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BASIC PRINCIPLES AND MECHANISMS OF SELECTIVE OIL AGGLOMERATION

Fossil Energy Interim Report

October 1, 1983 - September 30, 1992

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ABSTRACT

The overall objective of this investigation was to determine the basic principles and mechanisms which underlie selective oil agglomeration processes for beneficiating fine-size coal. The investigation focussed on the following key areas: (1) the relationship between particle recovery and various system parameters, (2) the separation of coal and pyrite, and (3) rate of agglomeration. Special laboratory equipment and experimental techniques were developed for studying particle agglomeration, including a method for continuously monitoring the progress of agglomeration in a batch mixing system by measuring the turbidity of the particle suspension. This method provided an indication of the rate of agglomeration. Since particle agglomeration depends on particle surface properties, several methods for measuring such properties were evaluated and found to yield comparable results.

Numerous agglomeration tests were conducted with several types of low-ash coal and graphite, high grade mineral pyrite, and other materials. Relatively pure hydrocarbons, including heptane and hexadecane, were used as agglomerants. Access of air to the system was controlled. Particle recovery by agglomeration was observed to depend on a number of system parameters. Among the most important parameters are the hydrophobicity of the particles and the oil dosage, so that the recovery of solids per unit of oil

administered is proportional to the hydrophobicity. The pH and ionic strength of the aqueous suspension affect particle recovery in different ways depending on the surface properties of the particles. On the other hand, the presence of air in the system generally improves particle recovery. The greatest effect of air was observed in a closely related study which showed that air had to be present to produce good agglomerates from a moderately hydrophobic coal in a mixer producing a lower shear rate.

The rate of agglomeration was found to be much greater for a strongly hydrophobic coal than for a moderately hydrophobic coal, and the rate was observed to be proportional to the oil dosage. Also the rate was enhanced by the presence of air in the system. For hydrophobic coals, the rate increased with increasing ionic strength of the aqueous medium, but it was not affected greatly by pH over a wide range.

The separation of coal and pyrite particles by selective agglomeration was found to depend on the relative hydrophobicity of the materials, the oil dosage, and the properties of the aqueous medium. Artificial mixtures of a hydrophobic coal and pyrite were separated successfully by suspending the materials in a basic solution and using a limited amount of oil. The separation was improved by increasing the ionic strength of the suspension or by adding a pyrite depressant. A number of pyrite depressants were identified and several were shown to improve the separation of coal and pyrite. One of the more promising depressants identified is thioglycolic acid.

TABLE OF CONTENTS

INTRODUCTION	1
DEVELOPMENT OF EXPERIMENTAL METHODS	4
Oil Agglomeration Methods	4
Surface Characterization Methods	6
SURFACE PROPERTIES AND OIL DOSAGE	8
Agglomerate Structure	9
Solids Recovery	10
Rate of Agglomeration	14
PROPERTIES OF THE SUSPENDING MEDIUM	16
Solution pH	16
Ionic Strength	17
Multivalent Cations	20
THE ROLE OF AIR	22
High Shear Rate Agglomeration	22
Related Work Based on a Lower Shear Rate	23
SEPARATION OF COAL AND PYRITE	25
Separation Difficulty	25
Pyrite Surface Properties	28
Pyrite Depressants	30
FURTHER CONSIDERATION OF SURFACE PROPERTIES	33
CONCLUSIONS	35
ACKNOWLEDGMENT	39
REFERENCES	40
APPENDIX	43

INTRODUCTION

A number of selective oil agglomeration processes have been proposed for cleaning fine-size coal in order to produce super clean coal with very low sulfur and ash contents.^a In these processes oil or a hydrocarbon liquid such as pentane or heptane is added to a vigorously agitated suspension of coal particles in water. The hydrophobic coal particles are selectively coated by the oil and stick together upon collision forming agglomerates, whereas the hydrophilic mineral particles are generally unaffected. Since relatively large agglomerates are produced, they can be separated from the other materials by floating, skimming, or screening.

Although the basic concepts underlying such processes have been known in the past, the scientific and engineering principles which control the agglomeration and separation of different materials have not been well understood, and technical development has followed a largely empirical course. Therefore, the commercial application of selective agglomeration processes has been more an art than a science. The present project was undertaken to remedy this situation with the overall objective being to determine the basic principles and mechanisms which underlie the selective oil agglomeration of fine-size coal.

