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Oil agglomeration of weakly hydrophobic coals and coal/pyrite mixtures

Abstract

Fine particle suspensions of various materials in water were agglomerated with heptane in a modified blender to determine the agglomeration characteristics of the solids. The materials included Upper Freeport coal, oxidized Upper Freeport coal, two batches of Illinois No. 6 coal, graphite, and iron pyrite. The response of these materials to oil agglomeration varied over a wide range and seemed to depend on their relative hydrophobicity. Treating the weakly hydrophobic materials with traces of sodium oleate greatly enhanced their response to oil agglomeration. The separation of mixtures of pyrite and various carbonaceous materials by selective agglomeration with heptane was also studied. While an excellent separation of graphite and pyrite was achieved, the separation of coal and pyrite proved elusive.

Disciplines

Catalysis and Reaction Engineering | Other Chemical Engineering | Petroleum Engineering

Comments

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Table III. Effect of Particle Size on Coal Surface/Interfacial Properties

param	(ash = 28.6%, SP = 1.52)		(ash = 23.5%, SP = 1.45)	
	-28 + 100 mesh	-100 mesh	-28 mesh	-200 mesh
θ in liquid CO ₂ , deg	140	149	136	145
surface area, m ² /g of coal	87	98	95	109
g of CO ₂ /g of coal at $P = P_0$	0.057	0.065	0.069	0.082
g of CO ₂ /100 m ² of coal at $P = P_0$	0.066	0.063	0.073	0.075
π_{sv} , N/m	0.0904	0.0889	0.0852	0.0816

surface areas, and adsorption isotherms for these samples were experimentally determined.

The results (Table III) show that the measured contact angles in the large particle size fractions (-28 + 100 mesh and -28 mesh) are slightly smaller than those in the small particle size fractions (-100 mesh and -200 mesh). This may be attributed to the apparent differences in surface condition of the compressed coal pellet samples formed with large and small particle sizes. Hence the measured contact angle for the large particle size coal tends to underestimate the true contact angle. This phenomenon was also observed by Murata.¹⁵ Considering the small differences in measured contact angles between these two size fractions of each group, it can be said that the particle size has only a minor effect on the contact angle.

As expected, the surface area is smaller for the large size fraction than the small size fraction of coal samples. It is also found that coal with the smaller size fraction adsorbed more CO₂ on a unit weight basis. The increase in

the external surface area for the finer coal particles is known to be the reason for the increased amount of CO₂ adsorption on a unit weight bases. However, when expressed on a unit surface area basis, the same amount of adsorption is observed. Similarly, the film pressure of each size fraction of these coal samples was compared, and little difference between the two size fractions was found for both of the tested groups. These results can be explained by the fact that when the coal particles are ground into smaller sizes, the increase in the total surface area is mostly due to the increase in the external surface area (assuming very few dead pores in the original coal particles), while the internal micropore surface area is the same for both the larger and smaller sizes of coal particles.

Conclusions

From the above discussion, it is clear that the LICADO process is a surface-property-driven process. The work performed so far indicates that the mechanism of the LICADO process is governed by the interactions among the interfacial, shear, and body forces present in the coal particle-liquid CO₂-water system. The shear and body forces are determined by the density and size of the coal particles as well as the hydrodynamic conditions in the separation process, which subsequently control the manner that the surfaces of coal particles are exposed to processing media. Therefore, it is possible to optimize the performance of the LICADO process by improving the quality of mixing.

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Registry No. CO₂, 124-38-9.

(15) Murata, T. *Fuel* 1981, 60, 744-746.

Oil Agglomeration of Weakly Hydrophobic Coals and Coal/Pyrite Mixtures[†]

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Fine particle suspensions of various materials in water were agglomerated with heptane in a modified blender to determine the agglomeration characteristics of the solids. The materials included Upper Freeport coal, oxidized Upper Freeport coal, two batches of Illinois No. 6 coal, graphite, and iron pyrite. The response of these materials to oil agglomeration varied over a wide range and seemed to depend on their relative hydrophobicity. Treating the weakly hydrophobic materials with traces of sodium oleate greatly enhanced their response to oil agglomeration. The separation of mixtures of pyrite and various carbonaceous materials by selective agglomeration with heptane was also studied. While an excellent separation of graphite and pyrite was achieved, the separation of coal and pyrite proved elusive.

Introduction

The need for industry to clean fine-sized coal is increasing steadily. One of the more promising techniques for cleaning such coal involves the selective agglomeration

of coal fines suspended in water with oil.^{1,2} Although this technique works well for hydrophobic coals because water is readily displaced from the surface of these coals by oil, it is less effective for weakly hydrophobic and hydrophilic

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(1) Wheelock, T. D.; Markuszewski, R. In *Chemistry and Physics of Coal Utilization*; Cooper, B. R.; Ellingson, W. A., Eds.; Plenum: New York, 1984; pp 81-87.

