities:
3" Diameter Packed Column (left)
2" Diameter Microbubble Column (right)

The dissolved-CO₂ flotation tests were performed at different dosages of kerosene, MIBC, and bottom input water rates in the packed column. The feed rate and the tank pressure were maintained the same. The ranges of the test conditions performed in the packed and the microbubble column are shown in Table 1. A few tests were performed in the 2-inch diameter microbubble column for comparison. Both the packed and the microbubble column were operated at similar conditions. Each column was not operated at its optimum conditions.

Table 1 Test Conditions for Dissolved-CO ₂ Flotation in the Packed Column and the Microbubble Column (Slurry solids content ~ 10%, pH = 7.7)	
Kerosene	10 ~ 25 lbs/ton of coal
MIBC (frother)	1 ~ 15 lbs/ton of coal
CO ₂ pressure	40 psig
Slurry feed rate	0.27 lb/minute
Water with dissolved CO ₂	1.0 ~ 4.5 lb/minute
Wash water rate	0.4 ~ 0.7 lb/minute
Residence time	4.0 ~ 13.5 minutes

The froth and the tail samples were collected for a period of 5 to 10 minutes after five column volumes of the liquid has passed through the columns. The froth and the tail samples were weighed and then dewatered using vacuum filtration. The samples were then dried in an oven at 225°F overnight before they were weighed and analyzed for Btu, pyritic sulfur, and total ash. The yield (weight of froth collected as compared to the weight of the feed to the column in the same period of time), the Btu recovery, the pyrite rejection, the ash rejection, and the separation efficiency were determined.

Dispersed-CO₂ and Dispersed-Air Flotation:

Flotation tests were also performed in the packed column using bubbles generated by dispersing CO₂ and air for comparison. In these tests the dosages and other operating conditions were maintained as close as to those used in dissolved-CO₂ flotation. No optimization of the chemical dosages and other operational conditions was performed. The tests conditions of the selected flotation tests are shown in Table 2.

Table 2 Test Conditions for Dispersed CO ₂ and Air Flotation (Slurry solids content ~ 10%, pH = 7.7)	
Kerosene	25 lbs/ton of coal
MIBC (frother)	10 lbs/ton of coal
CO ₂ and air pressure	20 psig
CO ₂ and air flow rate	6 liters/minutes
Slurry feed rate	0.27 lb/minute
Wash water rate	0.6 lb/minute
Bottom water rate	1.9 ~3.3 lb/minute
Residence time	4.3 ~ 6.5 minutes

Calculations of Flotation Performance:

The Btu recovery and ash rejection were calculated based on Equations 1 and 2.

$$\text{Btu recovery} = (\text{Btu/lb in froth} \times \text{yield}) / (\text{Btu/lb in feed}) \quad (1)$$

Ash rejection =

$$100 - (\text{ash content in froth}) \times \text{yield} / (\text{ash content in feed}) \quad (2)$$

It was assumed that froth flotation did not remove organic sulfur. The pyrite rejection was calculated by Equation 3.

Pyrite rejection =

$$100 - (\text{pyritic sulfur in froth} \times \text{yield}) / (\text{pyrite in feed}) \quad (3)$$

The separation efficiency was calculated from Equation 4 ^[11-13].

Separation Efficiency =

$$\text{Btu Recovery} + \text{Pyrite Rejection} - 100 \quad (4)$$

Removal of Trace Metals from Clean Coal by A Chelating Agent:

Three froth products obtained from dispersed-CO₂ flotation were further treated with a EDTA solution. EDTA is a chelating agent. It could form complexes with the trace metals in the clean coal.

Approximately 2 grams of each froth product was mixed with 100 ml of 5% EDTA. The pH of the EDTA solution was adjusted to about 6. The solution was slightly acidic such that some of the trace metals may be soluble. The temperature of the solution was raised to 180 to 200°F. The samples were shaken for 4 hours before they were filtered for trace metal analysis.

