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Desulfurization of Coal by Flotation of Coal in a Single-Stage Process

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Desulfurization of Coal by Flotation of Coal in a Single-Stage Process

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Abstract

A single-stage flotation process was developed in which *coal* was floated out and pyrite was depressed. Up to 90% of the pyritic sulfur content of bituminous coal could be removed at 75% coal recovery. The process was applied to three Canadian and two United States coals. Higher coal recoveries were obtained for low sulfur coals; up to 94.4% coal recovery was possible with 18.2% pyritic sulfur removal. Sulfate sulfur, trace elements, and ash were also removed.

The effects of particle size, temperature, slurry density, and flotation time were studied. From a simplified rate equation a nonintegral order was obtained for the flotation process.

INTRODUCTION

In the utilization of coal for energy, its sulfur content presents a pollution problem, and various processes aimed at removing sulfur from coal have been reported. These include washing (*1*), magnetic separation (*2*, *3*), solvent refining (*4*, *5*), ferric sulfate treatment (*1*), alkali leaching (*6*, *1*), molten salt reaction (*7–9*), and the use of gases (*10*, *11*).

Flotation involving coal has been known and used for a long time, but the emphasis has not been on the removal of sulfur (*12–14*). Flotation has also been used together with other processes to produce ultraclean coal for the production of carbon electrodes (*15*). A recent study (*16*) involves two-stage flotation for the removal of sulfur. In this, pyrite particles are floated out while coal is depressed. In one laboratory test the pyritic sulfur content of coal was reduced from 2.31 to 0.25% in two stages.

The air avidity of all coals, with the exception of lignite, is greatly enhanced by the use of an oily collector which increases the natural contact angle and decreases the induction period (*17*). Oxidizing agents greatly reduce the contact angle at a coal surface, and hence the floatability of the coal. In high concentrations, reducing agents can act as depressants for coal. Low-rank coals require more collector to effect a given recovery. Emulsification of the collector oil is shown to result in considerable economics in reagent consumption (*18*).

In this work the natural air avidity of coal is taken advantage of, and coal is floated off rather than the more customary impurities.

BASIC CONCEPTS

By analogy to chemical kinetics, an equation representing the kinetics of the flotation process can be written as

$$dC/dt = k_i \Pi C_i^{n_i}$$

where C_i represents the concentration of a particular species i in the cell, and n_i specifies the order of the process. With some loss of generality, every variable except the concentration of the floatable material, C, and the concentration of air, C_a, may be included in the rate constant, k'. Thus in

$$dC/dt = k' C^n C_a^{n_a}$$

k' is a complex function involving, among other things, reagent concentration, particle and bubble sizes, induction times, flotation cell design, rate of froth removal, previous treatment, and power input.

In the flotation of coal, all such variables, and also the air supply, remain substantially constant. A familiar form of the rate equation may then be applied:

$$dC/dt = -k_n C^n$$

where k_n is the flotation rate constant and n is the order of the process.

The slurry density W, defined as

$$W = \frac{\text{mass of solid}}{\text{total mass of slurry}} \times 100$$

is related to concentration through

$$W = C\frac{100}{\rho}$$

where ρ is the density of the slurry and is taken as constant for a given system.

The rate equation may be defined by

$$R = dC/dt = -kW^n$$

where k is the corresponding rate constant. A plot of log R vs log W gives a straight line of slope n.

Removal Efficiency

In this study, percent removal, R_s, is defined as

$$R_s = \frac{S_R - S_F}{S_R} \times 100$$

where S_R and S_F are the percent sulfur in the original and the desulfurized coal, respectively.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. A Denver flotation cell was used. Coal samples were ground and sized and stored in plastic bags.

Preliminary Experiments

Floating Out Sulfur-Bearing Species

A coal slurry of 10% solids was agitated for 0.5 hr in the overhead slurry reservoir. Some 10% solution of potassium amyl xanthate was added (5 ml/kg of solid coal). Pine oil (0.7 ml/kg coal) was also added and the slurry made to flow into the flotation cell. The slurry temperature was 28 °C, the air flow rate 2 l/min, and the impeller speed 1770 rpm.

The flotation was continued a further 5 min after the reservoir had been emptied.