To achieve the overall objective several key areas were identified which, from a review of the technical literature, appeared in need of serious study. The first area was the relationship between particle recovery by agglomeration and various system parameters such as particle surface hydrophobicity, oil properties, oil dosage, solution properties and

^a

C. E. Capes and R. J. Germain, "Selective Oil Agglomeration in Fine Coal Beneficiation," in: *Physical Cleaning of Coal, Present and Developing Methods*, Y. A. Liu (ed.), Marcel Dekker, New York, 1982, pp. 293-351.

presence or absence of air. The second area was the separation of coal and pyrite by selective agglomeration and its dependence on key system parameters. This area was closely related to the first area. The third area was the rate of agglomeration and its dependence on key system parameters. Although all of these areas were addressed subsequently, more consideration was given to the first two areas because more time was required to develop a method for measuring the rate of agglomeration than was required to develop methods for addressing the first two areas.

One of the first problems encountered was the lack of appropriate experimental techniques for studying the process of agglomeration and for characterizing the oleophilicity of coal and mineral particles. In the past, the process of agglomeration had been studied largely by using open kitchen blenders with no way of controlling air access. The blenders developed extremely high shear rates which were not typical of industrial practice, so equipment size scale up was difficult and unpredictable. Also, suitable equipment and methods were not available for investigating the rate of agglomeration. Furthermore, while it was known that particle agglomeration depends on the surface properties of the particles, it was not known whether conventional methods for assessing the hydrophobicity of solids were the most appropriate for characterizing particles in an oil agglomeration process.

Therefore, considerable effort was devoted to developing more suitable equipment and methods for investigating the process of agglomeration and to assessing certain methods for characterizing the surface of particles. The surface characterization methods

included techniques for measuring the three-phase contact angle, heat of wetting, infrared absorption spectrum, and induction time.

A rather basic approach was taken in this investigation in order to develop an understanding of fundamental process principles. Therefore, relatively pure materials were selected for most of the work, including several types of coal and graphite with a low ash content, high grade mineral pyrite, and other minerals which contained few impurities. Also, relatively pure hydrocarbon liquids including pentane, heptane, and hexadecane were used as agglomerants. By using these materials, the interpretation of experimental results was relatively straightforward. In the past, much of the work on oil agglomeration involved the use of complex materials and mixtures of hydrocarbons such as fuel oil or kerosene which were poorly characterized. Therefore, interpretation of results was very difficult and inaccurate. Also, in the present investigation, artificial mixtures of relatively pure solid components were used for studying the separation of different solids so the results would not be affected by incomplete liberation of one component from another.

After this investigation had been underway for several years, a closely related project was conducted under industrial sponsorship. This project made it possible to extend the study of particle agglomeration to a lower shear rate where the presence of air in the system was found to play a major role. Because of the close relationship between the two projects, the important results of the second project are included in this report.

Since most of the results of this investigation have been published in a series of technical papers, the present report provides only an extended summary of the results. The discussion that follows is keyed to the published papers which appear in the list of

references at the end of this report. The papers are included as an Appendix and may be consulted for further details.

DEVELOPMENT OF EXPERIMENTAL METHODS

Oil Agglomeration Methods

Special equipment and procedures were developed for investigating the oil agglomeration of coal particles in an aqueous suspension. To determine the yield of agglomerates with a given amount of oil, a special mixing unit was developed which utilized the base and agitator of a 14-speed kitchen blender and a 500 ml home canning jar which was nearly square in cross section (refs. 5,6). By inverting the jar and attaching it to the base, a closed mixing system was created from which air could be excluded. For most agglomeration tests, the jar was completely filled with an aqueous suspension of coal particles. Agitator speeds from 5000 to 20,000 rpm were used for these tests. For an agglomeration test, oil was injected with a syringe through a hole which had been drilled in the glass bottom of the jar. After coal particles had been agglomerated, the contents of the jar were poured onto a screen to recover the agglomerates. The agglomerates were subsequently dried in an oven, weighed, and analyzed.

Since the yield of agglomerates could not be measured directly, the overall recovery of agglomerates achieved by screening the treated suspension was used as a measure of the yield. The reported coal recovery was taken to be the ratio of the mass of dried agglomerates recovered to the initial mass of coal supplied on a dry basis.