RESULTS AND DISCUSSION

Waste Coal and Particle Size Analysis:

The analysis of Illinois No. 6 waste coal is shown in Table 3. The waste coal had a moisture content of 68.85%. The pH of the slurry was 7.7. The waste coal had an ash content of 48.99% (dry basis). The pyritic and the total sulfur were 1.41% and 2.58% (dry basis), respectively. The ash analysis of the waste coal is shown in Table 4.

The particle size analysis of the as-received waste coal (with a top size of 2400 microns) is shown in Table 5. The as-received waste coal is a bimodal distribution with peaks occurring at 150 and 9.38 microns. The mass mean diameter of the waste coal is 84.02 microns.

The particle size distribution of the ground coal with a top size of 75 microns (200 mesh) and of 44 microns (325 mesh) are shown in Tables 6 and 7, respectively.

Dissolved-CO₂ Flotation

The dosages for kerosene and MIBC used in flotation were increased substantially when the finely ground waste coals were used as the feed. This was because new surfaces were generated during grinding. It required higher dosages to cover the increased coal surface area.

The particle size distributions of the froth and tail samples obtained from the waste coal feed with a top size of 75 microns (200 mesh) are shown in Tables 8 and 9, respectively. The mass mean diameter of the froth and the tail sample was 8.09 and 12.06 microns, respectively. The mass mean diameter of the froth sample was less than that for the tail sample. This indicated that a significant portion of large particles rejected to the bottom of the column.

For coal surface modifications, the flocculant 3367L and 3395, and the nonionic surfactant Triton X-45, N-101, and N-42 showed some adverse effect on flotation. However, Triton X-100 and EDTA showed some improvement on separation efficiency.

Table 3 Waste Coal Analysis		
Basis	As-Received	Dry
Total Moisture, %	68.85	
Proximately Analysis:		
Moisture	68.85	
Volatile Matter	7.01	22.50
Fixed Carbon	8.88	28.51
Ash	15.26	48.99
Ultimate Analysis		
Moisture	68.85	
Carbon	12.39	39.78
Hydrogen	0.82	2.63
Nitrogen	0.20	0.63
Sulfur	0.80	2.58
Chlorine	0.11	0.36
Ash	15.26	48.99
Oxygen (by difference)	1.57	5.03
Gross Heating Value		
Btu per Lb.	2135	6854
Btu per Lb. (M&A Free)	----	13437
Sulfur Form		
Pyritic	0.44	1.41
Sulfate	0.05	0.16
Organic (by difference)	0.31	1.01
Total	0.80	2.58
pH	7.7	

Table 4 Ash Analysis of Illinois No. 6 Waste Coal	
Major Constituents	Concentration, % (by ICP)*
Silicon as SiO_2	52.37
Aluminum as Al_2O_3	18.33
Iron as Fe_2O_3	7.33
Titanium as TiO_2	0.65
Calcium as CaO	4.37
Magnesium as MgO	1.48
Sulfur as SO_3	6.26
Phosphorus as P_2O_5	0.73
Sodium as Na_2O^{**}	2.09
Potassium as K_2O^{**}	3.85
* Analysis by Inductively Coupled Plasma Spectroscopy (ICP).	
** Analysis by Flame Photometry.	

Table 5 Particle Size Distribution of As-Received Waste
Illinois No. 6 Coal

Microns	% Less	Difference
2400.00	100.00	0.45
1697.06	99.55	0.34
1200.00	99.21	0.36
848.53	98.86	0.26
600.00	98.60	1.99
424.26	96.61	1.41
300.00	95.20	2.65
212.13	92.55	4.59
150.00	87.96	11.28
106.07	76.68	6.88
75.00	69.80	7.31
53.03	62.49	6.97
37.50	55.52	3.62
26.52	51.90	6.17
18.75	45.73	5.38
13.26	40.36	4.14
9.38	36.21	8.73
6.63	27.48	8.45
4.69	19.03	5.65
3.31	13.38	3.93
2.34	9.44	3.23
1.66	6.22	2.31
1.17	3.90	1.82
0.83	2.08	1.27
0.59	0.82	0.82
0.41	0.00	0.00
0.29		
0.21		
CS (CALCULATED SURFACE AREA) = $0.93 \text{ m}^2 / \text{cm}^3$		
MMD (D43) = 84.02 microns		
SMD (D32) = 6.47 microns		