Floating Out Coal

The flotation experiment was repeated using 5.5 kg of slurry containing 500 g of coal. A 10-ml portion of 10% sodium sulfite (Na_2SO_3) solution

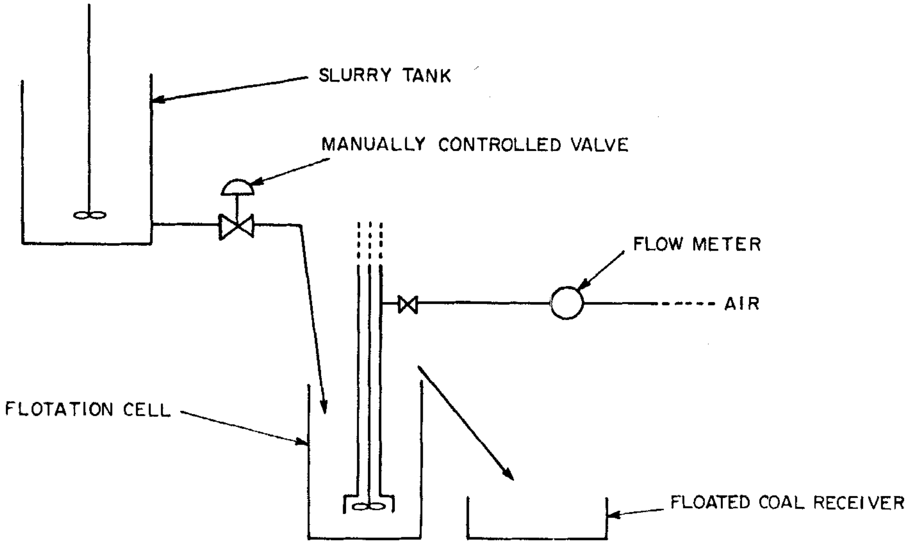

FIG. 1. Schematic diagram of the process.

was added and, after 10 min, 7 ml of kerosene (collector) was added. A 10-ml portion of cresylic acid (frother) was then added. The flotation cell was again operated with 2 l/min air flow and an impeller speed of 1770 rpm.

This experiment was repeated but with the following:

Frother: Pine oil, 0.2 g/kg solid
Depressant: Lime, 5 g/kg solid
Collector: Kerosene, 2 g/kg solid
Coal size: $-170 + 120$ U.S. mesh
Cell temperature: -29 °C
Slurry density: 5% solids

The flotation was run until no more solids floated.

Flotation Variables

Particle Size

Using kerosene, lime, and pine oil, the flotation was carried out for different particle size ranges while keeping other variables constant. The sizes were −40 + 70, −70 + 120, −120 + 140, −140 + 200, −200 + 250, and −250 U.S. mesh.

Pulp Density

Flotation runs were made for slurries containing 5, 10, 15, and 20% by weight of solid coal of size −140 + 200 U.S. mesh. All other variables were held constant.

Flotation Time

Flotation of a 10% solids slurry was carried out. The floated material was collected separately after 1, 3, 5, 10, 15, and 18 min. The particle size of coal used was −70 + 120 U.S. mesh. Other variables were also held constant.

Temperature

Flotation runs were made at 14, 23, 28, 35, 42, and 46°C with other variables held constant.

For this study of the effect of different variables, coal from West Virginia (WVB) was used.

Application to Different Coals

The flotation process was applied to coal samples from the United States and Canada, ground to pass 120 U.S. mesh. For each of the four coals, 550 g were added to 4950 g of water to make 10% slurry at 30°C. The slurry was well agitated and 2.75 g of lime added. Kerosene (0.75 ml) and pine oil (0.15 ml) were added. The air flow rate of 2 l/min was maintained through the cell and the operation was continued for 7 min.

Coals used included:

(1) Pennsylvania Bituminous Coal (PB2)
(2) Canadian High Volatile A Bituminous Coal (CHB2)
(3) Canadian Medium Volatile Bituminous Coal (CMB)
(4) Canadian Low Volatile Bituminous Coal (CLB)

RESULTS AND DISCUSSION

Preliminary Experiments

In floating out sulfur-bearing species, a coal recovery of 40% and a sulfur removal of 19.7% were obtained. Much coal floated along with the reject as no depressant was used.

