BASIC PRINCIPLES AND MECHANISMS OF SELECTIVE OIL AGGLOMERATION

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T. D. Wheelock, J. Drzymala, R. W. Allen,
Y.-C. Hu, D. Tyson, Qiu Xiaoping, and A. Lessa

Ames Laboratory^{*}
Iowa State University
Ames, Iowa 50011

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ABSTRACT

Since the surface characterization of coal is necessary to achieve an understanding of the principles of oil agglomeration, several methods of characterization are being evaluated, including measurement of the heat of immersion of coal in water and various organic liquids. Numerous measurements of the heat of immersion were conducted using several different particle size fractions of No. 2 Gas Seam coal from Raleigh County, West Virginia. The heat of immersion was determined in water, methanol, heptane, hexadecane and neohexane (2,2-dimethylbutane). A comparison of the results with those determined previously for Illinois No. 6 coal revealed some similarities as well as important differences. For both materials the heat of immersion appears to depend on wetting of both the external particle surface and some fraction of the internal pore surface. The fraction of internal surface which is wetted depends on the nature of the liquid and surface properties of the coal. For the relatively more hydrophobic No. 2 Gas Seam coal, a smaller fraction of the internal surface seems to be wetted by water than for the less hydrophobic Illinois No. 6 coal. Also for No. 2 Gas Seam coal, a larger fraction of the internal surface appears to be wetted by methanol or heptane than by water. A simple linear relationship was found between the heat of wetting per unit of surface area and particle size for a given type of coal and a given liquid. As expected, the heat of wetting per unit of external particle surface was found to be larger for Illinois No. 6 coal than for No. 2 Gas Seam coal when the materials were immersed in water.

A number of potential pyrite depressants for use in oil agglomeration of coal were screened by testing the response of sulfidized mineral pyrite to agglomeration with heptane in the presence of the potential depressant. Sulfidized mineral pyrite was employed since it is readily agglomerated by heptane in aqueous suspensions and, therefore, provides a severe test for a depressant. Sulfidization involved treating mineral pyrite with an acidified solution of sodium sulfide. The following materials were found to suppress the agglomeration of sulfidized pyrite when employed at appropriate pH levels: sodium dithionite, sodium thiosulfate, ferrous sulfate, ferric sulfate, titanous chloride, hydrogen peroxide, Oxone (a form of potassium monopersulfate), pyrogallol, quebracho (colloidal dispersant derived from tree bark), milk whey, and several organic thiols, i.e., compounds containing the sulfhydryl group (-SH).

One of the depressants, ferric chloride, was applied to mixtures of Upper Freeport coal and sulfidized mineral pyrite before subjecting the mixtures to agglomeration with heptane. By employing a ferric chloride concentration of 2×10^{-3} M and a heptane dosage of 12.5 v/w% (1.25 ml heptane/10 g solids) it was possible to agglomerate and recover 94% of the coal while rejecting 87% of the pyrite. The best results achieved without a selective depressant utilized 5 v/w% heptane which produced a coal recovery of 82% while rejecting 45% of the pyrite.

The design and development of a special batch mixing system for studying the kinetics of agglomeration were reported previously. This system has since been modified by adding a water jacket for temperature control and by improving the sample-withdrawing arrangement. Recent tests have shown that the mixing system is capable of producing a uniform particle suspension and that the improved sampling arrangement is capable of withdrawing small, representative samples of the suspension while the system is in operation.

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OBJECTIVE

The overall objective is to determine the basic principles and mechanisms which underlie a number of selective oil agglomeration processes that have been proposed for beneficiating fine-size coal. An understanding of the basic principles and mechanisms will greatly facilitate technical development and application of such processes to various types of coal.

INTRODUCTION

The investigation of the basic principles which underlie the oil agglomeration method advanced in three important areas. The first area involved further development of a coal surface characterization method based on measurement of the heat of immersion of coal in water or various organic liquids. The heat of immersion of No. 2 Gas Seam coal from Raleigh County, West Virginia, was measured in a number of liquids. In addition, a method was demonstrated for correlating the heat of immersion with coal particle size for a given coal immersed in a given liquid. The second area involved testing and evaluating a number of potential pyrite depressants against pyrite which had been sulfidized to increase its hydrophobicity and response to oil agglomeration. One of the more promising depressants, ferric chloride, was applied to the separation of mixtures of Upper Freeport coal and sulfidized pyrite. The third area involved further improvement and testing of a batch mixing system for studying the kinetics of agglomeration. Some progress was also made on other aspects of the investigation and will be reported in the future.

