IS--5018

DE91 004096

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Fossil Energy Quarterly Report

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Date Transmitted: October, 1989

Prepared for: Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Project Monitor: J. Balzarini

^{*}Operated for the U.S. Department of Energy
by Iowa State University
under Contract No. W-7405-Eng-82

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ABSTRACT

Measurement and control of the surface properties of coal and pyrite are important in the application of selective oil agglomeration for coal beneficiation and both received further study and consideration. One of the more promising methods of surface characterization for this application involves measuring the heat of immersion of coal in water or other liquids. To develop a useful and consistent measurement technique, numerous measurements were conducted with Illinois No. 6 coal to study the effects of coal particle size and moisture content on the heat of immersion in various liquids. The heat of immersion was nearly the same in water and heptane, lower in hexadecane, and higher in methanol. The effect of particle size indicated that the heat of immersion is dependent on the internal pore area as well as the external particle surface. The heat of immersion was also observed to decrease with increasing coal moisture content.

In seeking methods for controlling the surface properties of pyrite, ground mineral pyrite was pretreated with dilute solutions of sodium sulfide at various pH and then agglomerated with heptane. When the pretreatment was conducted in acidic solutions with 4×10^{-4} M Na_2S , the surface of pyrite appeared to become sulfidized for it became very hydrophobic and the pyrite responded readily to oil agglomeration. The

treated surface did not seem to be affected by washing with water, and the pretreated and washed pyrite responded readily to agglomeration over a wide range of pH. However, the agglomeration of the pretreated pyrite was suppressed by somewhat higher concentrations of sodium sulfide, particularly at high pH.

To achieve better control over the oil agglomeration process, oil agglomeration experiments were conducted with aqueous suspensions of graphite which were first degassed with a vacuum pump. This treatment was designed to remove minute amounts of air from the surface of the particles and seemed to result in more complete wetting of the surface because the response of the material was similar to that of graphite which had been wet ball-milled. The agglomeration recovery of the degassed graphite was highly reproducible and varied significantly with changes in the ionic strength of the suspending medium even at very low salt concentrations. Also the recovery decreased significantly when the pH was raised above 10.

Preliminary testing of the recently constructed batch mixing system for studying the kinetics of agglomeration showed the system to have good mixing characteristics. Also a satisfactory method of sampling the suspension of particles during operation was demonstrated.

MECHANISMS FOR SELECTIVE AGGLOMERATION OF COALS

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OBJECTIVE

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

INTRODUCTION

Since the surface properties of coal and associated minerals have an important effect on the oil agglomeration process, further study was given to the factors which affect the heat of immersion of coal particles in different liquids because it appears that the heat of immersion can be a useful method of surface characterization. However, to provide a meaningful comparison of surface properties of different materials, the method needs to be normalized or standardized so that the heat of immersion can be compared under comparable conditions. To establish these conditions, the heat of immersion of Illinois No. 6 coal was measured in different liquids using different particle sizes. In addition, the effect of coal moisture content was also studied.

The surface properties of pyrite create a serious problem in oil agglomeration because under some conditions the surface of pyrite is relatively hydrophobic and the material is readily agglomerated. On the other hand, under other conditions the surface of pyrite can be relatively

hydrophilic so that the material does not respond to agglomeration. To better understand the causes of pyrite hydrophobicity/hydrophilicity and to define the conditions which result in either a hydrophobic or hydrophilic pyrite surface, the response of pyrite to oil agglomeration was investigated after applying different surface treatments. These treatments included treating the surface with dilute solutions of sodium sulfide in various concentrations and having different pH values.

Although it has been known for some time (ref. 1) that the process of agglomeration is affected by the presence of air, it was not fully appreciated to what extent the process may be affected by the presence of even minute amounts of air. Such amounts may interfere with the complete wetting of hydrophobic coals and graphite. To evaluate this effect further, aqueous suspensions of graphite particles were degassed with a vacuum pump before agglomeration. The effects of oil dosage and pH on the agglomeration of degassed graphite were also investigated.

In addition, the mixing and sampling characteristics of a batch mixing system were evaluated to determine the adequacy of the system for further study of oil agglomeration kinetics.