Table 6 Particle Size Distribution of -75 Microns (-200 mesh) Illinois No. 6 Waste Coal

Microns	% Less	Difference
150.00		
106.07		
75.00	100.00	0.49
53.03	99.51	0.33
37.50	99.19	1.22
26.52	97.96	7.33
18.75	90.63	10.84
13.26	79.79	11.24
9.38	68.55	14.67
6.63	53.88	13.53
4.69	40.36	10.50
3.31	29.85	8.29
2.34	21.57	6.89
1.66	14.68	4.42
1.17	10.25	3.69
0.83	6.57	2.92
0.59	3.64	2.52
0.41	1.13	1.13
0.29	0.00	0.00
0.21		
CS (CALCULATED SURFACE AREA) = $2.07 \text{ m}^2 / \text{cm}^3$		
MMD (D43) = 8.39 microns		
SMD (D32) = 2.90 microns		

Table 7 Particle Size Distribution of -44 Microns (-325 mesh) Illinois No. 6 Waste Coal

Microns	% Less	Difference
150.00		
106.07		
75.00		
53.03		
37.50		
26.52	100.00	5.00
18.75	95.00	4.82
13.26	90.18	10.55
9.38	79.63	19.17
6.63	60.46	18.00
4.69	42.46	12.97
3.31	29.49	8.78
2.34	20.71	7.06
1.66	13.65	5.06
1.17	8.59	3.97
0.83	4.62	2.76
0.59	1.86	1.78
0.41	0.08	0.08
0.29	0.00	0.00
0.21		
CS (CALCULATED SURFACE AREA) = $1.93 \text{ m}^2 / \text{cm}^3$		
MMD (D43) = 6.70 microns		
SMD (D32) = 3.11 microns		

Table 8 Particle Size Distribution of Illinois No. 6
Froth Product Obtained from a Waste Coal Feed
with a Top Size of 75 Microns (200 mesh)

Microns	% Less	Difference
150.00		
106.07		
75.00		
53.03		
37.50		
26.52	100.00	6.84
18.75	93.16	10.50
13.26	82.66	14.06
9.38	68.61	18.84
6.63	49.77	16.04
4.69	33.73	10.70
3.31	23.03	7.12
2.34	15.91	5.88
1.66	10.03	3.87
1.17	6.16	2.96
0.83	3.20	1.99
0.59	1.21	1.21
0.41	0.00	0.00
0.29		
0.21		
CS (CALCULATED SURFACE AREA) = $1.59 \text{ m}^2 / \text{cm}^3$		
MMD (D43) = 8.09 microns		
SMD (D32) = 3.78 microns		

Table 9 Particle Size Distribution of Illinois No. 6
Tail Sample Obtained from a Waste Coal Feed
with a Top Size of 75 Microns (200 mesh)

Microns	% Less	Difference
150.00		
106.07		
75.00		
53.03	100.00	4.91
37.50	95.09	5.09
26.52	90.00	10.09
18.75	79.90	12.20
13.26	67.70	12.72
9.38	54.98	14.39
6.63	40.59	11.46
4.69	29.13	9.02
3.31	20.12	6.23
2.34	13.89	4.92
1.66	8.97	3.36
1.17	5.60	2.69
0.83	2.92	1.86
0.59	1.05	1.05
0.41	0.00	0.00
0.29		
0.21		
CS (CALCULATED SURFACE AREA) = $1.39 \text{ m}^2 / \text{cm}^3$		
MMD (D43) = 12.06 microns		
SMD (D32) = 4.32 microns		

The detailed test conditions of the selected feed samples with different top sizes in both the 3" diameter packed column and the 2" diameter microbubble column are shown in Table 10.