PROGRESSCoal Surface Properties

Measurements of the heat of immersion of Illinois No. 6 coal in water, methanol, heptane, and hexadecane, respectively, were reported previously (ref. 1). This work was extended to the measurement of the heat of immersion in neohexane (2,2-dimethylbutane). This liquid was selected because it has been reported that the penetration of the liquid into coal pores is negligible because of the presence of its t-butyl group (ref. 2). Also the heat of immersion of No. 2 Gas Seam coal from the Sundial Mine in Raleigh County, West Virginia, was measured in the same set of liquids. This coal was selected because of its low ash content (2.9%) and total sulfur content (0.9%). Also, the coal is much more hydrophobic and is of higher rank than Illinois No. 6 coal.

Both coals were prepared by grinding in the dry state with a high-speed impact mill and by separating into various size fractions by screening. Final screening was performed with a Sonic Sifter to improve the accuracy of separation. The mean particle size and specific surface area of each size fraction were determined with a Microtrac particle size analyzer for size fractions smaller than 100 mesh, while the mean particle size of larger size fractions was determined by automatic image analysis. In either case the specific surface area was based on the external surface of the particles and calculated from the size distribution of the particles by assuming the particles to be spherical. The specific surface area per gram was calculated by invoking the apparent density of the particles. These data were reported previously for Illinois No. 6 coal (ref. 1) and are listed in Table 1 below for No. 2 Gas Seam coal.

Before determining the heat of immersion of the various size fractions of coal, the particles were dried in a desiccator containing either magnesium perchlorate or a saturated solution of lithium chloride. The desiccator containing magnesium perchlorate was outgassed with a vacuum pump for several hours. This treatment left the coal with a moisture content of 2-3%.

The liquids used for heat of immersion measurements included deionized water, spectrophotometric-grade heptane from Burdick and Jackson Laboratories, 99% pure hexadecane and 99% pure neohexane from Aldrich Chemical Co., and 99.9% pure methanol (A. C. S. Certified) from Fisher Scientific. The heat of immersion was determined at 25°C with a Tronac model 450 microcalorimeter using the isoperibol method.

The heat of immersion of the two types of coal in different liquids is indicated by Figures 1 and 2, respectively. The heat of immersion based on the external particle surface area is plotted against the external particle surface area per gram for different particle size fractions. If only the external surface of the particles contributed to the heat of immersion, the heat of immersion per unit of external surface would remain constant as particle size varied. However, it is apparent that the heat of immersion per unit of external surface decreased as particle size decreased and the external surface area per gram increased. This result shows that the internal pore surface area was also involved and the involvement must have been greatest for the liquid which resulted in the greatest change in the heat of immersion as particle size varied.

For Illinois No. 6 coal, the greatest change in heat of immersion was observed with methanol (see Figure 1). A large change in heat of immersion as external surface varied was also observed with water. Smaller changes were observed with hexadecane and neohexane. These results suggest that a relatively

Figure 1. Heat of immersion per unit of external surface area (mJ/cm^2) for Illinois No. 6 coal.

Figure 2. Heat of immersion per unit of external surface area (mJ/cm^2) for No. 2 Gas Seam coal.

Table 1. Properties of No. 2 Gas Seam coal used for heat of immersion measurements.

Particle size, mesh (U.S. Std.)	Mean size, μm	Surface area		Ash, %	Total S, %
		$\frac{\text{cm}^2}{\text{cm}^3}$	cm^2/g		
-45/+70	284	191	146	3.21	0.76
-70/+100	181	427	327	3.08	0.76
-100/+200	113	888	679	3.66	0.82
-200/+400	71	1014	776	2.50	0.82
-400	20	5741	4392	3.31	0.84

larger proportion of the internal pore surface was accessible to methanol and water than to hexadecane and neohexane.

For No. 2 Gas Seam coal, the greatest change in heat of immersion as external surface varied was observed with heptane and the least change was observed with water. The change observed with methanol was close to that observed with heptane. Therefore, a larger proportion of the internal pore surface appeared to be accessible to heptane and methanol than to water.

The difference in accessibility of the internal pore surface to water exhibited by the two coals seems directly related to the relative hydrophobicity of the coals. It would be expected that water would penetrate the pores of a less hydrophobic material more than it would penetrate the pores of a more hydrophobic material.