PROGRESS

Coal Surface Properties

The heat of immersion of Illinois No. 6 coal was measured in different liquids under various conditions in order to study the effects of liquid type, particle size, and coal moisture content. The coal was from the River King Mine in St. Clair County, Illinois. The coal was ground in the dry state in a high-speed impact mill and separated into

various size fractions by screening. Final screening was performed with a Sonic Sifter to improve the accuracy of separation. The different size fractions were analyzed for ash and total sulfur contents, mean particle size, and specific surface area (see Table 1). The mean particle size and specific surface area 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. The latter was measured for -45/+70 mesh particles with a pycnometer by displacement of heptane and found to be 1.30 g/cm^3 .

Before determining the heat of immersion of the various size fractions in different liquids, the particles were placed in a dessicator containing magnesium perchlorate which was outgassed with a vacuum pump. This treatment left the coal with a moisture content of 2 wt %. To study the effect of coal moisture content on the heat of immersion, different portions of -100/+200 mesh coal were stored in different dessicators containing either water or sodium hydroxide solutions for several days. By using different sodium hydroxide concentrations the different coal samples were exposed to different relative humidities and the samples ended up with different moisture contents. The moisture content of the coal samples was determined by drying the samples in an oven at $110\text{--}120^\circ\text{C}$ for 1.5 hr.

Table 1. Composition of Illinois No. 6 coal used for heat of immersion measurements.

Particle size, mesh (U.S. Std.)	Mean size, μm	Surface area, ^a		Ash, ^b wt. %	Tot. S, ^c wt. %
		cm^2/cm^3	cm^2/g		
-45/+70	241	275	212	4.99	3.39
-70/+100	158	428	330	5.24	3.48
-100/+200	110	728	560	6.80	3.32
-200/+270	82	856	659	6.94	3.41
-270/+400	63	1172	902	7.32	3.53

^aExternal particle surface area.

^bDry basis.

^cAs received basis.

The liquids used for heat of immersion measurements included deionized water, spectrophotometric grade heptane from Burdick and Jackson Laboratories, 99% hexadecane from Aldrich Chemical Co., and 99.9% 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 effect of moisture content on the heat of immersion of Illinois No. 6 coal in water is shown in Figure 1. The trend of decreasing heat of immersion with increasing moisture content is similar to that reported previously (ref. 2).

The heat of immersion of Illinois No. 6 coal in different liquids is indicated in Figures 2 and 3. It can be seen that the heat of immersion was greatest in methanol and least in hexadecane. For intermediate size and larger particles, the heats of immersion in water and heptane were

Figure 1. Heat of immersion of Illinois No. 6 coal in water.

Figure 2. Heat of immersion per gram of Illinois No. 6 coal in different liquids.

Figure 3. Heat of immersion per unit of external surface in various liquids.

Figure 4. Turbidity of untreated pyrite mixed with increasing amounts of heptane.

nearly the same. The heat of immersion in hexadecane was about half of that in heptane which is consistent with results reported previously for Pocahontas No. 3 coal (ref. 3). In the case of Pocahontas No. 3 coal the heat of immersion in octane was about half of that in hexadecane. The larger heat of immersion in lower molecular weight alkanes was attributed to the greater accessibility of the inner pore surface to the smaller molecules. The relatively large heat of immersion of Illinois No. 6 coal in methanol may be due in part to coal swelling. It was reported previously that the most energetic step of wetting by methanol was the swelling process for high volatile bituminous coal and subbituminous coals (ref. 4).

Of considerable interest is the effect of particle size on the heat of immersion. It is believed that the heat of wetting per unit of surface area should be constant for a given coal and a given liquid. But the surface area which is wetted is difficult to measure because it probably consists of some of the internal pore surface as well as the external particle surface. Contributing to the difficulty is the presence of pores of different sizes, some of which are readily penetrated by the liquid and others which are not. If the internal pore surface area which is wetted greatly exceeds the external particle surface area, the heat of wetting per gram of coal should be nearly constant as the particle size is varied. On the other hand, if the external particle surface area greatly exceeds the pore surface accessible to the liquid, the heat of wetting per unit of external surface should be constant. An examination of the results for Illinois No. 6 coal in Figures 2 and 3 reveals that neither the heat of wetting per gram nor the heat of wetting per unit of external surface was

constant when plotted against particle size. However, it appears that the heat of wetting per gram may have varied somewhat less than the heat of wetting per unit of external surface when plotted against particle size. Hence, the results suggest that pore surface area made an important contribution to the observed heat of immersion.