In floating out coal using kerosene, cresylic acid, and sodium sulfite, 97.4% of coal was recovered with a total sulfur removal of 12.9%. Besides

TABLE 1
Elemental Distribution—Floating Out Coal

Element	Original coal	Floated material	Bottoms material
Co, ppm	4.81	4.20	7.83
U, ppm	0.684	0.68	1.30
Dy, ppm	1.03	0.940	1.87
Sm, ppm	6.78	5.28	11.1
Eu, ppm	0.250	0.216	0.440
Ba, ppm	119	111	472
Ti, ppm	540	532	1439
Sr, ppm	97.3	80.0	157
Br, ppm	16.7	17.9	10.6
Na, %	0.047	0.044	0.156
V, ppm	19.4	19.0	23.7
Al, %	0.945	0.870	3.51
Mn, ppm	34.3	29.2	126
Cl, ppm	1410	1420	820
Ca, %	0.324	0.250	1.37

TABLE 2
Elemental Distribution—Floating Out Coal

Element	Original coal	Floated material	Bottoms material
Co, ppm	5.29	3.73	6.48
U, ppm	0.681	0.566	0.949
Dy, ppm	0.891	0.748	1.05
Sm, ppm	7.20	4.27	8.85
Eu, ppm	0.248	0.185	0.273
Ba, ppm	143	84.1	189
Ti, ppm	534	499	850
Sr, ppm	91.1	87.6	119
Br, ppm	14.7	18.3	13.6
Na, %	0.050	0.029	0.053
V, ppm	21.1	17.9	24.9
Al, %	1.87	0.680	2.51
Mn, ppm	44.2	18.6	53.9
Cl, ppm	1460	1630	1180
Ca, %	0.545	0.220	0.757

the presence of sulfur in the sodium sulfite introduced, cresylic acid is known to have a collector action on the pyrite. The coal recovery was, however, satisfactory.

By using a narrow size range (−70 + 120 U.S. mesh), pine oil instead of cresylic acid, and lime as depressant, a sulfur removal of 40% was obtained at 88.3% coal recovery. The pyritic sulfur removal was 57.5%, reducing its concentration in the coal from 1.53 to 0.65%. Sulfate sulfur removal was 89.5% and the ash content was reduced from 12.2 to 6.0%. Dissolution of soluble sulfates might have contributed to the high sulfate sulfur removal.

The distribution of trace elements in the various portions separated by flotation was obtained by neutron activation analysis in the Slowpoke reactor. These are given in Tables 1 and 2 for the kerosene flotation. With the exception of bromine and chlorine, all the elements were concentrated in the bottoms (reject). This is desirable.

Effect of Flotation Variables

Particle Size

The effect of particle size on recovery is represented in Fig. 2. The decline

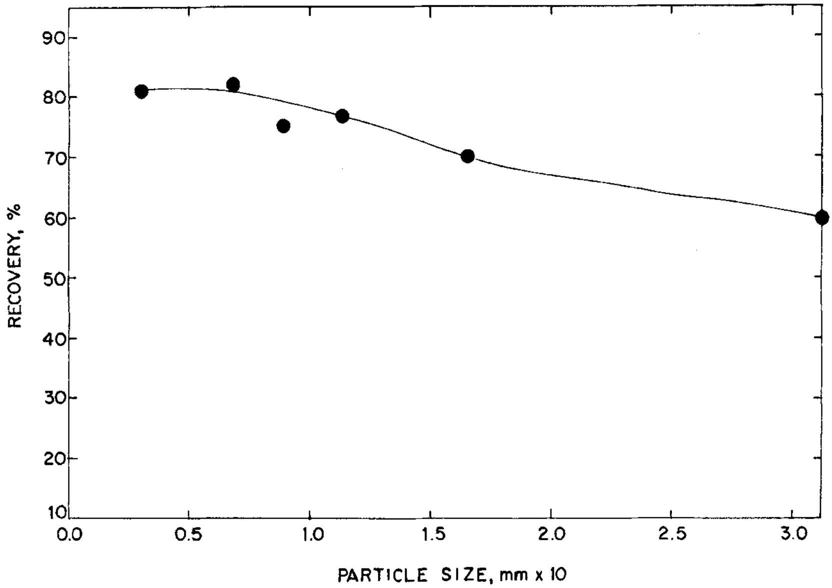

FIG. 2. Effect of particle size on recovery.