By assuming that the heat of immersion per unit of total surface area wetted by the liquid is a constant for a given type of coal and a given liquid, the following relation was developed:

$$\Delta H = A + B \cdot d_p$$

where ΔH = total heat of immersion per unit of external surface area, mJ/cm^2 .

A = heat of immersion due to wetting of external surface, mJ/cm^2 .

B = coefficient which represents wetting of internal pore but based on external surface area, $\text{mJ}/(\text{cm}^2)(\mu\text{m})$.

d_p = particle diameter, μm .

A represents the heat of wetting of the external surface of the particles, whereas B accounts for the heat of wetting of the internal pores and depends on the degree of penetration of the pores by the liquid. A and B are constants for a given coal of a given moisture content immersed in a given liquid. The validity of the preceding relationship was confirmed by plotting ΔH versus d_p for both types of coal (see Figures 3 and 4). Analysis of the data by linear regression produced the values of A and B listed in Table 2. Also listed is the correlation coefficient R. Since values of R were high in most cases ($R = 1.00$ being the maximum possible), the results seemed to be adequately represented by a linear relation. However, the results obtained with heptane appeared out of line with the others and will be rechecked by further measurements.

Table 2. Heat of immersion coefficients for different coals.

Coal type	Liquid type	A mJ/cm^2	B $\text{mJ}/(\text{cm}^2)(\mu\text{m})$	R ^a
Ill. No. 6	Water	4.63	0.459	0.985
	Methanol	7.36	0.711	0.983
	Heptane	26.12	0.325	0.886
	Hexadecane	6.63	0.239	0.955
	Neohexane	10.73	0.237	0.976
No. 2 Gas Seam	Water	2.36	0.030	0.822
	Methanol	3.64	0.105	0.936
	Heptane	1.58	0.130	0.977
	Hexadecane	3.40	0.058	0.871
	Neohexane	3.98	0.050	0.912

^aCorrelation coefficient for linear regression.

Figure 3. Heat of immersion per unit of external surface area (mJ/cm²) for Illinois No. 6 coal.

Figure 4. Heat of immersion per unit of external surface area (mJ/cm²) for No. 2 Gas Seam coal.

The values of A determined by immersing the two types of coal in water are of particular interest because they seem to reflect the relative hydrophobicity of the two materials. As expected the heat of immersion due to wetting of the external surface was larger for Illinois No. 6 coal than for No. 2 Gas Seam coal. Thus, the less hydrophobic material (Illinois No. 6 coal) interacted more strongly with water than the more hydrophobic material. Other workers (ref. 3) have observed similar behavior.

Screening of Potential Pyrite Depressants

A number of potential pyrite depressants for use in oil agglomeration were screened by applying them to sulfidized mineral pyrite. Relatively pure mineral pyrite from Huanzala, Peru, was employed because it had been shown previously (ref. 1) that this material could be made very hydrophobic by treating it with a solution of sodium sulfide under acidic conditions. The sulfidized pyrite was readily agglomerated in an aqueous suspension by heptane and, therefore, appeared to be a good material for testing agglomeration inhibitors or depressants.

The sulfidizing treatment was generally applied to pyrite which had been freshly ground to pass a 90 μ m screen. In the first version of the treatment scheme 160 g of ground pyrite was suspended in 200 ml water. To this suspension was added a freshly prepared mixture consisting of 140 ml of 0.10 M sodium sulfide and 35 ml of 1 M hydrochloric acid. In the second treatment version 160 g of pyrite was suspended in 400 ml water to which was added 30 ml of 1 M hydrochloric acid. Next 100 ml of 0.1 M sodium sulfide was introduced. In both methods the suspension was subsequently stirred for 30 min. at room temperature to complete the treatment. The pyrite was recovered by filtration, washed with water, and air-dried overnight at room temperature. The material was passed through a 90- μ m

screen to break up lumps. The response of the material to oil agglomeration was tested and if the response was weak, a second treatment was applied which was similar to the first treatment. In a few cases more than two treatments were applied to produce a responsive material.