Surface Properties of Pyrite

It was shown previously (refs. 5,6) that much can be learned about the agglomeration characteristics of coal and pyrite by monitoring the turbidity of a particle suspension undergoing oil agglomeration. The apparatus used for this purpose consists of a specially designed, closed mixing system which is connected to a photometric dispersion analyzer for measuring turbidity (ref. 5). To obtain the experimental results described below, relatively pure mineral pyrite from Huanzala, Peru, was utilized. The pyrite was ground with a high-speed impact mill to pass a No. 170 screen with 90 μ m openings. For most of the work the ground pyrite was stored in an unsealed glass jar for 3-4 weeks before being utilized. The material was agglomerated with n-heptane, 99% pure, obtained from Aldrich Chemical Co.

In one series of experiments the ground pyrite was treated with dilute sodium sulfide solutions in various concentrations and then agglomerated. For each experiment 8 g of pyrite was suspended in 450 ml of deionized water in the mixing vessel and an appropriate amount of sodium sulfide solution was added. The sodium sulfide solution was prepared by acidifying a given quantity of 0.1 M Na_2S with 1 M HCl just before adding it to the pyrite suspension. Sufficient deionized water was

added to completely fill the mixing system and eliminate air. The resulting suspension occupied a volume of 500 ml. The vessel was closed and the suspension was conditioned by stirring for 5 min. at 5500 rpm. Next heptane was introduced in a series of measured increments with a hypodermic syringe while stirring was continued at 5500 rpm. After each increment was added, the system was allowed to stabilize as indicated by the dispersion analyzer before adding the next increment. During this process the turbidity of the suspension was monitored and recorded.

Several baseline experiments were first conducted with pyrite which had not been treated with sodium sulfide. The results presented in Figure 4 showed that the response of pyrite to agglomeration depended on the pH of the suspension. At pH 1.5 the turbidity of the suspension decreased as more and more heptane was introduced which indicated that the pyrite was agglomerated to some extent. However, the change in turbidity with increasing amounts of heptane was moderate which indicated a modest response to agglomeration. At pH 4 the initial turbidity of the suspension was higher than at pH 1.5 which showed that the pyrite was more highly dispersed at the higher pH. Furthermore, the turbidity decreased less at pH 4 than at pH 1.5 when increasing amounts of heptane were added which indicated a lower response to agglomeration. At pH 5.5 the initial turbidity of the pyrite suspension was essentially the same as at pH 4, and the turbidity increased as more and more heptane was added which showed that the pyrite was not agglomerated significantly.

Since the greatest response of untreated pyrite to oil agglomeration was at pH 1.5, the first set of experiments in which pyrite was pretreated with sodium sulfide was also conducted at this pH. The results of the

Figure 5. Turbidity of pyrite treated with Na_2S after mixing with increasing amounts of heptane.

Figure 6. Effect of pH during the Na_2S treatment on the response of the treated pyrite to oil agglomeration.

pretreatment and oil agglomeration are presented in Figure 5 and indicate that the concentration of sodium sulfide had a major effect. When the pyrite was treated with an intermediate concentration of sodium sulfide (6×10^{-4} M), the pyrite responded most readily to agglomeration. At this level of treatment, the critical oil dosage (C_c) for the pyrite was only 4 v/w % (4 ml heptane/100 g pyrite) which indicates a very hydrophobic material. For comparison it was found previously (ref. 6) that the critical oil dosage for minus 200 mesh Upper Freeport coal, a relatively hydrophobic material, was 25 v/w %. This indicates that the treated pyrite was more readily agglomerated than Upper Freeport coal and that it would be very difficult to separate such pyrite from Upper Freeport coal by selective agglomeration.

Also of interest are the results obtained with either higher or lower concentrations of sodium sulfide, since these did not appear to affect the agglomeration of pyrite significantly. Thus, the results presented in Figure 5 for other than those obtained with 6×10^{-4} M Na_2S were not appreciably different from those shown in Figure 4 for untreated pyrite at pH 1.5.