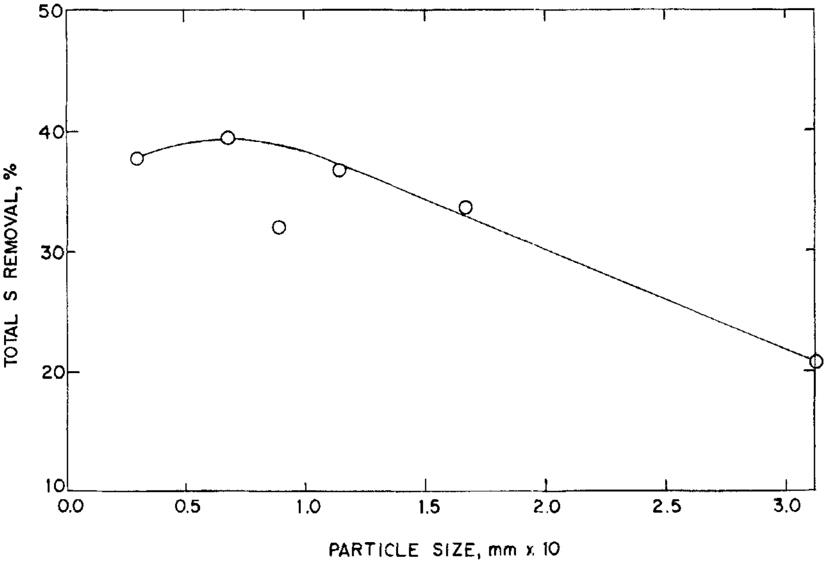

FIG. 3. Effect of particle size on total sulfur removal.

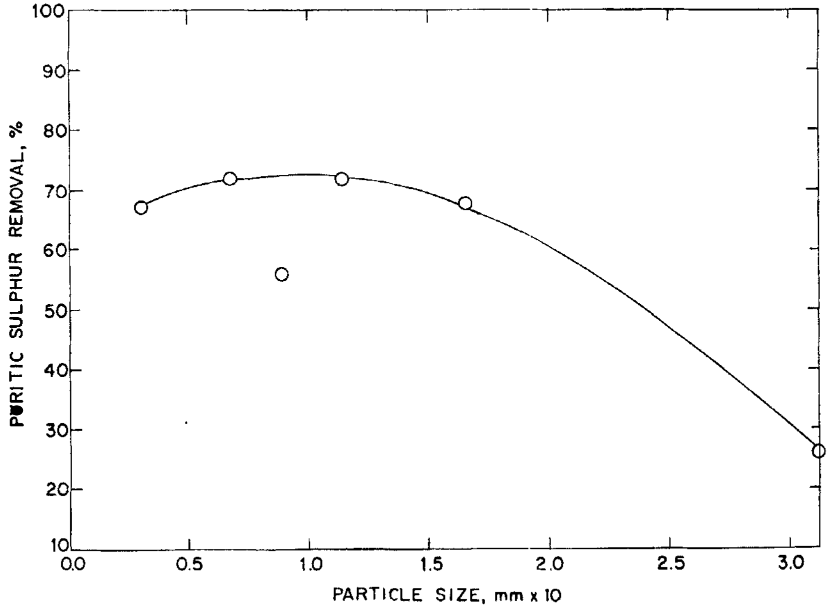

FIG. 4. Effect of particle size on pyritic sulfur removal.

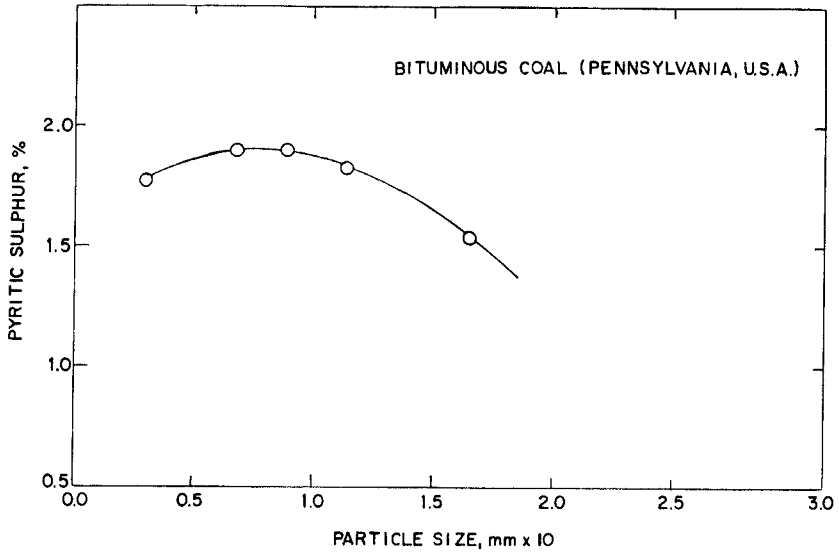

FIG. 5. Pyritic sulfur distribution in coal sizes.