The performance of the dissolved-CO₂ flotation was evaluated for yield, Btu recovery, pyrite rejection, ash rejection, and separation efficiency. The analyses of the selected froth samples and the corresponding flotation performance are shown in Table 11.

Effect of Column Type:

Comparing the flotation performance of the feed with a top size of 2400 microns obtained from the packed column with that from the microbubble column (Sample 3-3-1 vs. 6-17-1), the separation efficiency in the packed column and the microbubble column was 34.1% and 49.2%, respectively. The separation of coal was better in the microbubble column than in the packed column. The packing in the packed column seemed to hinder the separation. The rationale of inserting the packing in the column was that the packing can break large bubbles into smaller bubbles, prevent vertical mixing of the froth, increase bubble-particle interaction, and stabilize the froth on the top of the column ^[14]. However, in dissolved-CO₂ flotation, the bubbles are relatively small. The packing did not serve its original purpose. On the contrary, it retarded the coal from floating toward the top of the column. As a result, the separation efficiency was reduced.

Another reason for less separation efficiency in the packed column than in the microbubble column was that the froth in the packed column was not discharged as freely as in the microbubble column. In the microbubble column, the froth was collected from the overflow of the column. In the packed column, the froth went through a narrow pipe and then was forced out. A higher pressure was needed for discharge of the froth from the packed column. The bubbles generated by dissolved CO₂ did not provide high volume of gas flow. As a result, the pressure of the froth was low. Therefore, some of the coal particles were retained in the column and discharged to the bottom of the column.

Effect of Feed Size:

The separation efficiency for the feed with a top size of 2400 microns and of 75 microns in the packed column was 34.1% and 20.2%, respectively (Sample 3-3-1 and 4-26-2). The separation efficiency of the fine ground coal was less than the as-received waste coal. Similarly, in the microbubble column,

Table 10 Test Conditions for Dissolved-CO ₂ Flotation Tests								
Slurry Solids~ 10.0%, Slurry Feed Rate ~0.267 lb/minute, pH 7.7 CO ₂ Pressure ~ 40 psig								
Sample Number	Wash Water Rate (lb/m)	Water for Dissolved-CO ₂ (lb/m)	Residence Time (min)	Kerosene (lb/t)	MIBC (lb/t)	Top size micron	EDTA (lb/t)	Triton-X-100 (lb/t)
Dissolved-CO ₂ in 3" Diameter Packed Column								
3-3-1	0.7	1.59	8.5*	10	1	2400	0	0
4-26-2	0.7	1.60	8.4	10	6	75	0	0
5-9-1	0.7	1.73	8.0	10	6	75	0	5
5-25-1	0.7	1.67	8.2	10	6	75	15.5	0
Dissolved-CO ₂ in 2" Diameter Microbubble Column								
6-17-1	0.25	1.1	6.3*	10	1	2400	0	0
7-24-1	0.25	1.15	6.1	25	10	44	0	0
6-17-2	0.25	1.05	6.5	25	10	44	0	5
6-17-3	0.25	1.1	6.3	25	10	44	15.5	0
* The holdup volume for dissolved-CO ₂ was approximately 5% of the column volume.								

Table 11 Performance of Dissolved-CO ₂ Flotation Tests								
	Froth			Flotation Performance				
Sample Number	Gross Heating Value Btu/lb	Pyritic Sulfur % S	Ash %	Yield %	Btu Recovery %	Pyrite Rejection %	Ash Rejection %	Separation Efficiency %
Dissolved-CO ₂ Flotation in 3" Diameter Packed Column								
3-3-1	10862	0.76	19.08	32.5	51.6	82.5	87.3	34.1
4-26-2	9929	0.86	27.18	24.0	35.0	85.0	86.7	20.2
5-9-1	8289	1.19	37.2	59.7	72.1	49.7	54.7	21.8
5-25-1	8005	1.05	37.32	59.3	69.2	55.9	54.8	25.1
Dissolved-CO ₂ Flotation in 2" Diameter Microbubble Column								
6-17-1	10600	0.88	22.0	53.3	82.5	66.7	76.1	49.2
7-24-1	9494	1.02	30.18	58.1	80.5	58.0	64.0	38.4
6-17-2	9636	1.04	29.72	59.8	84.0	55.9	63.7	39.9
6-17-3	9596	0.96	29.14	57.8	80.9	60.7	65.6	41.6