To test a given pyrite depressant, 8 g of sulfidized pyrite was first placed in a 500 ml agglomeration vessel together with approximately 375 ml of deionized water. An appropriate amount of the depressant in solution was added and the mixture was stirred briefly to completely wet the solids. Then the vessel was filled completely with water. The pH of the suspension was determined. The contents of the closed vessel were subsequently stirred for 5 min. at 5500 rpm using the agitator from a 14-speed kitchen blender. Next heptane was introduced in a series of measured increments with a hypodermic syringe while stirring was continued at 5500 rpm. During this process the turbidity of the suspension was monitored and recorded. Afterwards the pH of the suspension was usually redetermined.

A number of pyrite depressants were identified by applying the above procedure. One of these depressants was potassium monopersulfate in the form of Oxone, manufactured by the Du Pont Co. This material is regarded as a strong oxidizing agent. Ye et al. (ref. 4) had shown this material to depress pyrite in fine coal flotation. Our results showed that it would also suppress the agglomeration of pyrite with heptane. Oxone was applied to sulfidized pyrite (batch III) which had been prepared on September 13 by applying the first version of the sulfidizing treatment twice. The sulfidized pyrite responded readily to agglomeration with heptane as can be seen from the baseline results presented in Figure 5. These results indicated that the material would be completely agglomerated by 4 v/w% heptane (0.32 ml/8 g pyrite) since the turbidity of the suspension approached zero with this amount of heptane. After the sulfidized

Figure 5. Effect of Oxone (potassium monopersulfate) on agglomeration of sulfidized pyrite.

Figure 6. Effect of ferric chloride on agglomeration of sulfidized pyrite.

pyrite was treated with 3×10^{-3} M Oxone on September 25 the pH of the resulting suspension was 2.4, and the material responded weakly to agglomeration. The large decrease in turbidity produced by 0.62 v/w% heptane followed by only a slight decrease in turbidity with larger additions of heptane suggest that the Oxone-treated material was not homogeneous at pH 2.4. Apparently some of the material responded to agglomeration whereas some did not. When the pH of the Oxone-treated material was raised to 7.5, the increasing turbidity of the suspension which accompanied the addition of heptane showed that agglomeration was largely suppressed.

Another batch of sulfidized pyrite (batch XIII1A) was prepared by two applications of the sulfidizing treatment (first version). A baseline experiment showed that this material responded readily to agglomeration with heptane (see Figure 6). The baseline results were similar to those observed with pyrite (III). Further agglomeration experiments were conducted after first treating pyrite (XIII1A) with ferric chloride. The results presented in Figure 6 showed that a ferric chloride concentration of 3×10^{-4} M suppressed the agglomeration of the pyrite only slightly. However, a concentration of 3×10^{-3} M suppressed the agglomeration almost completely, and intermediate concentrations had an intermediate effect. The natural pH of the suspensions containing ferric chloride is indicated in Figure 6. In the indicated range of pH, ferric ions and ferric hydroxy complex ions would have been present (ref. 5). Hydroxy complexes are known to be very surface active and strongly adsorbed by certain solids. Their adsorption on pyrite could have made the pyrite hydrophilic. While this phenomenon could have accounted for agglomeration suppression, another possibility is that the pyrite surface could have been oxidized since ferric chloride is a relatively strong oxidizing agent, known to oxidize pyrite.

Additional experiments were conducted to see whether the effect of the ferric chloride treatment was permanent. Different portions of pyrite (XIIIA) were treated with different concentrations of ferric chloride at room temperature for 5 min. in the agitated system. After this treatment the pyrite was recovered by filtration, the filter cake was washed with water, and the pyrite was resuspended in water for agglomeration. Although the ferric chloride treatment was conducted in a pH range of 2.6 to 3.0, the agglomeration step was conducted in a pH range of 4.5 to 5.0. The results of the agglomeration experiments are shown in Figure 7. The results are similar in general to those obtained before when agglomeration was conducted in the treatment solution. Therefore, it appeared that the effect of the ferric chloride treatment was permanent. Either a hydrophilic species was adsorbed very strongly on the surface of the pyrite or some other change in the chemical composition of the surface was produced by oxidation.

For testing several other pyrite depressants, additional sulfidized pyrite (batch XVI) was prepared. Several samples of pyrite which had been ground and stored for some time were combined and reground to pass a 90- μ m screen. The material was sulfidized twice using the second version of the treatment procedure. A baseline experiment conducted on October 4 showed that this material was readily agglomerated (see Figure 8), but the agglomeration characteristics of the material were not quite the same as those observed with the previous batch. The new batch appeared to be less homogeneous and required more heptane for complete agglomeration.