Later, the mixing system was modified in order to provide a means for continuously monitoring the turbidity of a suspension undergoing agglomeration (ref. 8). A single

vertical baffle was attached to the inner surface of the jar and an external loop of tubing was added to convey the suspension from the jar to a photometric dispersion analyzer for measuring the turbidity. The suspension was then returned to the jar. This arrangement made it possible to monitor the turbidity of a suspension continuously as the particles were agglomerated. Since the turbidity was directly proportional to the concentration of unagglomerated fine particles, the rate of change of turbidity was indicative of the rate of agglomeration (ref. 1). Also the relative change in the turbidity of a suspension over a given time interval was proportional to the extent of agglomeration which had taken place. Therefore, it was possible to show that the coal recovery from an agglomeration test was directly proportional to the relative turbidity change (refs. 24,28). Since the relative turbidity change was indicative of the extent of agglomeration, it was possible to use the relative turbidity change as a measure of agglomeration performance when only one solid component was treated. This measure was more convenient and less time consuming than measuring solids recovery and was widely used for determining the effects of various parameters and for evaluating or measuring the effect or performance of agglomeration depressants.

By monitoring the turbidity of a particle suspension undergoing agglomeration, it was possible to determine the rate of change of turbidity which is indicative of the rate of agglomeration (ref. 1). Therefore, this technique was used to determine the effects of different parameters on the rate of agglomeration of specific types of coal.

For a closely related investigation of oil agglomeration at a lower shear rate, another specially designed closed mixing unit was developed and used (refs. 22,23,30). A jar

similar to the one used in the other mixing units was employed except that it had a vertical baffle located in each corner. Agitation was provided by a turbine impeller with six vertical flat blades, and the impeller was driven at 1800 rpm. Therefore, the mixing system was a better model of a large production unit. The system was connected to the photometric dispersion analyzer for monitoring turbidity, and the system was used to observe the rate of agglomeration and to determine the extent of agglomeration.

Surface Characterization Methods

Since the agglomeration process seemed to be highly dependent on the nature of the particle surface, various methods were employed to characterize the surface of coal particles and to determine whether the methods were equally effective for correlating agglomeration performance. These methods included procedures for measuring the zeta potential of particles in aqueous suspensions, heat of immersion of particles in water, induction time or bubble-particle attachment time, and the three-phase contact angle. Two different procedures were used for measuring the coal-oil-water contact angle. One procedure involved placing a captive drop of oil in contact with a polished, flat surface of coal submerged in water and measuring the three-phase contact angle with a goniometer. Another procedure was a modified suction potential method which involved drawing water, oil, and air in succession into a bed of coal particles and measuring the pressure drop across the bed. The contact angle was calculated by applying the Laplace equation to the pressure drop data. All of these surface characterization methods had been developed and applied previously by other workers. However, the suction potential method was modified and greatly improved (ref. 25). The modification involved changing both the

apparatus and procedure in a way that greatly reduced the time required for a single measurement and improved the reliability of the method.

Another surface characterization method, which was employed to a limited extent, involved measuring the infrared absorption spectrum of a coal surface and using the data to calculate the hydrophilicity index (refs. 28,29). This index is equal to the ratio of the relative concentration of hydrophilic oxygen functional groups on or near the coal surface to the relative concentration of hydrophobic aliphatic and aromatic CH groups.

Two of the surface characterization methods were compared by measuring the induction time and heat of immersion for different types of coal and graphite, which represented a wide range of surface properties (ref. 16). For this series of materials, an excellent linear correlation was found between the two surface characterization parameters with the heat of immersion increasing in direct proportion to the induction time. Graphite being the most hydrophobic material exhibited the smallest induction time, and Illinois No. 6 coal being the least hydrophobic exhibited the largest induction time. In addition, the recovery of the different materials by agglomeration with a given heptane dosage correlated very well with the induction time.

Other comparisons of surface characterization methods were made by applying the methods to a series of coal samples which had been subjected to various levels of surface oxidation, thereby altering the surface properties of the material over a relatively wide range. For one series of oxidized coal samples an excellent linear correlation was found between the heat of immersion and the hydrophilicity index (ref. 28). For another series of oxidized coal samples, an excellent linear correlation was obtained between the heat of

immersion and the cosine of the three-phase contact angle measured by the modified suction potential method (ref. 25). For this series, excellent linear correlations were also observed between the hydrophobicity index and either the heat of immersion or the cosine of the contact angle. In addition, coal recovery by agglomeration with a given hexadecane dosage increased in direct proportion to the contact angle measured through the water phase.