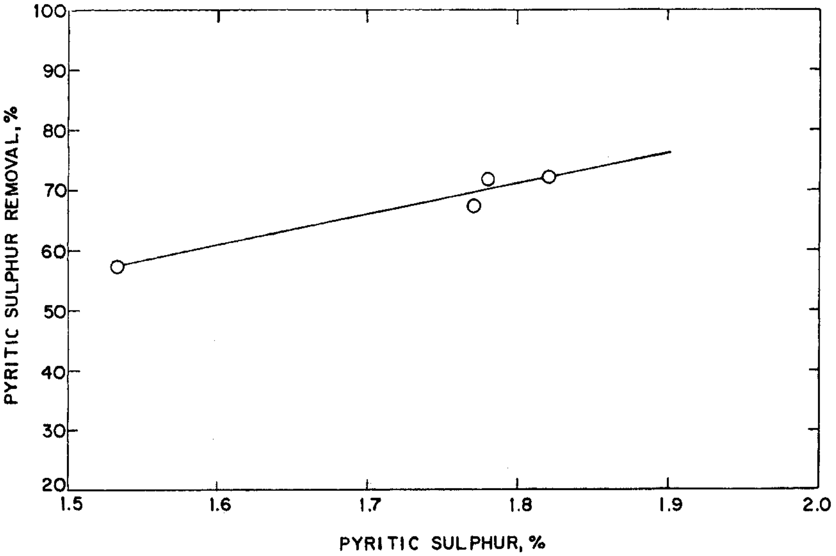

FIG. 6. Pyritic sulfur content and its removal.

of recovery at very fine particle sizes may be attributed to the onset of flocculation. The maximum recovery is obtained at about 75 μm. While this is in close agreement with the results of Smith (*19*), there is no agreement with the work of Bennett, Chapman, and Dell, as reported by Arbiter and Harris (*20*).

Generally, poor sulfur separation may be expected at high recoveries because of loss of selectivity. However, this was not the case here as can be seen from Figs. 3 and 4. This is explained by the fact that the pyrite in the coal was distributed at a size of about 70 μm (Fig. 5) at which maximum recovery was also obtained. Moreover the pyritic sulfur removal was found to be directly proportional to the pyritic sulfur content (Fig. 6), other functions remaining the same.

Slurry Density

The effect of slurry density on the mean flotation rate, calculated from the weight of dry solid floated over a period of 10 min, is shown in Fig. 7.

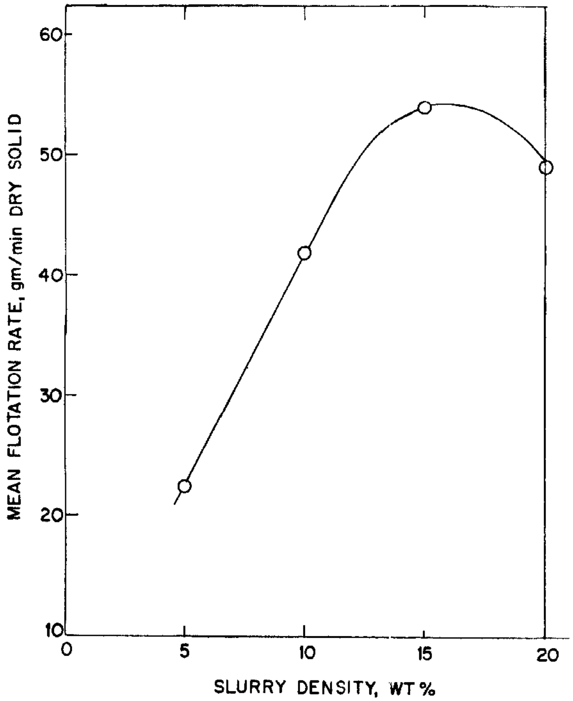

FIG. 7. Effect of slurry density on flotation rate.