When pyrite (XVI) was treated with 3×10^{-3} M sodium dithionite, its response to agglomeration was suppressed somewhat at pH 5.6 and was suppressed almost completely at pH 7.2. The lower pH was the natural pH of the treatment mixture whereas the higher pH was obtained by adding sodium hydroxide. The results

Figure 7. Effect of ferric chloride treatment followed by washing on agglomeration of sulfidized pyrite.

Figure 8. Effect of sodium dithionite on agglomeration of sulfidized pyrite.

appeared generally similar to those observed with Oxone even though sodium dithionite is a reducing agent, whereas Oxone is an oxidizing agent.

Pyrite (XVI) was also treated with a material believed to be milk whey which was prepared by allowing pasturized milk with 2% butter fat to ferment for two weeks. The fermented milk was heated and kept just below the boiling temperature for several hours to kill the bacteria and denature the protein. The material was subsequently filtered. The filtrate was recovered, boiled and again filtered. The clear liquid was used for treating sulfidized pyrite. To obtain the experimental results shown in Figure 9, a pyrite suspension was treated with 5 ml. of the whey-containing liquid. At either pH 5.3 (the natural pH of the suspension) or pH 8.0, agglomeration with heptane was largely suppressed. On the other hand, when a pyrite suspension which had been treated with whey was filtered, and the recovered pyrite was washed with water and resuspended, the resulting suspension did respond to agglomeration with heptane. This suggested that the agglomerability of pyrite was suppressed because whey was physically adsorbed on the pyrite surface. Subsequent washing removed the whey.

Another baseline experiment was performed with pyrite (XVI) on October 17. (see Figure 10). Since the material responded more readily to agglomeration than it had on October 4, it appeared that storing the sulfidized pyrite in an unsealed jar had changed its hydrophobicity through some unknown mechanism. When the pyrite was treated with 3×10^{-3} M pyrogallol either at pH 4.3 (the natural pH of the suspension) or at pH 8.1, agglomeration with heptane was largely suppressed. Pyrogallol is a well-known reducing agent.

The agglomeration of pyrite (XVI) was also largely suppressed by 3×10^{-3} M titanous chloride at pH 1.7, the natural pH of the suspension (see Figure 11). At pH 6.8 titanous chloride prevented the agglomeration of pyrite with small

Figure 9. Effect of milk whey on agglomeration of sulfidized pyrite.

Figure 10. Effect of pyrogallol on agglomeration of sulfidized pyrite.

Figure 11. Effect of titanous chloride on agglomeration of sulfidized pyrite.

Figure 12. Effect of quebracho on agglomeration of sulfidized pyrite.

amounts of heptane but not with large amounts. The effect of the treatment was not repealed by washing the treated pyrite. Titanous ions are strongly reducing.

It had been shown previously (ref. 6) that the agglomeration of oxidized pyrite could be suppressed by small amounts of quebracho. Quebracho is a high molecular weight material extracted from the bark of certain trees and is widely used as a dispersant for colloidal materials. As the results in Figure 12 indicate, quebracho also suppressed the agglomeration of sulfidized pyrite (XVI).

Hydrogen peroxide which is a strong oxidizing agent also proved to be a good depressant for sulfidized pyrite. As indicated by Figure 13, the agglomeration of pyrite (XVI) was suppressed markedly by 10^{-2} M hydrogen peroxide and was suppressed almost completely by 10^{-1} M hydrogen peroxide in both acidic and basic solutions. When pyrite was treated with hydrogen peroxide, the evolution of gas was noticeable, and the treatment was continued until the evolution abated. The natural pH of the suspension treated with 10^{-2} M hydrogen peroxide was 4.7 and that of the suspension treated with 10^{-1} M hydrogen peroxide was 3.6. The decrease in pH indicates that the surface of the pyrite was oxidized to form acidic products.

When pyrite (XVI) was treated with 10^{-2} M ferrous sulfate, agglomeration was largely suppressed at pH 4.2 and almost completely suppressed at pH 6.5 (see Figure 14). Suppression may have been greater at the higher pH because of the formation and adsorption of a ferrous hydroxy complex at that pH.

In a final set of experiments with pyrite (XVI), the material was treated with 3×10^{-3} M sodium thiosulfate, another known reducing agent. Agglomeration was largely suppressed at pH 5.8 and almost completely suppressed at pH 9.2 (see Figure 15).