These comparisons of methods for characterizing the surface properties of particles indicated that the different methods produced consistent results which appeared to be equivalent. In other words, the results of each method correlated well with the results of every other method. Also, agglomeration performance seemed to correlate well with results produced by any of the surface characterization methods, so it was difficult to choose between the methods. However, values of the three-phase contact angle are necessary for theoretical calculation of forces involved in particle bonding.

SURFACE PROPERTIES AND OIL DOSAGE

Although a number of parameters were found to control the course of an oil agglomeration process, two of the most important parameters are the oil dosage and the hydrophobic or oleophilic character of the solid surfaces. These parameters, either together or in concert with other parameters, were observed to have a large influence on the size and structure of the agglomerates, the rate of agglomeration, the yield of recoverable agglomerates, and the particle separation efficiency. Initially, the observed effects of oil dosage and particle surface properties on agglomerate structure, product

yield, and agglomeration rate will be reviewed. Other effects involving additional parameters will be discussed in subsequent sections of the report.

Agglomerate Structure

Previous workers^a had observed that the structure of agglomerates produced from coal depended on the amount of oil used. This dependency was investigated further in the present study to include coal and other materials representing a wide range of surface properties (ref. 7). When small amounts of oil were applied to agitated suspensions of hydrophobic coal or graphite particles, bulky flocs were produced which were loosely held together by pendular bridges of oil. With larger amounts of oil, more compact aggregates were formed which involved funicular bridging. With still larger amounts of oil, very compact, spherical agglomerates were produced in the case of highly oleophilic particles of graphite and some types of coal, but not in the case of weakly oleophilic materials. In the pendular state, and to a lesser extent in the funicular state of particle aggregation, water was trapped within the flocs and agglomerates. Also, gas pockets were incorporated in the agglomerates when air was present in the system. When materials which formed compact spherical agglomerates were agglomerated with increasing amounts of oil above and beyond the minimum amount required to form spherical agglomerates, the result was to produce larger, uniformly sized agglomerates (refs. 6,7). Consequently, when graphite particles underwent spherical agglomeration with heptane, the agglomerate diameter increased exponentially with heptane dosage.

Mineral particles were also observed to form agglomerates, but the structure of the agglomerates was quite different from that noted above because the mineral particles

tended to collect around oil droplets and form bridges between the droplets (ref. 7). While forming such bridges, the particles also prevented the droplets from coalescing. Weakly oleophilic pyrite particles which collected at the oil-water interface tended to be partly submerged in each phase, whereas hydrophilic quartz particles which collected at the interface tended to be submerged almost entirely in the water phase. While pyrite aggregates could be recovered by screening, quartz or kaolin aggregates were too weak to be recovered by this method.

Solids Recovery

Although the recovery of solids from a suspension by agglomeration with oil and then screening was observed to depend on a number of different parameters, attention will be focussed initially on how recovery was affected by oil dosage, particle surface properties, and screen aperture size. In general, for materials which could be recovered by oil agglomeration, the recovery of solids, as a percent of the amount supplied initially, increased steadily with increasing oil dosage up to a point and then leveled off. For strongly hydrophobic materials, the maximum recovery approached 100% (refs. 5-7,26,27), and the principal effect of supplying excess oil was to increase the size of the agglomerates (refs. 6,7). For weakly hydrophobic materials, the maximum recovery was much lower, and when the optimum oil dosage was exceeded, the recovery decreased (ref. 27).

The rate of increase of solids recovery with respect to oil dosage was strongly dependent on the hydrophobicity and/or oleophilicity of the material. In one series of agglomeration tests with different materials (ref. 7), the rate of increase, expressed as

grams solids per gram of oil, varied directly with the oil-water-solid contact angle (θ_c) as follows: 14.5 g graphite/g oil ($\theta_c = 113^\circ$), 7.2 g Ill. No. 6 coal/g oil ($\theta_c = 105^\circ$), 0.5 g pyrite/g oil ($\theta_c = 85^\circ$), and 0 g quartz/g oil ($\theta_c = 20^\circ$). Since the receding contact angle was measured through the water phase by the captive droplet method using a flat, polished surface, it was a measure of the oleophilicity of the solid. Therefore, the rate of increase in recovery varied directly with the oleophilicity of the material.

