

[54] **FLOTATION OF PYRITE FROM COAL**

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[56] **References Cited**

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[57]

ABSTRACT

Pyrite is removed from coal by means of a two-stage froth flotation process. In the first stage, coarse pyrite is removed as underflow in a conventional froth flotation operation. In the second stage, the froth product from the first stage is subjected to froth flotation using a coal flotation depressant and a pyrite flotation collector, thereby removing a substantial proportion of fine pyrite.

6 Claims, No Drawings

FLOTATION OF PYRITE FROM COAL

Sulfur content of bituminous coals ranges from less than 1 percent to as much as 6 percent or more. Pyritic sulfur, i.e., sulfur in the form of pyrite or marcasite, essentially FeS_2 , generally makes up about 40 to 80 percent of the total sulfur present, with the balance being chiefly organic sulfur compounds. The pyritic sulfur is present in macroscopic and microscopic forms, the macroscopic form occurring chiefly as veins, lenses or beds, nodules, or pyritized plant tissue. The microscopic pyrite occurs as finely disseminated globules, veinlets, or euhedral crystals as small as 1 or 2 microns.

Air pollution as a result of burning high-sulfur coals has come under increasing public scrutiny and efficient means for processing coals to lower their sulfur content are, therefore, of increasing importance. Obviously, the sulfur content of some coals could be significantly reduced if most of the pyrite were physically removed during coal preparation. However, because coal must be crushed to a fine size in order to liberate pyrite, such a separation is extremely difficult with conventional coal preparation techniques. Specific gravity separation methods are ineffective because of the extreme fineness of some of the crushed material, and conventional froth flotation suffers from the tendency for the fine-size pyrite to float with the coal.

It has now been found, according to the present invention, that these problems can be largely overcome by means of a process in which the coal, in a finely-divided form in an aqueous pulp, is initially subjected to froth flotation to float the coal and remove most of the coarse, or essentially free, pyrite as underflow, along with the other nonfloatable refuse such as clay and shale. The froth product from this first step of the process is then repulped with fresh water and froth flotation, using a coal flotation depressant and a pyrite flotation collector, is employed to float a substantial portion of the remaining fine-size pyrite, while removing the coal product as underflow.

The feed material in the process of the invention may be any coal containing a substantial proportion of pyritic sulfur. This will usually be a bituminous coal having a pyritic sulfur content as discussed above. It is employed in a finely divided form, i.e., in a particle size of less than about 35 mesh (500 microns). Suitable particle size reduction may be readily achieved by conventional techniques such as grinding, pulverizing etc.

The initial stage of the process consists of conventional froth flotation of the finely divided coal from an aqueous pulp consisting of about 8 to 15 percent coal. This pulp is prepared by conventional means comprising addition of the coal to water in a flotation cell, or prior to addition to the cell, followed by thorough dispersion, as by mechanical stirring means. The pH of the pulp is not critical but will usually be about 4.5 to 8.5. A conventional frother may also be added to the dispersion in an amount of about zero to 0.001 percent by weight. It has, however, been found that optimum results are obtained in the process of the invention when the amount of frother employed is held to near the minimum amount required to float the coal. Suitable frothers include those commonly used in the froth flotation of coal and other minerals, e.g., pine oil and aliphatic alcohols such as methyl isobutyl carbinol (MIBC) and 2-ethylisohexanol.

Flotation of the coal is then accomplished by aeration at a flow rate of about 0.3 to 1.2 cubic feet of air per minute per gallon of slurry, generally for a period of about 1 to 3 minutes. Subsequently or simultaneously, the resulting froth product is separated by conventional means such as froth scrapers or paddles.

In the second stage of the process, this froth product is repulped in the flotation cell with fresh water to form a pulp having about 6 to 14 percent solids content. The pH of this pulp should be from about 4.5 to about 8.0, since values substantially above or below this range may have an adverse effect on the pyritic sulfur content of the second stage froth concentrate refuse. This pulp is then subjected to froth flotation, employing a coal flotation depressant and a pyrite flotation collector in order to float a substantial proportion of the fine-size pyrite, with the desired coal product remaining as underflow.

Preferably the second-stage pulp is initially conditioned with the coal flotation depressant by maintaining about 0.002 to 0.007 percent by weight of the depressant dispersed in the pulp for a period of about 5 seconds to 1 minute. The depressant consists of an organic colloid. This material may consist of a carbohydrate such as dextrin or modified, i.e., the so-called soluble, starches, such as modified corn or potato starch.

The organic colloid depressant may also consist of a proteinaceous material such as glue, gelatin, albumin, casein or whey.