(2) Capes, C. E.; Germain, R. J. In *Physical Cleaning of Coal*; Liu, Y. A., Ed.; Marcel Dekker: New York, 1982; pp 293-351.

coals such as Illinois No. 6 coal and oxidized Upper Freeport coal. Generally, the latter require considerably more oil than the former for beneficiation, which increases the cost of treatment excessively.

In the present study the oil agglomeration characteristics of Illinois No. 6 coal and oxidized Upper Freeport coal were determined and compared to those of two hydrophobic materials, unoxidized Upper Freeport coal and graphite. In addition, since fatty acids are known to increase the hydrophobicity of various materials through adsorption thereon, the less hydrophobic materials were treated with sodium oleate to increase their hydrophobicity and were subsequently agglomerated to evaluate the effectiveness of the treatment. Also, since there is a general need to improve the separation of coal particles from iron pyrite particles for all types of coal, consideration was given to this problem.

Materials

Various samples of coal were used in this study, as well as relatively pure graphite from Sri Lanka and iron pyrite mineral from Huanzala, Peru. The graphite and pyrite were obtained from Ward's Natural Science Establishment. The sample of Upper Freeport coal used in this work was handpicked from the Lucerne No. 6 mine in Indiana County, PA, and had an ash content of 6–7% and a total sulfur content of 1.9–2.1%. A channel sample from the same source contained 0.93% moisture, 27.34% ash, and 1.29% total sulfur (0.91% pyritic plus 0.38% organic sulfur) on an as-received basis; it had a heating value of 10 872 Btu/lb and was medium-volatile bituminous in rank. The first Illinois No. 6 coal was a channel sample obtained from the Elm Mine near Trivoli, IL, and had a moisture content of 11–12%, an ash content of 9–10%, and a total sulfur content of 2.3–2.7%, all on an as-received basis; its heating value was 11 101 Btu/lb. The second Illinois No. 6 coal was obtained from the Illinois State Geological Survey. It was a channel sample from southwestern Illinois that had been processed and packaged in a nitrogen atmosphere by Argonne National Laboratory for the Illinois Basin Coal Sample Program; the as-received sample had a moisture content of 9–10%, an ash content of 18%, and a total sulfur content of 4.63% (2.55% pyritic and 2.08% organic sulfur); its heating value was 11 522 Btu/lb. In the following discussion the first Illinois No. 6 coal will be referred to as A and the second as B.

The Illinois coal was high-volatile bituminous C in rank. On the basis of qualitative observation of the relative difficulty of wetting, the fresh Illinois coal was weakly hydrophobic and the fresh Pennsylvania coal was highly hydrophobic.

All of the solids were ground in air in the dry state to –325 or –200 mesh by a high-speed impact mill. Various portions of the ground Upper Freeport coal were spread in thin layers on watch glasses and oxidized in a laboratory oven with natural air convection at 150 °C for up to 144 h.

Pure *n*-heptane (bp 98 °C) from Eastman Kodak Co. was used as the agglomerating oil. Sodium oleate (SOL) from J. T. Baker Co. was used as an anionic surfactant. Deionized water prepared by passing steam condensate through a Barnstead NANOpure II cartridge system was used in all experiments. The resistivity of the purified water was 17.9 mΩ cm. The pH of the particle suspensions was adjusted with either reagent grade hydrochloric acid or ammonium hydroxide.

Experimental Methods

Special procedures were used for measuring particle recovery by oil agglomeration and the ζ potential of suspended particles. A specially designed closed system was used for the agglomeration experiments in order to eliminate air from the system because air had been found previously to affect the results.³ This system, described in detail previously,³ utilized the motor and agitator from a 14-speed kitchen blender, but a 500-mL canning jar was substituted for the open vessel furnished with the blender. The