In another series of agglomeration tests with different types of coal and graphite, the relationship between solids recovery and the hydrophobicity of the material was clearly demonstrated (ref. 16). The hydrophobicity of the materials was determined by measuring the induction time, i.e., the time required for a particle to become attached to a gas bubble when the bubble was brought in contact with a bed of particles submerged in water. It was shown previously that the more hydrophobic the material, the shorter the induction time. The series of agglomeration tests showed that for any given heptane dosage, the recovery decreased exponentially with increasing induction time. In other words, the recovery decreased with decreasing hydrophobicity of the solids. Also, for any given heptane dosage there was a critical induction time below which the recovery was nearly 100%. Thus, for a heptane dosage of 15 v/w % (i.e., 1.5 ml heptane/10 g solids) the recovery was essentially 100% for any material having an induction time under 2 ms.

The effect of particle surface characteristics on solids recovery was also studied by conducting several series of agglomeration tests using samples of coal which had been subjected to different levels of surface oxidation. The surface characteristics of the samples were determined by measuring either the heat of immersion in water, the three-

phase contact angle, or the infrared absorption spectrum. The latter was used to determine the hydrophilicity index of the material. For one series of agglomeration tests, different samples of sized Upper Freeport coal from Pennsylvania were oxidized by air at 150°C for periods ranging from a few hours up to 144 hr (ref. 26). When the different samples of coal were agglomerated with a given amount of heptane, there was a steady decrease in recovery with increasing time of oxidation. Also, since there was a similar decrease in the receding oil-water-coal contact angle measured through the water phase, the results showed that the recovery decreased as the oleophilicity of the coal was reduced by oxidation. Furthermore, it was found that while coal which had been oxidized for only a few hours formed relatively large spherical agglomerates when treated with heptane, after 50-60 hr of oxidation, the material would no longer produce spherical agglomerates. However, the material could still be agglomerated even after 144 hr of oxidation. By employing hexadecane instead of heptane, the critical oxidation time beyond which spherical agglomerates were not produced was extended to 100 hr.

For another series of agglomeration tests, samples of No. 2 Gas Seam coal from Illinois were oxidized in the same manner as described above (refs. 24,28). The surface of the samples was characterized by measuring the heat of immersion in water. The heat of immersion of the less hydrophobic Colchester coal was consistently higher than that of No. 2 Gas Seam coal. However, in both cases the heat of immersion of the coal increased rapidly during the initial 24 hr of oxidation and then only gradually as the time of oxidation was extended to 72 hr. Agglomeration performance was determined by measuring the turbidity of a suspension as the particles were agglomerated with increasing amounts of

heptane. The results showed that the extent of particle agglomeration decreased steadily with increasing heat of immersion and, therefore, decreasing hydrophobicity.

The recovery of agglomerates from a suspension by screening depended on both the size distribution of the agglomerates and the screen aperture size (ref. 7). Since the agglomerates were not all the same size in any given suspension, the recovery would increase as the screen mesh size was reduced. For spherical agglomerates which were relatively uniform in size, the change in recovery with respect to screen size was sharp, whereas with other types of agglomerates which were less uniform in size, the change in recovery with respect to screen size was gradual. This meant that uniform, spherical agglomerates could be recovered almost completely with a screen having openings which were much larger than the size of the unagglomerated particles, whereas achieving a large recovery of agglomerates having a wide size distribution required using a screen with openings that were not much larger than the size of the unagglomerated particles. Thus, it was much more difficult to achieve a good separation of agglomerations from unagglomerated fines in the case of materials which did not form spherical agglomerates. Interestingly, it was also observed that even in the case of uniform spherical agglomerates having a diameter in the range of 0.08 to 2.5 mm, agglomerates of a given size could be recovered almost completely by a screen having openings which were significantly larger than the agglomerates themselves. This suggests that the agglomerates tended to stick or clump together while being screened.

As a consequence of this work it became apparent that it would be much more difficult to clean a weakly hydrophobic coal than a strongly hydrophobic coal for several

reasons. While nearly uniform, easily recoverable, spherical agglomerates can be produced with a limited amount of oil from a strongly hydrophobic coal, only nonuniform, non-spherical agglomerates can be produced from a weakly hydrophobic coal and only by using much more oil. The recovery and separation of the nonuniform agglomerates would be more difficult for the reasons outlined above. Moreover, the bulkier flocs or aggregates produced from weakly hydrophobic coal would be much more likely to trap unwanted mineral particles during screening than the compact spherical agglomerates produced from strongly hydrophobic coal.