the separation efficiency was 49.2% for the feed with a top size of 2400 microns as compared to 38.4% for the feed with a top size of 44 microns. The reduction in separation efficiency was more for the packed column than for the microbubble column. This could be attributed to more hinderance imposed on the fine ground particles by the packing material.

Effect of Additives:

The separation efficiency for the feed with a top size of 75 microns in the packed column was 20.2% (Sample 4-26-2). Addition of Triton X-100, the separation efficiency was increased to 21.8% (Sample 5-9-1). Using Triton X-100 in flotation increased the separation slightly.

EDTA was used in flotation mainly to modify the pyrite surface. Electrochemical studies of pure pyrite have shown that at low concentration of EDTA, the pyrite became more hydrophobic and at high concentration of EDTA, the pyrite surface became more hydrophobic ^[15-17]. This was due to interaction of EDTA with iron in pyrite to form Fe-S_x-Fe (hydrophobic species) and iron hydroxide (hydrophilic species). The hydrophilicity or hydrophobicity of the pyrite surface depends on the relative abundance of Fe-S_x-Fe and iron hydroxide. At high concentration of EDTA, the pyrite became more hydrophilic which is beneficial to coal cleaning by flotation.

When EDTA was added to the feed with a top size of 75 microns in the packed column, the separation efficiency was increased to 25.1% (Sample 5-25-1). In this case, it appeared that EDTA enhanced Btu recovery more than changing the surface of pyrite in coal. The overall effect of addition of EDTA in flotation was that EDTA improved flotation performance.

When the waste coal feed with a top size of 44 microns was subjected to flotation in the microbubble column, the separation efficiency was 38.4% (Sample 7-24-1). Addition of Triton X-100 and EDTA increased the separation efficiency to 39.9% and 41.6%, respectively.

Dispersed-CO₂ and Dispersed-Air Flotation:

The conditions of the selected flotation tests using dispersed-CO₂ and dispersed-air are shown in Table 12. The analyses of the froth products and the flotation performance of the tests are shown in Table 13.

The separation efficiency of the flotation tests using dispersed-CO₂ and dispersed-air was 71.2% and 71.9%, respectively (Sample 7-22-2 and 7-24-4). The separation

Table 12 Test Conditions for Dispersed-CO₂ and Dispersed-Air Flotation Tests

Slurry Solids~ 10.0%, Slurry Feed Rate ~0.267 lb/minute, pH 7.7

Sample Number	Wash Water Rate (lb/m)	Bottom Water Input Rate (lb/m)	Residence Time (min)	Kerosene (lb/t)	MIBC (lb/t)	Top size micron	EDTA (lb/t)	Triton-X-100 (lb/t)
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Dispersed-CO₂ in Packed Column

7-22-2	0.56	2.85	4.3*	25	10	44	0	0
7-21-5	0.56	2.85	4.3	25	10	44	1.8	0
7-22-6	0.56	2.85	4.3	25	10	44	0	0.5

Dispersed-Air in Packed Column

7-24-4	0.56	2.82	4.7*	25	10	44	0	0
7-24-5	0.56	2.82	4.7	25	10	44	1.8	0
7-24-6	0.56	2.82	4.7	25	10	44	0	0.5

* The holdup volume for CO₂ and air was approximately 30% and 25% of the column volume, respectively.