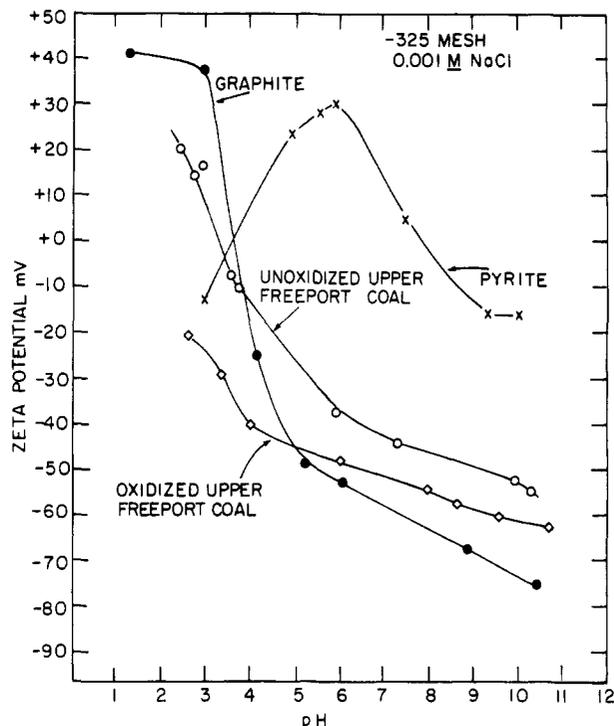


Figure 1. ζ potential of various materials.

jar was inverted and a hole was drilled in the bottom. The hole was plugged with a rubber septum through which oil could be introduced with a hypodermic syringe. For each experiment, the 500-mL jar was filled with a suspension containing 10 g of particles, and the suspension was conditioned for 3 min at the highest speed (18 000–20 000 rpm). Then the appropriate amount of oil was introduced quickly and mixing was continued at the highest speed for another 3 min. The agglomerated solids were recovered on a 100-mesh screen (U.S. Standard), dried overnight in an oven at 100–110 °C, and weighed to determine the recovery.

To determine the ζ potential of suspended particles, 0.02 g of material was mixed with 100 mL of 0.001 M sodium chloride, and the pH was adjusted to the desired level with hydrochloric acid or ammonium hydroxide. Next the suspension was stirred vigorously for 2 h and the final pH measured. The suspension was then placed in an ultrasonic bath and agitated for 5 min. The average ζ potential of 10 particles in each sample was subsequently measured with a Zeta-Meter 3.0 unit; it was reported as an average of three separate samples.

Results and Discussion

Electrokinetic Properties. The ζ potential measured for different materials in 0.001 M sodium chloride is shown as a function of pH in Figure 1. The ζ potential of pyrite at any given pH was similar to that reported previously for oxidized pyrite.⁴ Apparently the pyrite surface had become oxidized by exposure to the atmosphere. Above pH 3.5 the ζ potential of graphite was similar to that reported for unleached graphite by Solari et al.⁵ However, these workers did not report any values below pH 3.5, where graphite was found to have a strong electropositive charge in the present investigation. The ζ -potential curve for unoxidized Upper Freeport coal was found to lie slightly below the curve for graphite up to pH 4 and slightly above the curve for graphite beyond pH 4. The isoelectric point for the Upper Freeport coal occurred at pH 3.3 and for graphite at pH 3.7. The ζ -potential curve for Upper Freeport coal that had been oxidized at 150 °C for 120 h lay below that of the unoxidized coal.

(3) Drzymala, J.; Markuszewski, R.; Wheelock, T. D. *Int. J. Miner. Process.* 1986, 18, 277–286.

(4) Wen, W. W.; Sun, S. C. *Sep. Sci. Technol.* 1981, 16, 1491–1521.
(5) Solari, J. A.; De Araujo, A. C.; Laskowski, J. S. *Coal Prep. (Gordon & Breach)* 1986, 3, 15–31.

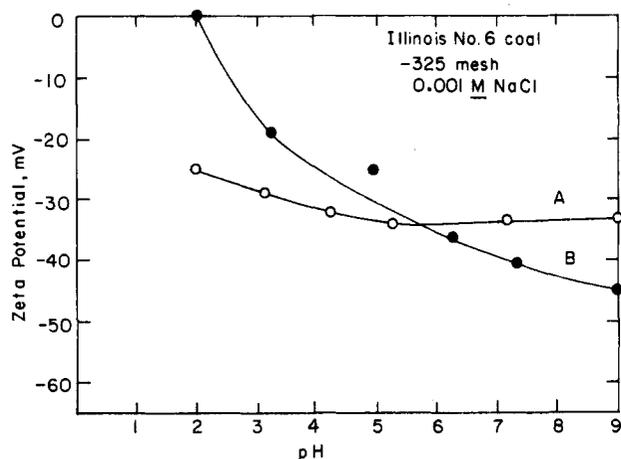


Figure 2. ζ potential of Illinois No. 6 coal (samples A and B).

For the two samples of Illinois No. 6 coal, the ζ potential is shown in Figure 2. The ζ potential of coal A was affected only slightly by changes in pH in contrast to the other materials. On the other hand, the electrokinetic behavior of coal B was similar to that of unoxidized Upper Freeport coal over much of the pH range. However, at low pH coal B was somewhat more electronegative than Upper Freeport coal. Consequently the isoelectric point for coal B occurred at pH 2, compared to pH 3.3 for unoxidized Upper Freeport coal.