The next set of experiments was designed to study the effect of pH on the sodium sulfide treatment. The pyrite was pretreated with 4×10^{-4} M Na_2S which was close to the concentration found to promote the agglomeration of pyrite. The results in Figure 6 show that the pH of the treatment was of major importance. Between pH 2.0 and 3.5 the results were similar to those obtained at pH 1.5 and presented in Figure 5 in that the different experiments indicated the same critical oil dosage (4 v/w

2). Between pH 4.1 and 4.9 the results with sodium sulfide were similar to those shown in Figure 4 for untreated pyrite at pH 1.5. Finally at pH 5.1 the results with sodium sulfide were similar to those shown in Figure 4 for untreated pyrite at pH 4.0.

Additional experiments were conducted to study the effect of pH in conjunction with a larger concentration of sodium sulfide. For these experiments pyrite was treated with $1.6 \times 10^{-3} \text{ M Na}_2\text{S}$ at different pH values. The results at pH 2-3 in Figure 7 were similar to those indicated in Figure 4 for untreated pyrite at pH 1.5. At pH 4 the results with pretreated pyrite (Figure 7) suggest that little or no agglomeration took place, whereas the result with untreated pyrite (Figure 4) indicate that some agglomeration occurred. Therefore, the results with the higher concentration of sodium sulfide suggest that at lower pH levels pretreatment had little or no effect on the agglomeration of pyrite whereas at higher pH levels sodium sulfide might tend to suppress agglomeration.

A diagram showing the combined effects of sodium sulfide concentration and pH on the nature of the pyrite agglomerates produced in the preceding experiments is presented as Figure 8. This diagram is semiquantitative since it is based on both visual observations and quantitative measurements. It shows a small region where the combined effects of sodium sulfide concentration and pH resulted in spherical agglomeration surrounded by a much larger region where some agglomeration occurred but the agglomerates were bulkier and unconsolidated. To the right of this region was a third region where no agglomeration seemed to take place.

Figure 7. Effect of pH during the Na_2S treatment on the response of the treated pyrite to oil agglomeration.

Figure 8. Treatment conditions which affect the response of pyrite to oil agglomeration.

In another series of experiments the ground pyrite was treated as before with 4×10^{-4} M Na_2S at pH 3.5. In each experiment after conditioning the suspension for 10 min., heptane was added in a single portion and the system was stirred for a number of minutes at 5500 rpm. When spherical agglomerates were produced, they were recovered by decanting the liquid, dried in air overnight, and measured with an optical microscope to determine their size. Since the spherical agglomerates tended to be uniform in size, the diameter of 10-15 agglomerates was measured and the mean diameter was based on the measured values.

The results of agglomerating pretreated pyrite as just described with different amounts of heptane are shown in Figure 9. In obtaining these results each suspension was agitated for 13 min. to agglomerate the particles after introducing heptane. As a consequence of the vigorous agitation the temperature of any given suspension increased approximately 20°C over room temperature during the combined conditioning and agglomeration stages. According to Figure 9 the logarithm of the average agglomerate diameter was directly proportional to the amount of heptane used. A similar relationship was found previously for hydrophobic graphite particles (ref. 1). When the amount of heptane was increased to 12.5 v/w %, the mixture of particles and oil formed an amalgam instead of discrete agglomerates.

Additional experiments were conducted in the same manner except that after the pretreatment and conditioning with 4×10^{-4} M Na_2S at pH 3.5 for 10 min., the pyrite was recovered by filtration, washed with water, and resuspended in fresh deionized water. The resulting suspension had a pH of 5-6. Heptane was then introduced and the suspension was stirred at

Figure 9. Results of agglomerating pretreated pyrite with a single dose of heptane.

Figure 10. Results of resuspending pretreated pyrite in fresh water and agglomerating with a single dose of heptane.

5500 rpm for 22 min. to agglomerate the pyrite. During the agglomeration stage the temperature rose approximately 20°C over room temperature. Since the results which are indicated in Figure 10 were very similar to those obtained in the preceding experiments (Figure 9), it is apparent that the surface properties of the treated pyrite were not affected significantly by the process of filtration, washing, and resuspension in fresh water.