It may also consist of complex polyhydroxy carboxylic acids and glucosides of high molecular weight such as quebracho extract, tannin or saponin.

About 0.001 to 0.005 weight percent of pyrite flotation collector is then added and the mixture again conditioned for a period of about 5 seconds to 1 minute. The collector consists of a xanthate, of the formula RO-C-SM , where R is an alkyl radical of at least about 3 carbon atoms and M is a metal such as potassium or sodium. Generally, the effectiveness of the compound increases with the number of carbon atoms in R, potassium amyl xanthate being a preferred compound. However, other xanthates such as sodium isobutyl xanthate and sodium isopropyl xanthate are also effective.

A frother such as those disclosed above is then added in similar amount, and the pulp is aerated in the same manner as in the first flotation stage.

The froth is again removed, as in the first stage, and the coal product recovered from the remaining slurry by means of conventional procedures such as vacuum filtration or centrifugation.

The invention will be more specifically illustrated by the following examples. In these examples, flotation tests were conducted in a standard laboratory rotor-stator flotation cell of the subaeration type. The impeller speed was set at 1,800 revolutions per minute, and the aeration rate was 0.33 cubic feet of air per minute. For the first stage of each test, 200 grams or 400 grams of minus 35 mesh bituminous coal was mixed in the cell with 2,300 milliliters of tap water, and the slurry was conditioned for 15 minutes to insure thorough wetting of the material. The 8 or 15 percent solids slurries had a pH ranging from about 5 to about 8.

The first stage of the process was a standard flotation procedure with minimum frother during which much of the coarse, or essentially free, pyrite was removed as

underflow with the other nonfloatable refuse. The froth product from the first stage was then repulped in the floatation cell with 2,300 milliliters of fresh water, and the slurry was treated with a coal floatation depressant. After a brief conditioning time, about 1 minute, the pyrite floatation collector was added. After another brief conditioning period, the frother was added, the air applied, and the froth product collected for 1 to 3 minutes.

Feed compositions, reagents and the results are given, in tabular form in the following examples. Tailings 1 in these examples is the underflow refuse from the first stage, tailings 2 the froth concentrate refuse in the second stage, and clean coal is the underflow product from the second stage. Hercules RT1712 is a trade name for pine oil, available from Hercules Powder Co. Aero Xanthate 350 is a trade name for potassium amyl xanthate, available from American Cyanamid Co. Aero Depressant 633 is a trade name for a carbohydrate colloid flotation depressant, available from American Cyanamid Co. The feed material in Examples 1 to 17 consisted of coal from the Lower Freeport coal bed in Cambria County, Pa., while those in Examples 18, 19 and 20 consisted of coal from the Lower Kittanning coal bed in Armstrong County, Pa., the Middle Kittanning bed in Lawrence County, Pa., and the Pittsburgh bed in Green County, Pa., respectively.

Example 1 shows the results obtained with no xanthate collector. Obviously, no selective pyrite flotation occurred. Examples 2 through 8, however, show the effect of increased amounts of xanthate in the second stage. The depressant dosage also had to be increased to avoid floating the coal, but this did not adversely affect pyrite flotation. The clean coal products in Examples 2 through 8, which amounted to 50 to 60 percent of the feed, contained only 0.29 to 0.56 percent pyritic sulfur, whereas the tailings 2 product contained 3.83 to 7.71 percent. That is, although tailings 2 represented only 3.4 to 10.7 percent of the feed product, it contained 45 to 75 percent of the pyrite available in the second stage. These results clearly demonstrate the selectivity of the process.

Examples 2 through 8 were run at reduced pH with HCl, but this step was not essential with this coal. Examples 9 and 10 show only slight adverse effect as a result of eliminating some, and then all of the HCl.

Examples 11 and 12 show that quebracho depresses the coal in the second stage as well as does the Aero Depressant 633. Example 13 shows results with modified cornstarch, which was also effective. And examples 14 and 15 show that methylisobutyl carbinol is as effective as pine oil as the frothing agent.

Examples 16 and 17 show results with the lower molecular weight xanthate collectors, sodium isobutyl xanthate and sodium isopropyl xanthate. Potassium ethyl xanthate was also tested, but it was not effective at concentrations below about 2 lb/ton of coal. These results indicate that the amyl xanthate is the most powerful collector, while the butyl, propyl, and ethyl xanthates are gradually less effective.

Examples 18, 19, and 20 show results with three additional coal samples to demonstrate the broad application of the process.