The electrokinetic behaviors of Upper Freeport coal and Illinois No. 6 coal B were similar to that observed for Pittsburgh seam coal by Campbell and Sun,⁶ who attributed the variation in ζ potential with pH to the adsorption of electropositive hydronium ions at low pH and electronegative hydroxyl ions at high pH. The results for graphite suggest that the same mechanism may have accounted for the variation in ζ potential of this material. The shift in ζ potential of Upper Freeport coal due to surface oxidation was similar to that observed by Wen and Sun⁴ upon applying a similar treatment to vitrain extracted from Pittsburgh seam coal. These workers found that hydronium and hydroxyl ions are not potential-determining ions for extensively oxidized coal, and they suggested that this was due to the presence of humic acids on the surface of the coal. Apparently hydronium and hydroxyl ions are not potential-determining ions for humic acids; therefore, this would account for the smaller variation in ζ potential with pH for the oxidized coal. Of course, the nature and distribution of oxygen-containing functionalities, not just the total oxygen content, have a significant effect on the ζ potential. The electrokinetic behavior of Illinois No. 6 coal A indicates that this sample may have been heavily oxidized since the ζ potential was virtually unaffected by pH. Although the sample had been stored under nitrogen, it was several years old when utilized and could have become oxidized because of air leakage or other problems with the storage system.

Agglomeration Characteristics of Individual Materials. The results of agglomerating various materials with heptane are shown in Figure 3. The oxidized Upper Freeport coal used for this set of results was treated at 150 °C for 144 h. The -325 mesh materials were agglomerated separately at the natural pH of the respective aqueous suspensions. The reported recoveries were based only on the total weight of the initial sample, but the agglomeration data were reproducible, being averages of three runs. The recovery curves for graphite and unoxidized Upper Free-

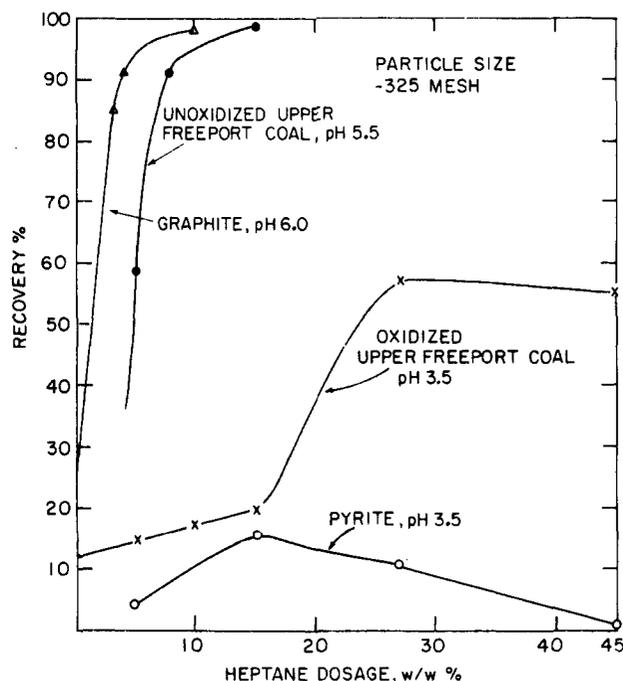


Figure 3. Effect of heptane dosage on agglomeration recovery of various materials.

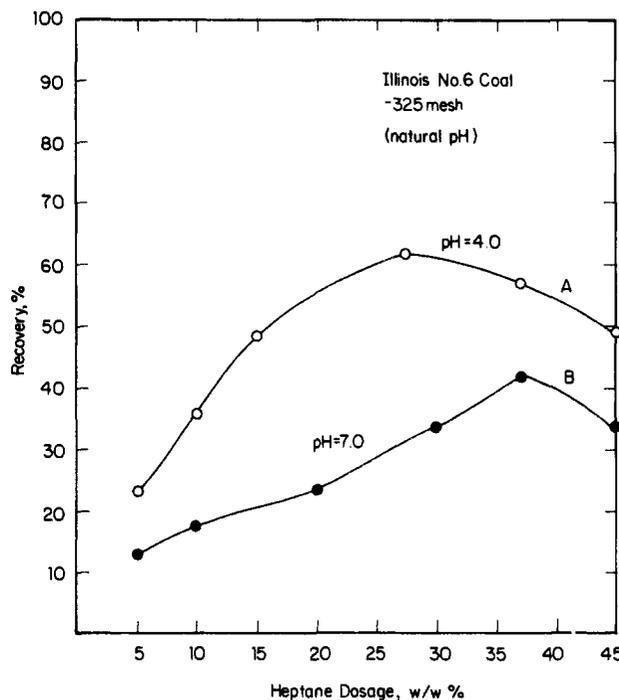


Figure 4. Effect of heptane dosage on agglomeration recovery of Illinois No. 6 coal A and B.