For a final series of experiments, 160 g of freshly ground pyrite (minus 90 μ m) was suspended in 200 ml of deionized water and treated with a solution prepared by mixing 140 ml of 0.1 M Na_2S with 25 ml of 1 M HCl. The sodium sulfide solution was somewhat milky, probably due to the precipitation of elemental sulfur; it was used immediately after preparation. The pyrite suspension was diluted with deionized water to 500 ml. The suspension having a pH of 2 was stirred for 30 min. The pyrite was recovered by filtration, washed with water, and air dried overnight. Small portions of the treated or sulfidized pyrite were subsequently used in a number of oil agglomeration experiments. These experiments were conducted by adding heptane in a series of small increments and observing the resulting effect on the turbidity of any given suspension as described above.

Some of the sulfidized pyrite (S-pyrite) was used to study the effect of pH during oil agglomeration. The natural pH of a sulfidized pyrite suspension was 4.6. From the results presented in Figure 11 it is apparent that the initial turbidity of the suspensions increased as the pH was raised. Although larger and larger amounts of heptane were required to reduce the turbidity to the same level as the pH increased, it was

Figure 11. Effect of pH on agglomeration of sulfidized pyrite.

Figure 12. Effect of Na_2S concentration on agglomeration of sulfidized pyrite.

still possible to achieve particle agglomeration even at pH 10. This is in sharp contrast to untreated pyrite which did not respond to agglomeration above pH 4 (see Figure 4). Thus, while the untreated pyrite lost its hydrophobicity at high pH, the sulfidized pyrite did not. The surface of the treated pyrite seemed to be passivated or coated with something which was not greatly affected by changes in pH. One possibility is that the surface of the treated pyrite was coated with elemental sulfur, a very hydrophobic material.

Another interesting characteristic of the sulfidized pyrite was that it could be agglomerated over a wide range of pH when separated from the treatment solution and resuspended in water, whereas it could only be agglomerated under acidic conditions when left in the treatment solution for agglomeration. This can be seen by comparing the results in Figure 11 with those in Figure 8. This suggested that sodium sulfide suppresses the agglomeration of sulfidized pyrite at intermediate and high pH levels. To investigate this possibility, several experiments were carried out in which sulfidized pyrite was resuspended in sodium sulfide solutions of various concentrations at pH 4.5-5.7 and agglomerated. Figure 12 shows that the agglomeration results in 3×10^{-4} M Na_2S were similar to those achieved in water. However, as the concentration of sodium sulfide was increased there was less and less tendency for the sulfidized pyrite to agglomerate, and at the highest concentration (10^{-2} M) no agglomeration was observed. Further results are shown in Figure 13 which compare the agglomeration of sulfidized pyrite in 10^{-3} M Na_2S with that in water both at pH 4.5 and at pH 10. These results indicate that at pH 4.5 there was less tendency for the sulfidized pyrite to agglomerate in 10^{-3} M Na_2S than

Figure 13. Effects of pH and Na_2S concentration on agglomeration of sulfidized pyrite.

Figure 14. Agglomeration recovery of degassed graphite.

in water, and at pH 10 the agglomeration of the material was suppressed completely by the sodium sulfide.

From the preceding results it is apparent that the surface of pyrite is rendered hydrophobic by treatment with a dilute sodium sulfide solution under acidic conditions. However, the concentration of sodium sulfide must be kept within very narrow limits. Once the sulfidized pyrite is removed from the treatment solution and resuspended in water it can be agglomerated with heptane over a wide range of pH. Interestingly, the agglomeration tendency of sulfidized pyrite is suppressed by sodium sulfide, particularly at high pH.