Figure 13. Effect of hydrogen peroxide on agglomeration of sulfidized pyrite.

Figure 14. Effect of ferrous sulfate on agglomeration of sulfidized pyrite.

Figure 15. Effect of sodium thiosulfate on agglomeration of sulfidized pyrite.

Figure 16. Results of treating sulfidized pyrite with thiols which suppressed pyrite agglomeration.

Since organic compounds containing the sulfhydryl group ($-SH$) and known as thio compounds are reputed to be strongly adsorbed by sulfide minerals, a series of such compounds was tested for pyrite depression. The compounds selected for testing also contained hydrophilic groups such as carboxyl, hydroxyl, or sulfonic acid groups. It was hypothesized that adsorption of such materials on pyrite would make the surface hydrophilic and prevent oil attachment. The compounds selected for testing included the following:

- 2-mercaptoethanesulfonic acid (MES)
- 2-mercaptoethanol (MET)
- 3-mercaptopropionic acid (MPA)
- mercaptosuccinic acid (MSA)
- thioacetic acid (TAA)
- thiobenzoic acid (TBA)
- thioglycolic acid (TGA)
- thiolactic acid (TLA)
- thiosalicylic acid (TSA)
- thioacetamide (TAM)

To test these materials, the sulfidizing treatment (second version) was applied four times in succession to the same batch (XVII) of $-90\ \mu m$ pyrite. For some unknown reason it required this many applications of the treatment to produce a readily agglomerable material. The treated material was rescreened with a $149\ \mu m$ screen to break up lumps. The results of a baseline agglomeration experiment without additives are shown in Figures 16 and 17. Although the baseline results were not quite the same as observed with other pyrite batches, they still provided a suitable basis for comparing the effectiveness of possible depressants.

For testing the thiols as depressants, the normal agglomeration procedure was employed except that after adding one of the depressants to a pyrite suspension, the pH of the suspension was increased to 7.5 by adding sodium hydroxide, and then the suspension was conditioned for only 2 min. by stirring at 5500 rpm. The thiols which were found to be effective depressants provided

Figure 17. Results of treating sulfidized pyrite with thiols which did not suppress pyrite agglomeration.

Figure 18. Results of agglomerating a mixture of Upper Freeport coal and sulfidized pyrite (batch XV) with different amounts of heptane.

the results presented in Figure 16, whereas those which appeared ineffective gave the results shown in Figure 17. All of the effective materials suppressed pyrite agglomeration with small amounts of heptane, and two of the materials (MES and MSA) suppressed pyrite agglomeration with relatively large amounts of heptane as well. Although the ineffective materials seemed to act as pyrite dispersants and increased the turbidity of the suspensions, they did not prevent agglomeration with heptane.

The thiols which proved to be effective pyrite depressants had a unique structure which consisted of a chain of two or more carbon atoms with either a carboxyl or sulfonic acid group on one end and a sulfhydryl group attached to one of the carbon atoms which was not part of the carboxyl group. Compounds having a benzene ring structure (TBA or TSA) were not effective depressants nor were compounds having a hydroxyl group (MET) or an amide group (TAM) in place of a carboxyl or sulfonic acid group. Also ineffective was a compound in which the sulfhydryl group was attached to the carbonyl group (TAA).

A number of compounds were tested which did not prove to be effective depressants when applied to sulfidized pyrite in either acidic or basic suspensions. These compounds are listed in Table 3. Agglomeration tests were conducted at the indicated pH and in most cases using a concentration of 3×10^{-3} M of the compound in question.

Application of a Selective Pyrite Depressant

One of the materials which was found to suppress the agglomeration of pyrite was selected for more detailed studies of its performance when applied to coal/pyrite mixtures. The material was ferric chloride, and it was applied to the separation of Upper Freeport coal and sulfidized mineral pyrite. The coal was a hand-picked sample from Indiana County, Pennsylvania, with a total sulfur

Table 3. Materials which were not effective pyrite depressants in 3×10^{-3} M concentration at the indicated pH.