port coal were very similar and characteristic of hydrophobic materials. In each case only a relatively small amount of heptane was required to achieve a high recovery of solids. Thus a recovery of 98% or more was achieved with 10 w/w% heptane (i.e., 1 g heptane/10 g solids) in the case of graphite and with 15 w/w % heptane in the case of Upper Freeport coal. As expected, the weakly hydrophobic and hydrophilic materials responded less well to oil agglomeration. The maximum recovery of oxidized Upper Freeport coal was 57%, and it required a heptane dosage of 27 w/w %. Moreover, the maximum recovery of pyrite was only 15%. For Illinois No. 6 coal, Figure 4 indicates that the maximum recovery of coal A was 62% and coal B was 42%. These recoveries were achieved with

(6) Campbell, J. A. L.; Sun S. C. *Trans. Soc. Min. Eng. AIME* 1970, 247, 111-122.

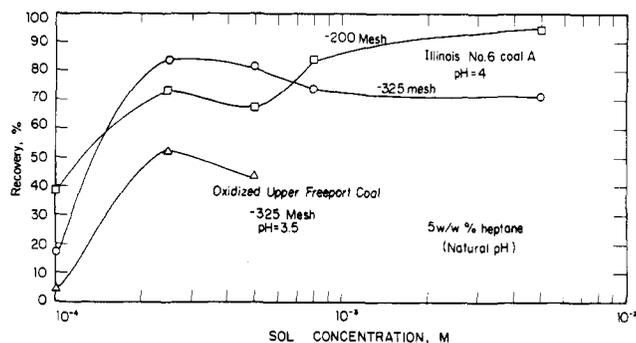


Figure 5. Effect of initial sodium oleate concentration on agglomeration recovery of Illinois No. 6 coal A and oxidized Upper Freeport coal.

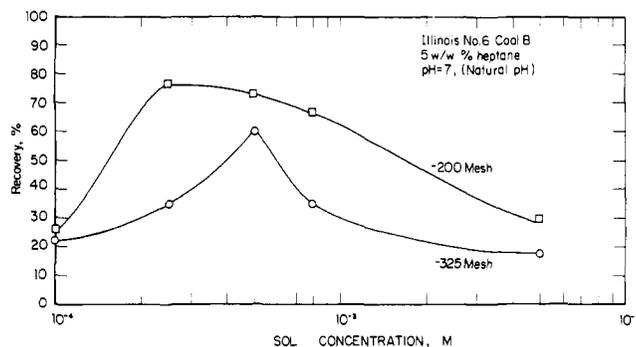


Figure 6. Effect of initial sodium oleate concentration on agglomeration recovery of Illinois No. 6 coal B.

a heptane dosage of 27 w/w % in the case of coal A and 37 w/w % in the case of coal B. The results with Illinois No. 6 coals seemed inconsistent since the electrokinetic behavior of the materials indicated that coal A was probably oxidized whereas coal B was not. However, the difference in agglomeration characteristics of the two samples may have been due to other factors, such as a difference in the concentration of finely disseminated hydrophilic minerals. Coal B was known to have a higher ash content than coal A. Furthermore, the inherent hydrophobicity of Illinois No. 6 coal from different sources has been known to vary.

With the application of excessive amounts of heptane, the recovery of the less hydrophobic materials declined, which may seem surprising. However, Capes and Germain² also observed a decrease in coal recovery under similar circumstances and attributed the decline to the formation of a weak coal-oil amalgam that passed through the collecting screen. It is also known that hydrophilic powders can stabilize oil-in-water emulsions, and such emulsions would be likely to pass through a collection screen, leading to the loss of both the hydrophilic material and oil.

Effect of Sodium Oleate. The effect of small amounts of sodium oleate (SOL) on the agglomeration recovery of Illinois No. 6 coal and oxidized Upper Freeport coal is shown in Figures 5 and 6. The Upper Freeport coal had been oxidized at 150 °C for 144 h. The different coals were suspended individually in dilute SOL solutions and conditioned at the natural pH of the suspensions for 3 min before agglomerating with 5 w/w % heptane. With an initial SOL concentration of 10^{-4} M, coal recovery was slight, but with an initial concentration of 2.5×10^{-4} M, coal recovery was considerably greater. For some coal samples the maximum recovery was achieved by starting with 2.5×10^{-4} M SOL, but for -200 mesh Illinois No. 6 coal A the highest recovery (95%) was achieved with 5×10^{-3} M SOL, and for -325 mesh Illinois No. 6 coal B the highest recovery was realized with 5×10^{-4} M SOL.