EXAMPLE 1

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur

Feed	100.0	31.3	2.21	1.78
Tailings 1	36.1	68.2	3.47	3.31
Tailings 2	2.7	9.5	1.15	0.56
Clean coal	61.2	10.5	1.52	0.93

5	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		0.5	
	Hercules RT 1712		0.1	
	Final pH=5.6			

EXAMPLE 2

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	31.7	2.22	1.79
Tailings 1	36.8	67.5	3.31	3.21
Tailings 2	7.7	11.5	4.50	3.83
15 Clean coal	55.5	10.8	1.18	0.56

15	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		0.5	
	Aero Xanthate 350		0.2	
	Hercules RT1712		0.1	
20	Final pH=6.2			

EXAMPLE 3

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	34.3	2.38	1.91
Tailings 1	43.1	65.7	3.58	3.46
Tailings 2	6.0	12.0	4.63	4.24
Clean coal	50.9	10.3	1.10	0.32

30	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		0.5	
	Aero Xanthate 350			0.3
	Hercules RT1712		0.1	
	Final pH=5.7			

EXAMPLE 4

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	25.2	2.12	1.77
Tailings 1	34.1	57.2	3.52	3.52
Tailings 2	5.8	12.1	5.63	5.23
40 Clean coal	60.1	8.4	0.99	0.45

40	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		0.5	
	Aero Xanthate 350		0.3	
	Hercules RT1712		0.1	
45	Final pH=5.7			

EXAMPLE 5

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	32.2	2.29	1.92
Tailings 1	36.6	70.1	3.43	3.42
Tailings 2	4.7	15.5	7.66	6.91
Clean coal	58.5	9.9	1.12	0.56

50	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		0.7	
	Aero Xanthate 350		0.5	
	Hercules RT1712		0.05	
55	Final pH=6.2			

EXAMPLE 6

Product	Analyses, percent			
	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	31.2	2.23	1.79
Tailings 1	36.3	68.1	3.49	3.29
Tailings 2	3.4	17.8	8.47	7.71
Clean coal	60.3	9.7	1.12	0.56

60	Reagents	Pounds per ton of coal		
	Hydrochloric acid		0.9	
	Aero Depressant 633		1.0	
	Aero Xanthate 350		0.5	
	Hercules RT1712		0.05	
65	Final pH=6.2			

EXAMPLE 7

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	32.1	2.28	1.85
Tailings 1	37.6	68.1	3.40	3.34
Tailings 2	10.7	11.6	4.71	4.13
Clean Coal	51.7	10.1	0.96	0.29

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Aero Depressant 633		0.7	
Aero Xanthate 350		0.5	
Hercules RT1712		0.1	
Final pH=6.2			

EXAMPLE 8

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	32.2	2.30	1.84
Tailings 1	34.6	73.3	3.55	3.34
Tailings 2	8.7	14.4	5.96	5.57
Clean coal	56.7	10.0	0.97	0.35

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Aero Depressant 633		1.0	
Aero Xanthate 350		0.5	
Hercules RT1712		0.1	
Final pH=6.4			

EXAMPLE 9

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	26.8	2.24	1.91
Tailings 1	41.7	52.1	3.53	3.46
Tailings 2	4.9	11.7	5.18	4.55
Clean coal	53.4	8.5	0.97	0.45

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.6	
Aero Depressant 633		0.5	
Aero Xanthate 350		0.3	
Hercules RT1712		0.1	
Final pH=6.4			

EXAMPLE 10

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	25.8	2.29	1.86
Tailings 1	35.4	57.0	3.72	3.43
Tailings 2	9.8	9.7	3.99	3.44
Clean coal	54.8	8.6	1.07	0.56

Reagents		Pounds per ton of coal	
Aero Depressant 633		0.5	
Aero Xanthate 350		0.3	
Hercules RT1712		0.1	
Final pH=8.1			

EXAMPLE 11

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	25.3	2.19	1.78
Tailings 1	33.4	58.7	3.48	3.48
Tailings 2	6.0	11.5	5.30	4.65
Clean coal	60.0	8.3	1.17	0.56

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Quebracho		0.5	
Aero Xanthate 350		0.3	
Hercules RT1712		0.1	
Final pH=5.6			

EXAMPLE 12

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	26.2	2.26	1.78
Tailings 1	33.1	61.5	3.86	3.86
Tailings 2	7.5	11.8	5.39	4.57
Clean coal	59.4	8.4	0.97	0.27

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Quebracho		0.7	
Aero Xanthate 350		0.4	
Hercules RT1712		0.1	
Final pH=5.6			

EXAMPLE 13

Product	Analyses percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	29.1	2.25	1.80
Tailings 1	36.3	65.3	3.63	3.48
Tailings 2	5.4	11.2	3.53	2.86
Clean coal	58.3	8.3	1.27	0.65