The result at 20% slurry density cannot be explained exactly; however, at the high slurry densities the concentration of flotation reagents increases in the slurry water. The high lime concentration makes the solution very alkaline (pH 13). Only 0.15 ml of pine oil instead of 0.32 ml (on the basis of 0.24 g/kg of coal) was found necessary to produce a stable froth.

A plot of log (rate) vs log (slurry density) in Fig. 8 gives an order of 0.82 if the fourth point is neglected, or 0.61 by a least mean squares fit for all points. Since the density ρ changes (decreases) with the progress of the flotation process, a higher order would be obtained if concentration C were used instead of the slurry density, W. The majority of investigators have argued for a first- or second-order rate equation (*20*), but there is no reason why there cannot be a nonintegral order.

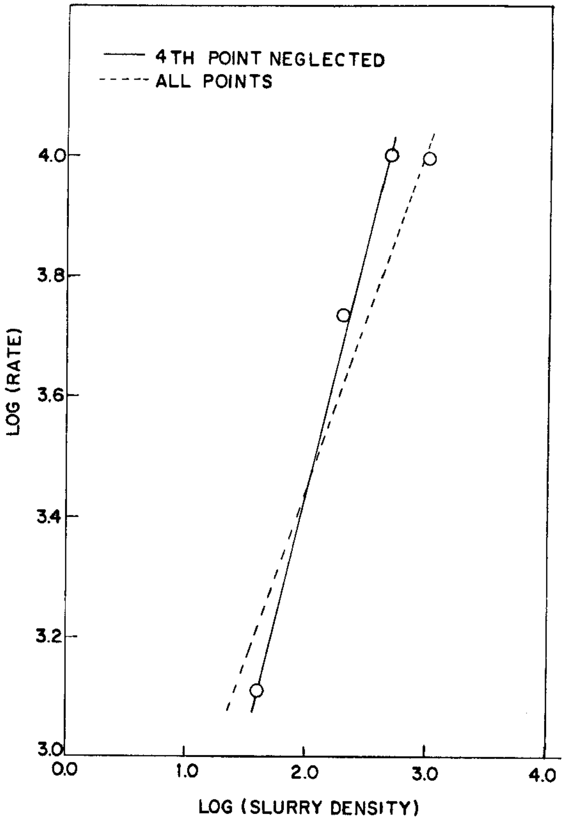

FIG. 8. Log (rate) vs log (slurry density).

Temperature and Time

The effects of temperature and time are shown in Figs. 9 and 10. The highest recoveries were obtained around 35 °C (Table 3), at which sulfur removal was poorest, probably due to loss of selectivity at the high recovery. The viscosity, interfacial tension, and solubility change with temperature. These affect the effectiveness of the collection and frothing. Moreover, with a temperature rise, salts and other compounds may be leached from the coal, and air will come out of solution, appearing as small bubbles at the coal surface. The rate of most chemical reactions also

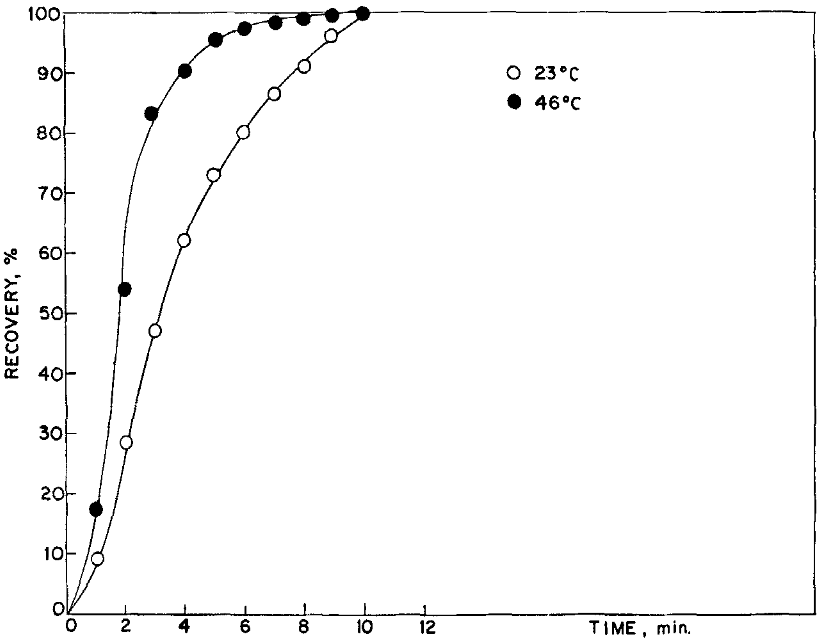

FIG. 9. Recovery vs flotation time.