Table 13 Performance of Dispersed-CO ₂ and -Air Flotation Tests								
	Froth			Flotation Performance				
Sample Number	Gross Heating Value Btu/lb	Pyritic Sulfur % S	Ash %	Yield %	Btu Recovery %	Pyrite Rejection %	Ash Rejection %	Separation Efficiency %
Dispersed-CO ₂ Flotation in 3" Diameter Packed Column								
7-22-2	12296	0.66	10.72	53.7	96.3	74.9	88.3	71.2
7-21-5	12512	0.68	9.43	54.0	98.7	73.9	89.6	72.6
7-22-6	12694	0.57	8.98	52.7	97.6	78.7	90.3	76.3
Dispersed-Air Flotation in 3" Diameter Microbubble Column								
7-24-4	13114	0.35	6.16	43.2	82.6	89.3	94.6	71.9
7-24-5	13189	0.37	5.42	46.8	90.1	87.7	94.8	77.8
7-24-6	12722	0.48	8.50	54.0	103.5	80.5	93.0	84.0

efficiency for both dispersed-CO₂ and dispersed-air flotation was comparable. However, it appeared that the froth was more stable and the froth height was increased when CO₂ was used than when air was used.

When EDTA and Triton X-100 were added in the waste coal feed, the flotation efficiency of dispersed-CO₂ flotation was increased to 72.6% and 76.3% (Sample 7-21-5, 7-22-6), respectively. For dispersed-air flotation, the flotation efficiency was increased to 77.8% and 84.0% (Sample 7-24-5 and 7-24-6), respectively. The increase in separation efficiency by adding EDTA and Triton X-100 was more for air than for CO₂.

Removal of Trace Metals by EDTA:

The concentrations of the trace metals in the three froth products (Sample 7-22-2, 7-21-5, and 7-22-6) and the waste coal feed are shown in Table 14. The concentration of iron in the waste coal feed and the froth products are also shown in the same table.

Comparing the waste coal feed with the froth product using dispersed-CO₂ flotation with no Triton X-100 or EDTA, the concentration of arsenic, cadmium, chromium, nickel, lead, and selenium in the froth products was significant lower than that in the feed coal. The reduction of arsenic, cadmium, chromium, nickel, lead, and selenium was approximately 45%, 58%, 40%, 50%, 54%, 10%, respectively. This indicated that froth flotation reduced most of the trace metals.

The froth products which were collected with the addition of either Triton X-100 or EDTA (Froth 7-21-5 and 7-22-6) had significant lower concentration of chromium, nickel, and selenium than that for the froth product without the additives (Froth 7-22-2). This indicated that EDTA and Triton X-100 enhanced removal of chromium, nickel, and selenium.

Except for lead, addition of EDTA to further treat the froth products did not show significant reduction of trace metals.

The concentration of iron in the froth products was much less than that in the feed. Also, applying EDTA to further treat the froth products removed more than 30 to 35% of iron from coal.

It appeared that EDTA had favorable removal of lead and iron at pH of 6. The pH of EDTA can be adjusted such that it can be targeted to remove a particular trace metal in coal.

Table 14 Removal of Trace Metals by EDTA							
Trace Metal	Concentration, ppm						
	Feed Coal (44 microns top size)	Froth from Dispersed CO ₂ Flotation with no Additives (Sample 7-22-2)		Froth from Dispersed CO ₂ Flotation with EDTA (Sample 7-21-5)		Froth from Dispersed CO ₂ Flotation with Triton X-100 (Sample 7-22-6)	
		Before Addition of EDTA	After Addition of EDTA	Before Addition of EDTA	After Addition of EDTA	Before Addition of EDTA	After Addition of EDTA
Arsenic, AS	6.0	3.3	3.1	2.6	3.1	2.4	1.7
Beryllium, Be	0.09	0.18	0.95	0.46	0.61	0.58	0.72
Cadmium, Cd	0.85	0.36	0.35	0.42	0.33	0.40	0.29
Cobalt, Co	< 1.2	< 1.6	< 1.5	< 1.7	< 1.6	< 1.6	< 1.8
Chromium, Cr	383	231	155	158	157	150	160
Nickel, Ni	199	98	67	51	81	73	76
Lead, Pb	10	4.6	3.4	5.8	2.9	5.6	3.4
Mercury, Hg	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Selenium, Se	7.2	6.5	6.3	5.5	5.8	5.6	5.7
Iron, Fe	40,990	13,830	9,780	12,700	8,270	12,100	8,930