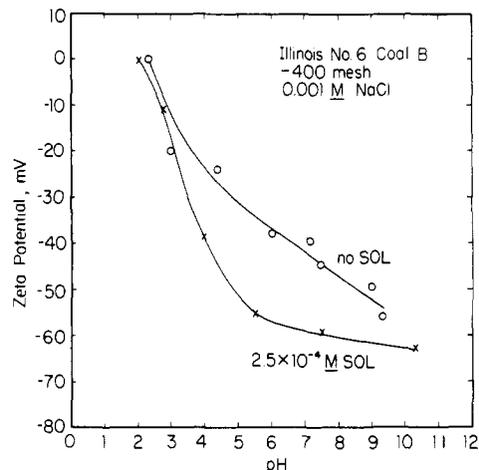


Figure 7. Effect of sodium oleate on ζ potential of Illinois No. 6 coal B.

These results appear to have been strongly affected by the adsorption of oleic acid or its ionization products on the coal surface with a corresponding increase in hydrophobicity of the material. In the lower pH range (3.5–4) of the coal suspensions, nonionized oleic acid should have been the predominant species present.⁷ Furthermore, because of the low solubility of oleic acid in water (2.5×10^{-8} kmol/m³), particularly at pH 4 and below, it is likely that a colloidal precipitate would have formed that could have coated the coal particles and rendered them more hydrophobic. Alternatively, oleic acid molecules may have been adsorbed by the coal surface due to hydrogen bonding between the carboxylic acid heads of the molecules and oxygen-containing functional groups on the coal surface. At low pH the results seemed to favor the mechanism involving adsorption of the precipitated oleic acid. Thus, at pH 3.5–4 a large increase in coal recovery was observed when the initial SOL concentration was increased from 10^{-4} M to 2.5×10^{-4} M (see Figure 5), yet at the pH of the coal suspensions the concentration of dissolved oleic acid would have been fixed by the solubility limit which remained constant. In other words, only the quantity of precipitated oleic acid would have increased and could have accounted for the increased recovery.

At pH 7 various anionic species of oleic acid would have been present in significant concentrations,⁷ and the adsorption of one or more of these species may have controlled the hydrophobicity of the coal. The results presented in Figure 6 tend to support this mechanism. As the initial SOL concentration increased, coal recovery increased to a peak and then decreased. Increasing recovery could have been due to the buildup of a monolayer of adsorbate and decreasing recovery to the adsorption of a second layer consisting of reverse-oriented oleate. The results of ζ potential measurements also suggest that oleate anions were adsorbed by the coal at high pH since the Illinois No. 6 coal B was more electronegative in the presence of SOL from pH 4 to 9 than it was with no SOL present (see Figure 7).

Sodium oleate was also found to have a remarkable effect on the agglomeration of -325 mesh pyrite with 5 w/w % heptane (see Figure 8). When pyrite was suspended in plain water and agglomerated, the maximum recovery was only 11%, but when pyrite was suspended in 10^{-4} M or higher concentrations of sodium oleate and agglomerated, the recovery jumped to 92–97%. Increasing the

(7) Morgan, L. J.; Ananthapadmanabhan, K. P.; Somasundaran, P. *Int. J. Miner. Process.* 1986, 18, 139–152.

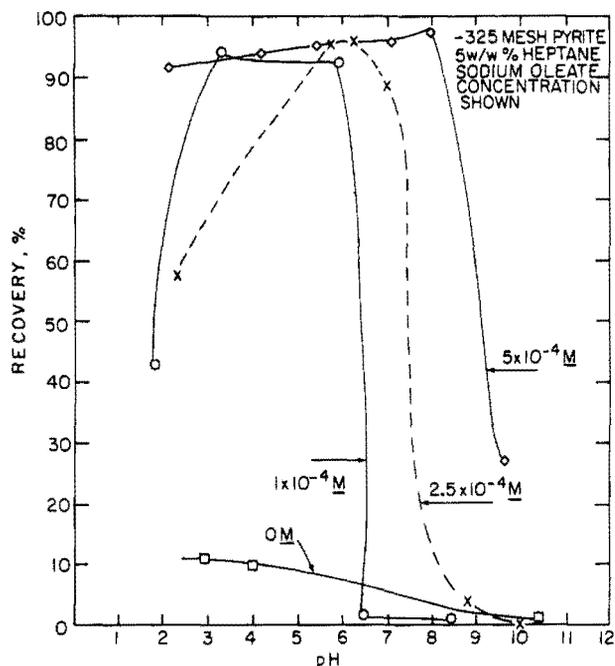


Figure 8. Effects of sodium oleate concentration and pH on agglomeration recovery of pyrite.

concentration of sodium oleate broadened the pH range over which pyrite recovery was enhanced. Also, at the highest concentration (5×10^{-4} M SOL) spherical agglomerates were produced whereas at lower concentrations less compact, irregular-shaped agglomerates were formed.