Material	pH	Material	pH
Malic acid	3.2 ^a 6.8	Hydroquinone	4.3 ^a 8.7
Lactic acid ^b	2.8 ^a 7.8	Hydrazine sulfate	2.7 ^a 7.5
Glycolic acid	3.4 ^a 8.1	EDTA	4.6 ^a 8.3
Tartaric acid	2.7 ^a 7.2	Potassium iodide	5.2 ^a 8.8
β -Hydroxybutyric acid	6.9 ^a 9.1		

^aNatural pH of treated pyrite suspension

^bConcentration was 10^{-3} M

content of 2.2% and ash content of 13%. It was prepared by combining equal amounts of coal which had been ground at two different times with a high-speed impact mill. The pyrite (batch XV) was a mixture of five different batches (X to XIV) which previously had been twice sulfidized. The starting material was high-grade mineral pyrite from Peru. Both coal and pyrite were fine enough to pass a 90- μ m screen. Also both materials were very hydrophobic and readily agglomerated by heptane.

To study the separation of coal/pyrite mixtures, 4 g of coal and 4 g of pyrite were first placed in a 500 ml agglomeration vessel together with approximately 375 ml of deionized water. After mixing the materials briefly, an appropriate amount of ferric chloride in solution was added, and then the vessel was filled completely with water. The contents of the closed vessel were subsequently stirred for 5 min. at 5500 rpm using the agitator from a 14-speed

kitchen blender. Next a single dose of heptane was introduced with a hypodermic syringe and stirring was continued for 5 min. The resulting agglomerates were recovered on a 150 μ m screen, washed into a bowl, and then recovered by filtration. The filter cake was dried in an oven, weighed and analyzed for total sulfur. Unagglomerated solids which passed through the screen were recovered by filtration, dried, and analyzed. A sulfur material balance was used to determine the distribution of pyrite between the agglomerated product and tailings.

An initial set of experiments was conducted without a pyrite depressant to obtain baseline data at the natural pH (4.5) of the system. The heptane dosage was varied among these experiments to see how the recovery of each component was affected by the overall mass yield of agglomerates. The results presented in Figure 18 show that the recovery of both coal and pyrite increased with increasing heptane dosage. However, the recovery of coal was always greater than the recovery of pyrite for any given heptane dosage so some separation was achieved. The greatest difference in the recoveries or separation efficiency was observed with 5 v/w% heptane which produced an overall agglomerate yield of 69%. At this yield, coal recovery was 82% and pyrite recovery was 55% and the difference between these recoveries, which is one measure of separation efficiency, was 27%. Increasing the heptane dosage to 6.25 v/w% increased coal recovery to 86% and pyrite recovery to 62% resulting in a separation efficiency of 24%.

The separation of coal and pyrite was greatly improved by introducing a pyrite depressant. This was demonstrated by another set of experiments in which the concentration of ferric chloride was constant at 6.25 v/w%. The results presented in Figure 19 show that with a ferric chloride concentration of 10^{-3} M the recovery of coal was 80% and the recovery of pyrite was 8% which gave a

Figure 19. Agglomeration of a mixture of Upper Freeport coal and sulfidized pyrite (batch XV) with 6.25 v/w% heptane and following concentrations of FeCl_3 : (a) $3 \times 10^{-3} \text{M}$, (b) 10^{-3}M , (c) $3 \times 10^{-4} \text{M}$, (d) 10^{-2}M .

Figure 20. Agglomeration of a mixture of Upper Freeport coal and sulfidized pyrite (batch XV) in $2 \times 10^{-3} \text{M}$ FeCl_3 with different amounts of heptane.

separation efficiency of 72%. Neither larger nor smaller concentrations of ferric chloride improved the separation.

To see whether a higher coal recovery could be achieved while maintaining a high separation efficiency, a final set of experiments was conducted in which the heptane dosage was varied while holding the ferric chloride concentration constant at 2×10^{-3} M. The results presented in Figure 20 show that by using 12.5 v/w% heptane it was possible to achieve a coal recovery of 94% and pyrite recovery of 13%. This provided a separation efficiency of 81%. A larger heptane dosage was counterproductive and resulted in a lower coal recovery and lower separation efficiency.

Kinetics of Agglomeration

The batch mixing system which was designed and built for studying the kinetics of agglomeration was modified and improved. The original design of the system was described previously (ref. 7). To improve the system, a water jacket was added for temperature control and the sampling tubes were redesigned to facilitate collecting samples of the suspension undergoing agglomeration. The sampling tubes are a key feature since representative samples of the particle suspension must be collected while the system is in operation. The modified system is shown in Figure 21, and it has been tested to demonstrate the effectiveness of the improved sampling tubes. It has been established that each sampling tube must penetrate at least 5 mm into the mixing vessel to ensure good sampling.