CONCLUSIONS

Dissolved- CO_2 flotation tests were performed in a 3-inch diameter packed column and a 2-inch diameter microbubble flotation column. The separation efficiency for the fine ground and as-received Illinois No. 6 coal ranged from 20.2% to 34.1% in the packed column and 38.4% to 49.2% in microbubble column. The separation efficiencies in microbubble column were significantly higher than those obtained from the packed column. The packing material in the packed column appeared to hinder the coal separation.

The separation efficiencies of the ground waste coal samples (75 microns and 44 microns top size) were less than those for the as-received waste coal in both columns.

When the waste coal was subjected to flotation by coarser bubbles generated by dispersing CO_2 and air, the separation efficiency was 71.2% and 71.9%, respectively. The separation efficiencies by dispersed- CO_2 and dispersed-air were comparable. However, the froth was more stable and the froth height was increased for CO_2 than for air.

Addition of Triton X-100 and EDTA increased the separation efficiency of the waste coal by 1.5% to 12%. The increase in separation efficiency was more when the dispersed bubbles were generated by air than by CO_2 .

Most of the trace metals in the waste coal were reduced by the flotation to a different degree. The reduction of arsenic, cadmium, chromium, nickel, lead, and selenium in dispersed CO_2 flotation was approximately 45%, 58%, 40%, 50%, 54%, 10%, respectively.

Addition of either Triton X-100 or EDTA removed significant amount of chromium, nickel, and selenium. Except for lead, further addition of EDTA to the froth products did not show significant reduction of trace metals.

RECOMMENDATIONS

The collection of the froth in the packed column can be modified such that little pressure is required to discharge the froth. Also, to reduce the hinderance to coal separation by the packing, most of the packing in the packed bed, particularly in the lower and the middle section of the packed column need to be taken out. However, a tighter packing may be needed at the top section of the column to stabilize the froth and increase the froth height.

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PROJECT MANAGEMENT REPORT
June 1, 1994 thru August 31, 1994

Project Title: **REMOVAL OF PYRITE AND TRACE ELEMENTS FROM
WASTE COAL BY DISSOLVED-CO₂ FLOTATION AND
CHELATING AGENTS**

DOE Grant No.:	DE-FC22-92PC92521 (Year 2)
ICCI Project No.:	93-1/5.1B-3P
Principal Investigator:	S. Y. Shiao Babcock & Wilcox Company
Project Manager:	Dr. Ken K. Ho, ICCI

COMMENTS

This project has been completed within budget.
Details and results of the test program are contained in
the Technical Report.

08/31/94

Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits (General Overhead)	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	0	0	0				0	0
	Estimated	252	554	0				202	1008
Sept. 1, 1993 to Feb. 28, 1994	Projected	3251	7152	293				2674	13370
	Estimated	6471	14237	5933				5994	32635
Sept. 1, 1993 to May 31, 1994	Projected	11359	24422	1825	31	4067		10883	52587
	Estimated	11116	23899	1602	31	4067		10817	51532
Sept. 1, 1993 to Aug. 31, 1994	Projected	19779	42525	3215	1101	4067		17592	88279
	Estimated	19486	41604	2739	582	4067		16697	85175

*Cumulative by Quarter

08/31/94

COSTS BY QUARTERRemoval of Pyrite and Trace Elements from Waste Coal by Dissolved- CO2
Flotation and Chelating Agents

Months and Quarters

O = Projected Expenditures \$88,279

△ = Estimated Actual Expenditures \$85,175

Total Illinois Clean Coal Institute Award \$88,279

SCHEDULE OF PROJECT MILESTONES

REF NO. 93-1/5.1B-3

08/31/94

Hypothetical Milestones:

- A. Project Management Activities
- B. Procurement of Waste Coal
- C. Characterization of Waste Coal
- D. Surface Modification
- E. Performing of Flotation Tests
- F. Removal of Trace Metals by Chelating Agents
- G. Data Analysis
- H. Project management reports prepared and submitted

Comments: All work is complete.