The preceding results suggested a need for some means of increasing the hydrophobicity of weakly hydrophobic coals. One method which was found involved suspending coal particles in a dilute solution of sodium oleate (ref. 26). By treating a heavily oxidized coal in this way, it became possible to produce spherical agglomerates using heptane as an agglomerant and conditions which otherwise would not have produced such agglomerates. Since only a very small concentration of sodium oleate (e.g., 2.5×10^{-4} M) was required and the treatment was most effective at pH 6.5, it appeared that the hydrophobicity of the coal was increased due to the adsorption of the acid-soap dimer $[(RCOO)_2H^-]$ of oleic acid. The principal disadvantage of the treatment is that it seems to be nonselective. Subsequent work showed that the agglomerability of pyrite particles was also greatly enhanced by sodium oleate (ref. 27).

Rate of Agglomeration

The rate of agglomeration of strongly hydrophobic No. 2 Gas Seam coal was determined by monitoring the rate of change of turbidity of a particle suspension after

introducing an appropriate amount of hexadecane (ref. 1). A closed mixing system was employed which used the agitator from a kitchen blender and from which air could be excluded. An agitator speed of 5500 rpm was used for agglomeration. Preliminary agglomeration tests showed that particle agglomeration started almost immediately when hexadecane was introduced and continued at a constant rate until most of the fines disappeared. Hence, the initial rate of agglomeration dominated the process. Subsequent tests showed that the initial rate of agglomeration depended on oil dosage as well as on how the coal was prepared. When the coal was prepared by dry grinding, the initial rate of agglomeration with any given oil dosage was considerably higher than when the coal was prepared by wet grinding. While the rate increased monotonically with increasing oil dosage for coal prepared by either method, the character of the relationship between the rate and the oil dosage differed for the coals prepared differently. For coal prepared by wet grinding, there was essentially a linear relationship between the rate and the oil dosage, whereas for coal prepared by dry grinding there was a more complex relationship.

At least part of the difference in results attributable to the coal preparation method was due to the presence of air on the surface of the dry ground coal even after the material had been suspended in water because vacuum degassing of the suspension reduced the initial rate of agglomeration. However, the rate for the degassed suspension was not as low as that for a suspension of wet ground coal. Part of the difference in results may have been due to the difference in particle size distributions because the dry ground coal was somewhat finer than the wet ground coal or because wet grinding did a better job of wetting surfaces than dry grinding and degassing.

In a related research project it was shown that for a given heptane dosage and with air present, the rate of agglomeration of highly hydrophobic No. 2 Gas Seam coal was much greater than that of moderately hydrophobic Colchester Seam coal (refs. 23,30). For this project, a lower shear rate was employed and air was essential for promoting the agglomeration of Colchester Seam coal. Nevertheless, the results indicated the strong dependence of agglomeration rate on coal surface properties.

PROPERTIES OF THE SUSPENDING MEDIUM

Both the pH and ionic strength of the medium in which particles are suspended for oil agglomeration were found to affect process performance, the extent of the effect depending on the nature of the particle surface and oil dosage. Also, the presence of certain multivalent cations was found to suppress coal agglomeration within certain pH ranges.

Solution pH

In most cases involving the agglomeration of unoxidized, moderately hydrophobic or highly hydrophobic coal with heptane in closed systems without visible air present, coal recovery was affected only slightly by changes in the pH of the suspension over a pH range of 3 to 11 (refs. 18,26). Generally the maximum recovery was achieved within a pH range of 6 to 8, and the maximum recovery seemed not to occur at the isoelectric point of the suspension. For pH values above or below the optimum value, the recovery was slightly lower. This effect was observed whether the coal was suspended either in water or a sodium chloride solution of moderate concentration (i.e., 0.5 to 1.5 M).

Interestingly, after the oleophilicity of Upper Freeport coal was reduced substantially by air oxidation at 150°C for 144 hr, the agglomerability of the coal was reduced and pH was found to exert a greater effect on coal recovery (ref. 26). Consequently when the pH was increased above 6, the recovery decreased markedly.