To demonstrate the effectiveness of the mixing and sampling arrangement, an experiment was conducted using a suspension of silica particles having a size distribution similar to that of an agglomerating suspension of coal particles. To obtain a suitable size distribution, six discrete size fractions

Figure 21. Batch mixing system for studying the kinetics of agglomeration.

of silica particles were combined. The particles were mixed with water to provide a suspension with 20 wt.% solids which filled the 500-ml agglomeration vessel. The turbine agitator in the vessel was operated at 1100 rpm to produce an apparently uniform suspension. After 5 min. of agitation, sampling was started. Two samples of the suspension were withdrawn in rapid succession from ports located on opposite sides of the mixing vessel. Sampling was repeated at 5 min. intervals over a period of 25 min. The volume of each sample was 35 ml, and as each sample was withdrawn, water was introduced to keep the vessel full. The samples were filtered; the particles were dried overnight, weighed, and subjected to a dry sieve analysis.

The overall mean size distribution of the 10 samples collected during the experiment is shown in Figure 22. Also shown is the standard deviation from the mean for each size class. A given size class was based on the geometric mean of the upper and lower screen sizes which bounded the class. Since the coefficient of variation was 8% or less for any given size class and under 5% for the majority of size classes, there was excellent agreement between samples. Therefore, sampling was highly reproducible and the particle size distribution did not change significantly as material was withdrawn from the mixing vessel. The contents of the vessel must have been well-mixed to provide a uniform suspension and all particle sizes must have had an equal chance of being withdrawn by the sampling arrangement. In other words, the samples must have been truly representative of the contents of the vessel. This conclusion was confirmed by determining the size distribution of the material remaining in the vessel at the end of the experiment and comparing it with the size distribution of the feed (see Figure 23). The close agreement between these distributions showed that material removed by sampling had to have been identical to that in the vessel or to state it another way sampling was unbiased. This can also be seen by comparing the mean size distribution of the samples (Figure 22) with the size distribution of the vessel contents (Figure 23).

Figure 22. Mean size distribution of 10 samples collected over 25 min.

Figure 23. Initial and final size distributions of the mixing vessel contents.

SUMMARY

The heat of immersion of No. 2 Gas Seam coal from Raleigh County, West Virginia, was determined in water and several organic liquids. A comparison of the results with those determined previously for Illinois No. 6 coal revealed some similarities as well as important differences. For both materials the heat of immersion appears to depend on wetting of both the external particle surface and some fraction of the internal pore surface. The relative contribution of each type of surface to the total heat of immersion varies with the type of coal and nature of the liquid. For the more hydrophobic No. 2 Gas seam coal, the internal pore surface appears to make a relatively larger contribution to the total heat of immersion in methanol or heptane than to the total heat of immersion in water. For the less hydrophobic Illinois No. 6 coal, the internal pore surface appears to make a relatively large contribution to the total heat of immersion in either methanol or water and to make a smaller contribution to the total heat of immersion in paraffinic hydrocarbons, particularly higher molecular weight materials. For a given type of coal and a given liquid, a simple linear relationship seems to account for the relative contribution of each type of surface as coal particle size varies.

A number of potential pyrite depressants for use in oil agglomeration of coal were screened by testing the response of sulfidized mineral pyrite to agglomeration with heptane in the presence of the potential depressant. The following materials were found to suppress the agglomeration of sulfidized pyrite: sodium dithionite, sodium thiosulfate, ferrous sulfate, ferric sulfate, titanous chloride, hydrogen peroxide, Oxone, pyrogallol, quebracho, milk whey, and several organic thiols, i.e., compounds containing the sulfhydryl group ($-SH$). The extent of pyrite suppression varied with the pH of the particle suspension and the effect of pH differed among the depressants. A number of

materials were also tested which did not appear to be effective pyrite depressants.

The use of ferric chloride as a selective depressant for sulfidized mineral pyrite in the presence of Upper Freeport coal was demonstrated by agglomerating a mixture of the materials in the presence of small concentrations of ferric chloride. By using this depressant, most of the pyrite was prevented from agglomerating while the coal was largely agglomerated and recovered. Without the depressant both pyrite and coal were largely agglomerated.

The batch mixing system previously developed for studying the kinetics of oil agglomeration was modified by adding a cooling water jacket for temperature control and by improving the sample withdrawing arrangement. The sampling arrangement was subsequently tested and shown to be very effective.

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