Agglomeration of Degassed Graphite

To determine the agglomeration characteristics of degassed and completely wetted graphite particles, a number of agglomeration experiments were conducted with graphite particles which were first suspended in water and degassed with a vacuum pump. Relatively pure graphite from Sri Lanka was ground with a high-speed impact mill and screened to provide -200/+325 mesh particles. An analysis of the particles with a Microtrac particle size analyzer produced the following size distribution:

<u>Size, μm</u>	<u>wt. %</u>
-176/+125	9.4
-125/+88	26.3
-88/+62	36.1
-62/+44	19.9
-44/+31	3.6
-31/+22	2.3
-22/+16	2.0
-16	0.4
	<u>100.0</u>

For each experiment 10.0 g graphite was suspended in enough water to nearly fill the 500 ml agglomeration vessel. The suspension was placed in a vacuum flask which was attached to a vacuum pump. The contents of the vessel were stirred with a magnetic stirring bar while the pressure was reduced to 110-120 mm Hg. After the suspension had been stirred for 10 min. under the reduced pressure, the system was returned to atmospheric pressure and the suspension was transferred to the agglomeration vessel. Sufficient water was added to completely fill the vessel. The vessel, which was fitted with the agitator from a 14-speed kitchen blender, was closed to prevent air from being mixed with the suspension. The suspension was conditioned for 5 min. by stirring at the lowest speed setting (8000 rpm). The agitation was interrupted and the required amount of n-heptane from Aldrich Chemical Co. was introduced with a hypodermic syringe. Agitation was then continued for another 5 min. at the lowest speed setting. The agglomerates were recovered on a 100 mesh screen, dried, and weighed.

Figure 14 shows the agglomeration recovery of the degassed graphite with various amounts of heptane. For the heptane range from 0 to 0.6 ml, the recovery was considerably lower than previously reported (ref. 7) for -325/+400 mesh graphite which had not been degassed with a vacuum pump after being ground in an impact mill. On the other hand, the recovery of the degassed graphite over the heptane range from 0 to 1.2 ml heptane was similar to that observed previously with wet, ball-milled graphite (ref. 1). However, the comparison is somewhat tenuous since the particle size distribution of the ball-milled graphite is unknown.

Figure 15 shows the effect of pH on the agglomeration recovery of degassed graphite with 8 v/w % heptane (0.8 ml heptane/10 g graphite). Also shown is the effect of pH on the measured induction time. For the induction time measurements, -140/+170 mesh particles were used. These were suspended in water and degassed with a vacuum pump as described above. Afterwards they were placed on a 170 mesh screen and washed to remove fines. The particles were resuspended in water and stirred for 10 min. The induction time was then determined as previously described (ref. 7).

The graphite suspension had a natural pH of 6 and at this pH the agglomeration recovery was about 60% with 8 v/w % heptane. Interestingly, the recovery increased when the pH of the suspension was either reduced below or increased above the natural pH. However, when the pH was increased above 10, the recovery decreased and continued to decrease with further increases in pH. This variation was not random in nature, since several of the experiments were closely duplicated. It seems likely that the variation in recovery was due to changes in the ionic strength of the suspension as hydrochloric acid was added to reduce the pH or sodium hydroxide was added to increase the pH. Although it had been shown previously that graphite recovery was enhanced by an increase in ionic strength (ref. 7), the levels of ionic strength which had been used to produce this effect were greater than those involved here. Therefore, additional agglomeration experiments were conducted to study the effect of ionic strength at very low levels. For this study the graphite was suspended in dilute salt solutions for degassing and agglomeration. The results presented in Figure 16 show that even very small concentrations of

Figure 15. Effect of pH on the agglomeration recovery and induction time of degassed graphite.

Figure 16. Effect of salt concentration or ionic strength on agglomeration recovery of degassed graphite.

sodium chloride affected the recovery of graphite significantly. An unexpected result was the minimum recovery observed in 0.04 M NaCl which was similar to the recovery observed when the graphite was suspended in deionized water. Why the recovery should increase below this salt concentration cannot be explained yet.

Returning to Figure 15 it can be seen that the induction time of the degassed graphite was unaffected by changes between pH 2 and 8. However, above this range the induction time increased with increasing pH. This trend seemed to reflect a decrease in hydrophobicity which was also reflected by the decrease in agglomeration recovery.