Another exception to the general trend was encountered when Illinois No.6 coal was agglomerated with heptane in an open system so air was present (ref. 32). The maximum recovery was achieved at pH 3.9 which corresponded to the isoelectric point. At either higher or lower pH levels, the recovery declined sharply.

The initial rate of agglomeration of two different types of coal with hexadecane was not affected greatly by pH over a wide range (ref. 2). For highly hydrophobic No. 2 Gas Seam coal the rate was a maximum at pH 9, but the rate decreased only slightly when the pH was reduced to 3 or increased to 12. For moderately hydrophobic Colchester Seam coal, the rate was a maximum at pH 3, and the rate declined only slightly when the pH was increased to 11. However, the rate dropped markedly when the pH was raised from 11 to 12.

Ionic Strength

In most cases the ionic strength of the particle suspending medium had a pronounced effect on agglomeration performance (refs. 14-16,32). For highly hydrophobic coals and graphite, an increase in ionic strength produced a major increase in coal recovery and caused a corresponding decrease in measured induction time. For example, an increase in salt concentration from 0 to 1.5 M caused the recovery of Upper Freeport coal with 3 v/w % heptane to rise from a level of 10% to a level of 72% and also caused the

induction time to fall from 1.96 ms to 1.58 ms (ref. 15). Similar changes were also produced with Pittsburgh coal following a similar increase in ionic strength (ref. 16). Furthermore, different salts produced much the same effect when compared at the same ionic strength, providing complexation of the ions was avoided (refs. 14,18).

It appeared that the underlying effect of increasing ionic strength is to compress the electrical double layer surrounding the individual particles in a suspension (refs. 14,16, 32). This in turn destabilizes the water film in contact with the solid, according to Laskowski and Iskra.^b Consequently, the water film is more easily ruptured between colliding particles and oil droplets or between oil-coated particles. In a similar way, the induction time is reduced because the water film between any given particle in contact with a gas bubble also is ruptured more easily.

Further support for the preceding theory was the evidence that an increase in the ionic strength of a suspension of Upper Freeport coal reduced the bulk volume of agglomerates made with a given heptane dosage (ref. 14). In other words, the agglomerates produced in 1.5 M sodium chloride were more compact than those produced in water.

For weakly hydrophobic coals and pyrite, the effects of increasing salt concentration on particle recovery and induction time were opposite to those noted above for strongly hydrophobic materials (refs. 14-16). Thus, for weakly hydrophobic Illinois No. 6 coal and pyrite the agglomeration recovery decreased and the induction time increased as the salt concentration rose. The results with these materials suggested that the materials were

^b J. Laskowski and J. Iskra, "Role of Capillary Effects in Bubble-Particle Collision in Flotation," *Transactions Institution Mining and Metallurgy, Sec. C, Mineral Processing and Extractive Metallurgy*, **79**, C6-C10 (1970).

made more hydrophilic and, therefore, less oleophilic through adsorption of hydrated sodium ions (ref. 16). In support of this suggestion was the evidence that Illinois No. 6 coal adsorbed a larger quantity of sodium ions than more highly hydrophobic Upper Freeport coal adsorbed. Also, pyrite is known to adsorb sodium ions.^c

The preceding results indicated that the separation of a highly hydrophobic coal from pyrite would be improved by suspending the materials in a salt solution for conducting the oil agglomeration process because the agglomeration of coal particles would be improved, whereas the agglomeration of the pyrite would be suppressed. The validity of this concept was demonstrated by conducting a series of oil agglomeration tests with a mixture of Upper Freeport coal and mineral pyrite suspended in either water or a salt solution (refs. 14,16). The results showed that as the salt concentration was increased from 0 to 1.5 M, coal recovery increased sharply and pyrite recovery dropped. Consequently, the separation efficiency increased greatly.

Furthermore, since an increase in ionic strength tended to suppress the recovery of weakly hydrophobic coals as well as pyrite, it was anticipated that the separation of a mixture of such coal and pyrite would not be improved by increasing the ionic strength. This indeed proved to be the case when a mixture of weakly hydrophobic Illinois No. 6 coal and pyrite was suspended in either water or a salt solution and agglomerated with heptane (ref. 16). As expected, the recovery of both coal and pyrite was reduced by an increase in ionic strength, and the separation efficiency suffered.

