

## AGGLOMERATION CHARACTERISTICS OF HYDROPHILIC COALS AND PYRITE/COAL MIXTURES

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### Introduction

The need for industry to clean fine-size coal is increasing steadily. Selective oil agglomeration of coal fines suspended in water is a practical technique for beneficiating hydrophobic coals, but the technique is less well developed for beneficiating weakly hydrophobic and hydrophilic coals such as Illinois No. 6 coal and oxidized Upper Freeport coal. The oil agglomeration characteristics of the latter were investigated in this study and compared to those of two hydrophobic materials, unoxidized Upper Freeport coal and graphite. 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. In addition, the effect of sodium oleate, a well-known anionic surfactant, on the agglomeration characteristics of these materials was studied.

### Materials

Handpicked samples of coal were obtained to minimize their ash content. A sample of Illinois No. 6 coal was obtained from a fresh underground face at the River King Mine No. 1 in St. Clair county, Illinois, and a sample of Upper Freeport coal from the Lucerne No. 6 mine in Indiana county, Pennsylvania. The Illinois coal had an ash content of 7-10% and the Pennsylvania coal an ash content of 6-7%. The rank of the Illinois coal was high volatile bituminous C and that of the Pennsylvania coal medium volatile bituminous. The fresh Illinois coal was weakly hydrophobic and the fresh Pennsylvania coal highly hydrophobic. Pure graphite from Sri Lanka and pure iron pyrite from Peru were obtained from Ward's Natural Science Establishment. All of these materials were ground in the dry state 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 hr.

Pure n-heptane (b.p. = 98°C) from Eastman Kodak Company was used as the agglomerating oil. Sodium oleate (SOL) from J. T. Baker Company 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 megohm-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 zeta 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 (1). This system 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 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 jar was filled with a suspension containing 10 g. of particles, and the suspension was conditioned for 3 min. at the highest speed. The 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 zeta 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 hr. and the final pH measured. The suspension was then placed in an ultrasonic bath and agitated for 5 min. The zeta potential of the particles was subsequently measured with a Zeta-Meter 3.0 unit.

## Results and Discussion

### Electrokinetic Properties

The measured zeta potential for different materials in 0.001 M sodium chloride is shown as a function of pH in Figure 1. The zeta potential of pyrite at any given pH was similar to that reported previously (2, 3). Above pH 3.5 the zeta potential of graphite was similar to that reported for unleached graphite by Solari et al. (4). 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 zeta 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 zeta potential curve for Upper Freeport coal which had been oxidized at 150°C for 120 hr. lay below that of the unoxidized coal. Although the zeta potential of Illinois No. 6 coal was similar to that of oxidized Upper Freeport coal at pH 3.5-4, it was affected less by pH so that at higher pH the zeta potential of Illinois No. 6 coal was noticeably greater than that of oxidized Upper Freeport coal.

For bituminous coal the variation of zeta potential with pH as indicated in Figure 1 was attributed by Campbell and Sun (5) to the adsorption of electro-positive hydronium ions at low pH and electronegative hydroxyl ions at high pH. The present results for graphite suggest that the same mechanism may have accounted for the variation in zeta potential of this material. The greater electronegativity of the oxidized Upper Freeport coal compared to the unoxidized material may have been due to the introduction of carboxylic acid groups through oxidation which upon ionization would tend to increase the negative charge. Although this explanation could account for the difference in zeta potential at high pH, it would not account for the difference at low pH where the carboxylic acid groups would not be ionized. At low pH, oxidation of the coal surface seemed to interfere with the adsorption of hydronium ions. This may also explain why the zeta potential of the Illinois No. 6 coal was negative at low pH, because this coal is known to have a relatively high oxygen content.

### Agglomeration Characteristics of Individual Materials

The results of agglomerating various materials with heptane are shown in Figure 2. The oxidized Upper Freeport coal used for this set of results was treated at 150°C for 144 hr. The -325 mesh materials were agglomerated separately at the natural pH of the respective aqueous suspensions. The recovery curves for graphite and unoxidized Upper Freeport 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 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 Illinois No. 6 coal was 62% and oxidized Upper Freeport coal 57%, and to achieve these recoveries an oil dosage of 27 w/w % was required. The recovery of pyrite was even lower with a maximum recovery of 15% being realized. With a large amount of heptane the recovery of these materials declined, which may seem surprising. However, Capes and Germain (6) also observed a decrease in coal recovery with excessive amounts of oil and attributed the decline to the formation of a weak coal-oil amalgam which passed through the collecting screen. It is also known that hydrophilic powders can stabilize oil-in-water emulsions (7) and such emulsions would be likely to pass through the collecting screen leading to the loss of both the hydrophilic material and oil.