Kinetics of Agglomeration

The batch mixing system designed and built to study the kinetics of agglomeration using practical shear rates was described previously (ref. 6). One of the unique features of this system is a specially designed sampling tube for withdrawing samples while the system is in operation. To provide meaningful data the samples must be representative of the particle suspension undergoing agglomeration. Several experiments were conducted to determine whether or not the sampling system is capable of taking representative samples. The most recent experiment will be described. For conducting this experiment six discrete size fractions of silica particles were combined to provide a size distribution which would approximate an agglomerating suspension of coal particles. The actual size distribution of the silica particle mixture was determined by dry sieve analysis. The mixture was combined with water to produce a suspension with 20 wt. % solids which filled the 500 ml agglomeration

vessel. The vessel is equipped with a turbine agitator which was operated at 1100 rpm to produce a nearly 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 size distributions of the feed and the samples collected during the experiment are shown in Table 2. The mean particle size for each sample is also listed. It can be seen that there was little variation in the size distribution between samples in any given pair and no trend in the size distribution over time. There was also good agreement in the mean particle size between samples in any given pair and no obvious trend in mean particle size over time. These results indicate that the sampling system provided reproducible samples. Also the samples were representative since there was good agreement between the size distributions of the samples collected over time and the size distribution of the feed. Furthermore, removing a significant amount of material from the mixing vessel did not change the size distribution of the particles in suspension which shows that the sampling system did not exhibit a preference for a particular size of particle. The results further suggest that the suspension was well-mixed and uniform in composition.

Table 2. Size distributions of feed and samples of product collected at time indicated.

Size, μm	Feed	Size distribution, wt. %									
		5 min.		10 min.		15 min.		20 min.		25 min.	
		a	b	a	b	a	b	a	b	a	b
-1000/+710	14.95	14.40	13.93	12.26	12.71	13.96	13.21	13.60	12.58	13.30	13.16
-600/+425	25.83	29.18	28.19	28.50	26.50	27.27	27.13	24.32	25.44	25.09	24.95
-355/+250	30.71	31.20	32.29	32.40	31.43	32.83	32.02	31.13	30.98	31.92	32.26
-212/+150	13.38	13.55	13.45	14.25	14.61	13.66	13.86	14.87	15.26	14.65	14.40
-125/+90	9.90	6.72	6.51	6.70	7.87	7.49	7.89	8.83	8.60	8.57	9.17
-75/+38	5.23	4.95	5.63	5.90	6.88	4.78	5.89	7.25	7.14	6.45	6.06
<u>Mean particle size, μm</u>											
	411	420	414	404	396	412	404	393	390	396	395

SUMMARY

The heat of immersion of Illinois No. 6 coal was determined in various liquids at 25°C using different particle sizes. The liquids included water, methanol, heptane, and hexadecane. The heat of immersion was greatest in methanol and least in hexadecane. It was nearly the same in water and heptane. The heat of immersion per gram increased with decreasing particle size, whereas the heat of immersion per unit of external particle surface decreased with decreasing particle size. These results suggest that the heat of wetting is dependent on the internal pore surface as well as the external particle surface. The heat of immersion was also observed to decrease with increasing coal moisture content.

Pure mineral pyrite particles were treated with dilute solutions of sodium sulfide at various pH levels and agglomerated with heptane in aqueous suspensions. When the treatment was conducted in an acidic solution using a sodium sulfide concentration of approximately 4×10^{-4} M, the surface of the pyrite appeared to become very hydrophobic and responded readily to oil agglomeration. Moreover, when the treated pyrite was resuspended in water free of sodium sulfide, it responded to oil agglomeration over a wide range of pH. However, agglomeration of the treated pyrite was suppressed by somewhat higher concentrations of sodium sulfide, particularly at high pH. Therefore, sodium sulfide appeared capable of both activating and depressing pyrite depending upon the conditions of application.

Oil agglomeration characteristics were determined for suspensions of graphite particles in water which were degassed with a vacuum pump. The trend in graphite recovery with oil dosage appeared similar to that of

graphite which had been thoroughly wetted by grinding in a ball mill. Also the recovery was highly reproducible and was observed to vary significantly with the ionic strength of the suspending medium even at very low salt concentrations. Above pH 10 the recovery decreased appreciably with a further increase in pH. This decrease was matched by an increase in induction time.

Preliminary experiments were conducted to evaluate the mixing and sampling characteristics of the newly constructed batch mixing system for studying the kinetics of oil agglomeration. These indicate that the system is well-mixed and that representative and reproducible samples of the suspension can be obtained over time.

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12 / 11 / 90