TABLE 3
Effect of Temperature

Temperature (°C)	14	23	28	38	42	46
Recovery (%)	33.0	38.1	75.1	72.5	12.2	26.3
Total sulfur removal (%)	38.6	38.6	31.8	34.6	45.1	41.6

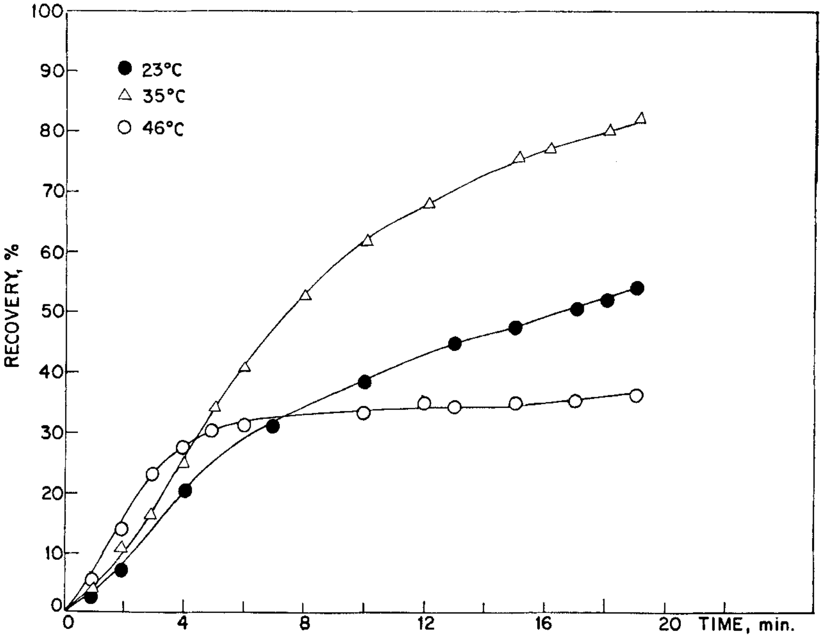

FIG. 10. Recovery vs time.

increases with temperature. The extent of the contribution of any one factor can only be determined by further work.

The effect of flotation time on sulfur removal is shown in Fig. 11, the similarity in shape of the plots for total and pyritic sulfur being in accordance with the fact that only inorganic sulfur (mostly pyritic) is removed by the flotation.

Application to Other Coals

The results obtained by applying the flotation process to four coals are shown in Table 4.

An important consideration in the flotation of coal is the subsequent need for dewatering. It was observed that the kerosene-floated coal dried relatively fast, particularly if the froth from the flotation cell was not collapsed. Drying experiments are required for process evaluation.

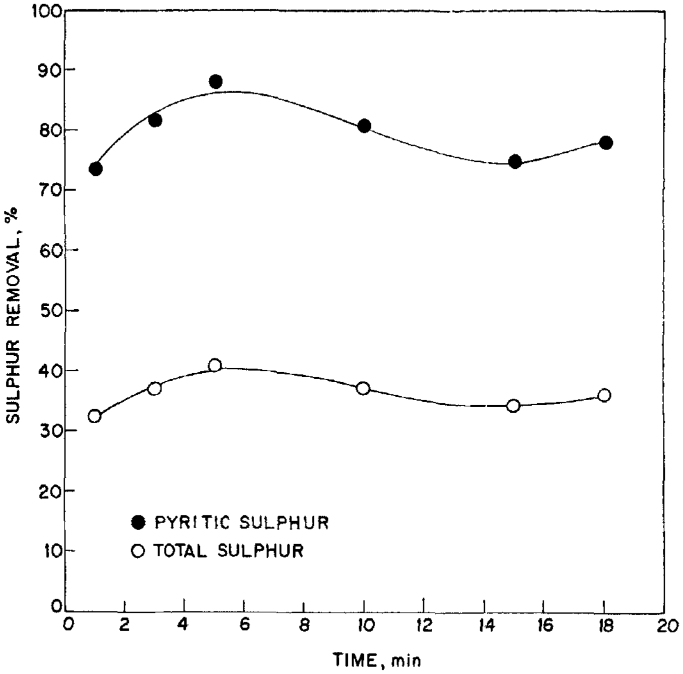

FIG. 11. Sulfur removal vs flotation time.