#### Effect of Sodium Oleate

The effect of small amounts of sodium oleate on the agglomeration recovery of Illinois No. 6 coal and Upper Freeport coal (oxidized for 144 hr.) is shown in Figure 3. For these results only 5 w/w % heptane was used in treating the suspensions of the individual materials at their natural pH. Without sodium oleate, coal recovery was slight, but with an initial concentration of  $2.5 \times 10^{-4}$  M in the suspension, the recovery of -200 mesh Illinois No. 6 coal or -325 mesh Upper Freeport coal (oxidized for 144 hr.) increased sharply. On the other hand, the recovery of -325 mesh Illinois No. 6 coal was not affected by sodium oleate over the indicated range of concentration. However, in a subsequent experiment when the concentration of sodium oleate was increased to  $8 \times 10^{-4}$  M, the recovery of -325 mesh Illinois No. 6 coal increased to 85%.

These results appear to have been strongly affected by either the adsorption or deposition of oleic acid on the coal surface with a corresponding increase in hydrophobicity of the material. In the pH range of the coal suspensions, nonionized oleic acid should have been the predominant oleate species present (8). Furthermore, because of the low solubility of oleic acid in water at pH 4 it is quite likely that a colloidal deposit would have formed which 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 carboxylic acid groups on the coal surface or possibly due to hydrophobic interaction between the hydrophobic tails of the molecules and hydrophobic regions on the coal surface.

Sodium oleate was also found to have a remarkable effect on the agglomeration of -325 mesh pyrite with 5 w/w % heptane (see Figure 4). 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 concentration of sodium oleate broadened the pH range over which pyrite recovery was enhanced. Also, at the highest concentration ( $5 \times 10^{-4}$  M) spherical agglomerates were produced whereas at lower concentrations less compact, irregular-shaped agglomerates were formed.

In Figure 4 it can be seen that for any given sodium oleate concentration there was a sharp drop in recovery when a certain pH was exceeded. Moreover, the upper limit of pH for agglomeration to occur increased with increasing sodium oleate concentration. The shift in the pH limit suggests that precipitation onto the pyrite surface may have played a dominant role. Morgan *et al.* (8) have

pointed out that for oleic acid the pH of precipitation is a sensitive function of concentration. Thus by reducing the pH from 8 to 6, the oleate activity is reduced about 100 fold. Consequently the upper agglomeration limits indicated in Figure 4 could very well correspond to the pH of oleic acid precipitation. Another possibility at high pH would be the adsorption of various anionic oleate species.

#### 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. 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 achieved was based on the following relation between the carbonaceous material (C.M.) and pyrite:

$$\text{Sepn. Eff. (\%)} = \text{C.M. Recovered (\%)} - \text{Pyrite Recovered (\%)}$$

The results of agglomerating various particle mixtures are presented in Table 1. 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. When either of these coals was mixed with pyrite, the recovery of pyrite generally exceeded the recovery of coal. Moreover, the recovery of pyrite

Table 1. Separation of a 50:50 mixture of a carbonaceous material and pyrite by selective agglomeration. All solid materials were -200 mesh

| Carbonaceous material | Heptane, w/w % | Final pH | Recovery, % |      |        | Separation Eff., % |
|-----------------------|----------------|----------|-------------|------|--------|--------------------|
|                       |                |          | Overall     | C.M. | Pyrite |                    |
| 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               |
| Up. Freep. coal       | 10             | 2.2      | 97.0        | 94.0 | 100.0  | -6.0               |
| Up. Freep. coal       | 10             | 4.9      | 97.1        | 97.8 | 96.2   | 1.6                |
| Up. Freep. coal       | 10             | 9.6      | 93.1        | 86.1 | 100.0  | -13.9              |
| Ill. No. 6 coal       | 1              | 4.2      | 8.8         | 0.5  | 17.1   | -16.6              |
| Ill. No. 6 coal       | 3              | 4.2      | 28.3        | 12.7 | 43.9   | -31.2              |
| Ill. No. 6 coal       | 5              | 4.2      | 47.9        | 25.0 | 70.7   | -45.7              |
| Ill. No. 6 coal       | 10             | 4.1      | 52.7        | 34.8 | 70.6   | -35.8              |
| Ill. No. 6 coal       | 15             | 4.0      | 63.4        | 39.2 | 87.8   | -48.6              |
| Ill. No. 6 coal       | 5              | 10.4     | 6.1         | 4.1  | 8.0    | -3.9               |
| Ill. No. 6 coal       | 10             | 10.2     | 29.5        | 21.8 | 37.1   | -15.3              |
| Ill. No. 6 coal       | 15             | 10.2     | 22.8        | 20.2 | 25.2   | -5.0               |