EQUIPMENT INVENTORY REPORT
Equipment Inventory
September 1, 1993, through August 31, 1994

Project Title: Removal of Pyrite and Trace Elements from Waste
Coal by Dissolved-CO₂ Flotation and Chelating
Agents

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.1B-3P
Principal Investigator: S. Y. Shiao, Babcock & Wilcox
Project Manager: K. Ho, Illinois Clean Coal Institute

List of Equipment Purchased

<u>Acct.#</u>	<u>Date</u> <u>Acquired</u>	<u>Short</u> <u>Description</u>	<u>Cost</u>	<u>Tag#.</u>	<u>Bldg. &</u> <u>Rm. #</u>
43196	3-15-94	3" ID x 8 ft Packed Column	\$2800,	C43198-003	Highbay Flotation Facility
43196	1-28-94	Backpressure Regulator	\$188,	C43196-006	Highbay Flotation Facility
43196	2-2-94	Flowmeter	\$134,	C43196-004	Highbay Flotation Facility
43196	1-18-94	Filter Bottle	\$398.21,	C43196-001	Highbay
		Filter Bottle	\$398.21,	C43196-002	Flotation Facility

HAZARDOUS WASTE REPORT
September 1, 1993, through August 31, 1994

Project Title: Removal of Pyrite and Trace Elements from
Waste Coal by Dissolved-CO₂ Flotation and
Chelating Agents

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.1B-3P
Principal Investigator: S. Y. Shiao, Babcock & Wilcox
Project Manager: K. Ho, Illinois Clean Coal Institute

In this project, Babcock & Wilcox used flotation to separate pyrite and mineral matter from Illinois No. 6 waste coal by Dissolved-CO₂ Flotation. No hazardous materials were purchased, used, or generated during the course of the project.

PUBLICATIONS AND PRESENTATIONS
September 1, 1993, through August 31, 1994

Project Title: Removal of Pyrite and Trace Elements from
Waste Coal by Dissolved-CO₂ Flotation and
Chelating Agents

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.1B-3P
Principal Investigator: S. Y. Shiao, Babcock & Wilcox
Project Manager: K. Ho, Illinois Clean Coal Institute

1. "Removal of Pyrite and Trace Elements from Waste Coal by
Dissolved-CO₂ Flotation and Chelating Agents", Paper
Presented at the ICCI/ICDB 12th Annual Contractors'
Technical Meeting, August 2-3, 1994, Champaign, Illinois.

A copy of the abstract is attached.

**REMOVAL OF PYRITE AND TRACE ELEMENTS FROM WASTE COAL
BY DISSOLVED-CO₂ FLOTATION AND CHELATING AGENTS**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.1B-3P
Principal Investigator: S. Y. Shiao, Babcock & Wilcox
Project Manager: K. Ho, Illinois Clean Coal Institute

ABSTRACT

In dissolved-CO₂ flotation, ultrafine bubbles are generated by CO₂ dissolved in water. The ultrafine bubbles have the potential to improve the separation efficiency in fine coal cleaning. Chemicals were used prior to or during dissolved-CO₂ flotation to improve the separation efficiency of pyrite and other minerals including trace metals from coal.

The ground Illinois No. 6 waste coal samples with a top size of 200 mesh (75 microns) and of 325 mesh (44 microns) were subjected to dissolved-CO₂ flotation in a 3" diameter packed column under different conditions. The surface of the coal was modified with two non-ionic surfactants, a flocculant, and a chelating agent. The froth and reject samples were analyzed for Btu, ash, and pyrite. A few selected froth samples will be analyzed for major trace metals. The particle size distributions of the selected froth and tail samples were determined by Microtrac analyzers.

The clean coal obtained from the dissolved-CO₂ flotation tests will be further treated with chelating agents to remove additional trace metals.