TABLE 4
Flotation Effects on Various Coals

Coal		PB2	CHB2	CMB	CLB
Total S (%),	original	3.77	2.97	0.55	0.73
	product	2.20	2.08	0.53	0.64
Pyritic S (%),	original	2.60	1.33	0.24	0.44
	product	0.80	0.56	0.23	0.36
Ash (%),	original	12.20	11.20	10.0	7.80
	product	6.00	3.96	7.43	6.40
	reject	24.20	38.6	70.3	72.1
Recovery (%)		76.2	80.0	87.6	94.4
Sulfur (pyritic)	removal (%)	69.2	57.9	4.2	18.2

CONCLUSIONS

While organic sulfur could not be removed, pyritic and sulfate sulfur were successfully removed by a froth flotation process in which coal was floated out, using kerosene (1.07 g/kg coal) as collector, pine oil (0.24 g/kg coal) as frother, and lime (5 g/kg coal) as depressant for pyrite. Although up to 90% of the pyritic sulfur could be removed under one set of conditions, lower removals may be obtained under practical conditions.

The removal of ash and trace elements is a desirable side benefit of the desulfurization. The presence of keorsene on coal surfaces hinders water-wetting, facilitating subsequent dewatering and drying of the coal product.

Acknowledgments

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REFERENCES

1. N. P. Chopey, "Taking Coal's Sulfur Out," *Chem. Eng.*, 86–89 (July 24, 1972).
2. S. Ergun and E. H. Bean, *Rep. Invest. U.S. Bur. Mines, No. 7181* (1968).
3. S. C. Trindale et al., "Magnetic Desulphurization of Coal," *Fuel*, *53*(3), 178–181 (1974).
4. A. L. Yergey et al., "Nonisothermal Kinetics of Hydro-desulphurization of Coal," *Ind. Chem. Eng., Process Des. Dev.*, *13*(3), (1974).
5. M. E. Frank and B. K. Schmid, "Design of a Coal-Oil-Gas Refinery," *Chem. Eng. Prog.*, *68*(3), 62–64 (1973).
6. L. Reggel et al., "Preparation of Ash-Free, Pyrite-Free Coal by Mild Chemical Treatment," *Am. Chem. Soc., Div. Fuel Chem., Prepr.*, *17*(1), (1972).
7. A. R. Glueck, "Molten Salt Processes for Sulphur Emission Control," *Chem. Eng. Prog.*, *69*(3), 56–57 (1973).
8. S. J. Lukasiewics and G. C. Johnson, "Desulphurization of Petroleum Coke," *Ind. Eng. Chem.*, *52*(8), 675–677 (1960).
9. T. Sutandar, B.A.Sc. Thesis, Department of Chemical Engineering, University of Toronto, 1975.
10. R. D. Snow, *Ind. Eng. Chem.*, *24*, 9031 (1932.
11. P. S. Maa et al., "Sulphur Transformation and Removal for Western Kentucky Coals," *Fuel*, *54*(1), 62–69 (1975).
12. D. J. Brown, in *Froth Flotation, 50th Anniversary Volume* (W. D. Fuerstenau, ed.), AIME, New York, 1962, pp. 519–538.
13. A. M. Gaudin, *Flotation*, 2nd ed., McGraw-Hill, New York, 1957, pp. 532–543.
14. A. F. Taggart, *Handbook of Ore Dressing*, Wiley, New York, 1927, pp. 901–904.

15. A. Crawford, "The Preparation of Ultra-clean Coal in Germany," *Trans. Inst. Mine. Eng., London, 111*, 204–218 (1952).
16. *Coal Age*, April 1974, p. 99.
17. R. M. Horseley and H. G. Smith, *Fuel, 30*, 54 (1951).
18. R. M. Horseley, "Oil Collectors in Coal Flotation," *Trans. Inst. Min. Eng., London, 111*, 886–900 (1952).
19. H. G. Smith and D. J. Brown, *Ibid., 113*, 1001 (1954).
20. N. Arbiter and C. C. Harris, in *Froth Flotation, 50th Anniversary Volume* (W. D. Fuerstenau, ed.), AIME, New York, 1962.

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