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, oxidized Upper Freeport coal, Illinois No. 6 coal, unoxidized Upper Freeport coal, and 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 may have accounted for an increase in hydrophobicity and recovery. An attempt to separate mixtures of carbonaceous materials and pyrite produced divergent results which require further explanation. On the one hand, a good separation of graphite and pyrite was achieved by selective agglomeration with heptane whereas, on the other hand, a similar separation was not achieved with coal and pyrite.

#### Acknowledgement

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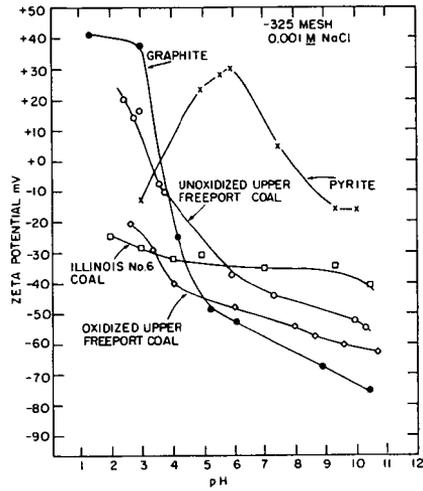


Figure 1. Zeta potential of various materials.

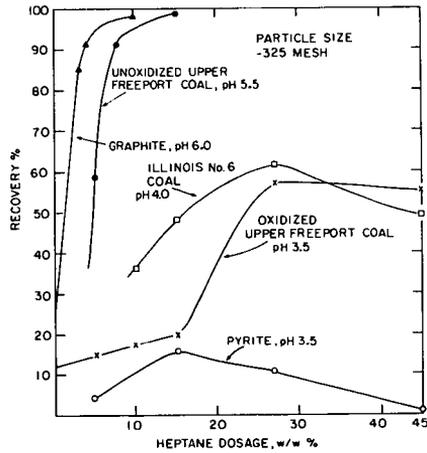


Figure 2. Effect of heptane dosage on agglomeration recovery of various materials.

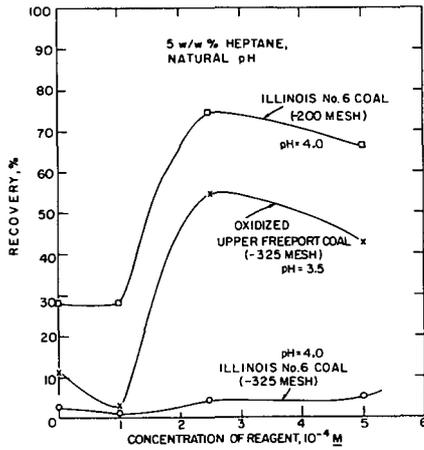


Figure 3. Effect of sodium oleate concentration on agglomeration recovery of coal.

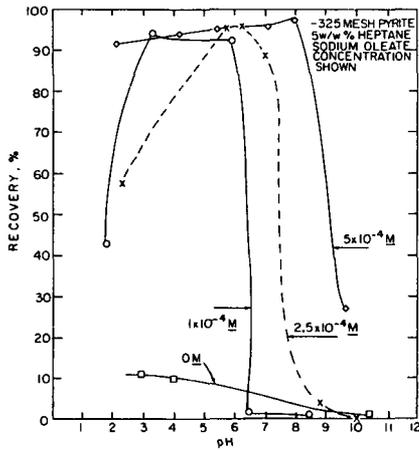


Figure 4. Effects of sodium oleate concentration and pH on agglomeration recovery of pyrite.