Reagents		Pounds per ton of coal	
First stage: Methyl isobutyl carbinol		0.1	
Second stage: Water soluble cornstarch		0.7	
Aero Xanthate 350		0.7	
Methylisobutyl carbinol		0.1	

EXAMPLE 14

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	25.7	2.25	1.87
Tailings 1	34.6	57.9	3.66	3.66
Tailings 2	6.5	11.5	5.63	4.87
Clean coal	58.9	8.4	1.05	0.48

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Aero Depressant 633		0.5	
Aero Xanthate 350		0.2	
Methylisobutyl carbinol		0.1	
Final pH=5.5			

EXAMPLE 15

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	26.2	2.24	1.81
Tailings 1	34.5	58.5	3.70	3.70
Tailings 2	8.8	11.3	4.78	4.34
Clean coal	56.7	8.8	0.95	0.27

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.9	
Aero Depressant 633		0.5	
Aero Xanthate 350		0.3	
Methylisobutyl carbinol		0.1	
Final pH=5.7			

EXAMPLE 16

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	24.9	2.48	1.95
Tailings 1	30.8	61.2	4.45	4.18
Tailings 2	10.4	11.0	4.44	4.07
Clean coal	58.8	8.4	1.10	0.41

Reagents		Pounds per ton of coal	
Hydrochloric acid		0.6	
Aero Depressant 633		0.7	
Sodium isobutyl xanthate		0.5	
Methylisobutyl carbinol		0.08	
Final pH=7.5			

EXAMPLE 17

Product	Analyses, percent			Pyritic sulfur
	Weight	Ash	Total sulfur	
Feed	100.0	23.4	2.29	1.72
Tailings 1	31.7	55.5	4.01	3.67
Tailings 2	7.5	8.0	1.86	1.16
Clean coal	60.8	8.5	1.44	0.77

Reagents		Pounds per ton of feed	
Aero Depressant 633		0.7	
Sodium isopropyl xanthate		0.5	
Methylisobutyl carbinol		0.08	
Final pH=8.1			

EXAMPLE 18

Analyses, percent

Product	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	22.4	2.89	2.43
Tailings 1	20.0	65.8	6.18	6.18
Tailings 2	11.1	17.0	6.56	6.56
Clean coal	68.9	10.7	1.34	0.68

Reagents

	Pounds per ton of coal
First stage: Methylisobutyl carbinol	0.25
Second stage: Hydrochloric acid	1.1
Aero Depressant 633	1.0
Aero Xanthate 350	0.7
Methylisobutyl carbinol	0.08

Final pH=7.3

EXAMPLE 19

Analyses, percent

Product	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	6.8	2.87	2.35
Tailings 1	11.3	31.7	12.30	12.13
Tailings 2	9.9	12.2	7.83	7.23
Clean coal	78.8	2.6	0.89	0.34

Reagents

	Pounds per ton of coal
First stage: Kerosine	0.6
Methylisobutyl carbinol	0.16
Second stage: Aero Depressant 633	1.0
Aero Xanthate 350	0.7
Methylisobutyl carbinol	0.08

Final pH=5.3

EXAMPLE 20

Analyses, percent

Product	Weight	Ash	Total sulfur	Pyritic sulfur
Feed	100.0	15.3	2.45	1.52

Tailings 1	16.3	56.7	5.68	5.35
Tailings 2	9.1	10.6	4.57	3.62
Clean coal	74.6	6.8	1.48	0.43

Reagents

	Pounds per ton of coal
First stage: Methylisobutyl carbinol	0.25
Second stage: Hydrochloric acid	1.1
Aero Depressant 633	0.7
Aero Xanthate 350	1.0
Methylisobutyl carbinol	0.08

Final pH=7.6

I claim:

1. A two-stage process for removal of pyrite from coal comprising the steps of (1) forming an aqueous pulp of the coal in a finely divided state, and frothing the pulp to collect the coal in the froth and leave a residual pulp containing coarse pyrite and (2) removing and repulping the froth product from step (1), conditioning the pulp with a coal flotation depressant and a pyrite flotation collector, and frothing the pulp to collect a substantial portion of fine pyrite in the froth and leave a residual pulp containing a product coal of low pyritic sulfur content.
2. The process of claim 1 in which the depressant employed in stage 2 is an organic colloid.
3. The process of claim 2 in which the depressant is a carbohydrate.
4. The process of claim 2 in which the depressant is quebracho extract.
5. The process of claim 1 in which the collector employed in stage 2 is a xanthate.
6. The process of claim 5 in which the xanthate is potassium amyl xanthate.

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