To investigate the nature of attachment of oleic acid or its ionization products to the pyrite surface, two portions of -325 mesh pyrite were treated with 10^{-4} M SOL at pH 3.5. One portion was subsequently washed repeatedly with absolute ethanol while the other portion was washed repeatedly with ethyl ether. The treated materials were then suspended in water at pH 3.5 and agglomerated with 5 w/w % heptane. The portion that had been washed with ethanol was recovered almost completely (i.e., 92.5%), whereas the portion washed with ether was recovered incompletely (i.e., 22%). Since the recovery of the ethanol-washed pyrite was almost the same as that of pyrite which had been suspended in 10^{-4} M SOL and then directly agglomerated (see Figure 8), the ethanol did not appear to remove whatever oleate species were adsorbed by the pyrite. On the other hand, since the recovery of the ether-washed pyrite was similar to that of pyrite which had not been treated with SOL, ether did seem to remove the adsorbate. The results suggest that one or more oleate species were chemisorbed by the pyrite; otherwise, they would have been removed by the ethanol. Polkin and Najfonow⁸ claimed that ether can remove chemisorbed oleates from mineral surfaces whereas ethanol does not. Their work suggests that oleate anions reacted with positively charged iron species on the surface of the pyrite to form relatively insoluble iron oleate.

Separation of Particle Mixtures. The separation of various mixtures of carbonaceous materials and pyrite was attempted by selective agglomeration with heptane. For this series of experiments all of the solids were ground to pass a 200 mesh screen (U.S. Standard). Equal amounts by weight of ground pyrite and either ground graphite or coal were introduced into the agglomeration apparatus.

Table I. Separation of a 50:50 Mixture of a Carbonaceous Material (CM) and Pyrite by Selective Agglomeration with Heptane^a

CM	heptane, w/w %	final pH	recovery, %			
			overall	CM	pyrite	SE, %
graphite	5	5.1	58.3	96.2	20.4	75.8
graphite	10	5.1	56.2	96.5	16.3	80.2
graphite	15	5.1	50.7	96.5	5.2	91.3
Upper Freeport coal	10	2.2	97.0	94.0	100.0	-6.0
Upper Freeport coal	10	4.9	97.1	97.8	96.2	1.6
Upper Freeport coal	10	9.6	93.1	86.1	100.0	-13.9
Ill. No. 6 coal A	1	4.2	8.8	0.5	17.1	-16.6
Ill. No. 6 coal A	3	4.2	28.3	12.7	43.9	-31.2
Ill. No. 6 coal A	5	4.2	47.9	25.0	70.7	-45.7
Ill. No. 6 coal A	10	4.1	52.7	34.8	70.6	-35.8
Ill. No. 6 coal A	15	4.0	63.4	39.2	87.8	-48.6
Ill. No. 6 coal A	5	10.4	6.1	4.1	8.0	-3.9
Ill. No. 6 coal A	10	10.2	29.5	21.8	37.1	-15.3
Ill. No. 6 coal A	15	10.2	22.8	20.2	25.2	-5.0

^aAll solid materials were -200 mesh.

The heptane dosage was based on the total weight of solids (10 g). For graphite/pyrite mixtures, the agglomerated product was analyzed by leaching with a hot solution containing equal parts of concentrated nitric and hydrochloric acids, which dissolved the pyrite but not the graphite.⁹ For coal/pyrite mixtures the agglomerated product was analyzed for total sulfur and a sulfur balance was used in estimating the recovery of each component. The separation efficiency (SE) achieved was based on the following relation between the carbonaceous material (CM) and pyrite:

$$SE (\%) = CM \text{ recovered } (\%) - \text{pyrite recovered } (\%)$$

The results of agglomerating various particle mixtures are presented in Table I. A good separation of graphite and pyrite was achieved, and the separation efficiency or selectivity of the process improved as the amount of heptane was increased because the amount of pyrite recovered decreased. This result was similar to that observed previously.⁹ However, a good separation of coal and pyrite was not achieved with either unoxidized Upper Freeport coal or Illinois No. 6 coal A. When either of these coals was mixed with pyrite, the recovery of pyrite generally exceeded the recovery of coal. Moreover, the recovery of pyrite with a given amount of heptane was usually greater than the recovery obtained when pyrite alone was treated under similar conditions. Therefore, the presence of coal in the system promoted the agglomeration of pyrite whereas the presence of graphite did not. Furthermore, under some conditions the recovery of Upper Freeport coal was lower than it would have been if agglomerated by itself. Hence, the pyrite either monopolized more of the oil or suppressed coal agglomeration. An explanation for these results cannot be traced to the electrokinetic properties or to the agglomeration characteristics of the individual materials. On both counts, graphite and Upper Freeport coal exhibited similar properties and characteristics. This intriguing phenomenon is being investigated further.

Conclusions

When various carbonaceous materials and pyrite were agglomerated individually, the recovery with a given amount of heptane increased in the following order: pyrite

(8) Polkin, S. I.; Najfonow, T. V. *Proceedings, VII International Mineral Processing Congress, 1964*; Gordon & Breach: New York, 1965; pp 307-318.

(9) Drzymala, J.; Markuszewski, R.; Wheelock, T. D. *Coal Prep. (Gordon & Breach) 1986*, 3, 89-98.

< Illinois No. 6 coal B < oxidized Upper Freeport coal < Illinois No. 6 coal A < unoxidized Upper Freeport coal < graphite. This order seems indicative of the relative hydrophobicity of the materials. Adding traces of sodium oleate to the agglomeration system markedly increased the recovery of pyrite, oxidized Upper Freeport coal, and Illinois No. 6 coal. The results suggest that deposition of oleic acid onto the coal or pyrite surface or possibly adsorption of various oleate species accounted for an increase in hydrophobicity and recovery. An attempt to separate mixtures of carbonaceous materials and pyrite produced divergent results that require further explanation. On the one hand, a good separation of graphite and pyrite was

achieved by selective agglomeration with heptane; on the other hand, a similar separation was not achieved with coal and pyrite.

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Registry No. Graphite, 7782-42-5; pyrite, 1309-36-0; heptane, 142-82-5; sodium oleate, 143-19-1.

Low-Temperature Coal Weathering: Its Chemical Nature and Effects on Coal Properties[†]

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A systematic study was performed in which both hvAb and mvb coals were weathered for up to 500 days at 25–80 °C under closely controlled conditions in the laboratory. Periodic samples were analyzed by a wide range of elemental, spectroscopic, physical, and empirical methods. These systematic and closely controlled experiments confirmed many conclusions reached by others using less rigorous experimental designs. Gieseler plastometry and Audibert–Arnu dilatometry were found to be the most responsive to the early stage of weathering, thus demonstrating that moderate weathering will destroy coal thermoplasticity. The higher rank coal weathered significantly more slowly. The weathering rate is highly dependent on temperature. This study also allowed several new conclusions regarding coal weathering. Rates of change with time of log Gieseler fluidity, heating value, and carbon and oxygen contents show similar dependencies on temperature. The principal chemical changes from organic matrix weathering were the loss of aliphatic groups and the production of carbonyl groups. These reactions occurred rapidly at 80 °C, moderately fast at 50 °C and slowly, if at all, at 25 °C. Froth flotation tests, performed on the hvAb coal, showed that losses in flotation recovery from weathering are strongly affected by pyrite oxidation at 25 °C and by organic matrix oxidation at 80 °C. The different temperature dependencies of pyrite and organic matrix oxidation underscore the importance of using realistic temperatures to study natural weathering.

Introduction

Weathering can affect the behavior of coal in many production and end-use processes.¹ Extensive laboratory research has been performed to determine the chemical nature of coal weathering or oxidation. However, as has been reported,^{2–5} published studies have come to significantly different conclusions concerning the chemical nature of coal weathering. Most reported coal weathering simulation experiments have been conducted at temperatures greater than 100 °C to accelerate the oxidation rate. However, the mechanism and chemical nature of coal weathering are reportedly different at temperatures above and below about 70–80 °C.^{5,6} The chemical structural changes induced by coal weathering are also reportedly dependent on coal rank and humidity.^{1,6,7,8} As noted by Gethner,² ill-defined or poorly controlled coal weathering

experiments can result in inaccurate conclusions. The work reported here is a systematic laboratory study of coal weathering at realistic temperatures and times using different ranks of coal under well-controlled experimental conditions. The objectives of this study are (1) to determine the effects of weathering on coal properties with emphasis on froth flotation and thermoplastic properties, (2) to compare the abilities of various techniques to measure the degree of weathering, and (3) to better define the chemical nature of low-temperature coal weathering.

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