^c A. M. Gaudin and W. D. Charles, "Adsorption of Calcium and Sodium on Pyrite," *Transactions of AIME*, 196, 195-200 (1953).

Another case where an increase in ionic strength did prove advantageous was in the separation of a mixture of hydrophobic coal and kaolin particles (ref. 32). By suspending the mixture in 1.5 M sodium chloride and agglomerating the particles with 6 v/w % paraffin oil, 95% of the coal was recovered and over 90% of the kaolin was rejected. Coal recovery was 265% greater than that achieved when the mixture was suspended in water and agglomerated with the same amount of oil.

For either No. 2 Gas Seam coal or Colchester Seam coal, the initial rate of agglomeration with a given hexadecane dosage was increased by an increase in salt concentration (ref. 2). The increase in rate for a given increase in salt concentration was greater for No. 2 Gas Seam coal than for Colchester Seam coal. This difference can be related directly to the greater hydrophobicity of No. 2 Gas Seam coal. Thus, it appears that the more hydrophobic the material, the more beneficial an increase in ionic strength.

Multivalent Cations

The agglomeration recovery of both Upper Freeport coal and Illinois No. 6 coal was suppressed greatly by the presence of certain multivalent cations in the suspending medium providing the pH was at a corresponding level (ref. 18). The multivalent cations in question included calcium (II), magnesium (II), iron (III), and aluminum (III) ions. These cations are known to form positively charged metal hydroxy complexes at specific pH values.^d For example, the equilibrium concentration of the magnesium hydroxy

^d M. C. Fuerstenau and B. R. Palmer, "Anionic Flotation of Oxides and Silicates," in: *Flotation, A. M. Gaudin Memorial Volume*, M. C. Fuerstenau (ed.), AIME, New York (1976), pp. 148-196.

complex $\text{Mg}(\text{OH})^+$ in a dilute solution is a maximum at pH 10, and the maximum equilibrium concentrations of other metal hydroxy complexes occur at the following pH levels: $\text{Ca}(\text{OH})^+$ at pH 13, $\text{Al}(\text{OH})^{2+}$ at pH 5, and $\text{Fe}(\text{OH})^{2+}$ at pH 2.7. Adsorption of these complexes by Upper Freeport coal was indicated by measurement of the zeta potential of coal particles suspended in the different electrolytes over a wide range of pH. Thus, when coal particles were suspended in a dilute magnesium chloride solution, a particle charge reversal from negative to positive was observed at pH 10 indicating adsorption of $\text{Mg}(\text{OH})^+$ ions. Furthermore, when Upper Freeport coal was suspended in 0.5 M magnesium chloride and a series of agglomeration tests was conducted at different pH levels, a large recovery was achieved except for a narrow range of pH centered at about pH 10. Agglomeration suppression by any of the other multivalent cations was also observed to take place at a pH level corresponding to the pH where the cation was most likely to be present as a hydroxy complex. Therefore, the evidence strongly indicates that agglomeration of coal particles was suppressed by adsorption of the metal hydroxy complexes.

The recovery of acid-cleaned mineral pyrite by oil agglomeration was also suppressed by calcium and magnesium salts but in a manner which differed considerably from that noted above (ref. 18). The degree of suppression increased gradually as the pH was raised from a very acidic solution to a basic solution. The recovery became negligible at pH 9 in a 0.5 M magnesium chloride solution and at pH 11 in a 0.5 M calcium chloride solution. Over a wide range of pH, agglomeration was suppressed to a greater extent by the magnesium salt than by the calcium salt. Although agglomeration

may have been suppressed by the metal hydroxy complexes at high pH, the suppression observed at lower pH levels indicates adsorption of other species as well.

THE ROLE OF AIR

High Shear Rate Agglomeration

A large amount of evidence was accumulated which indicated that an oil agglomeration process can be affected markedly by the presence of air in the mixing system where agglomerates are produced. Initial agglomeration tests conducted with a closed mixing system from which air could be excluded showed that the presence of air in the system greatly increased the recovery of highly hydrophobic graphite with a limited amount of heptane (ref. 6). For one set of tests, the graphite was ground in a wet ball mill to insure that no air was introduced with the solids. The particles were agglomerated in a modified kitchen blender operated at about 20,000 rpm which resulted in an impeller tip speed of 47 m/s and a very high shear rate. With a heptane dosage of 6 v/w %, the recovery of graphite was 100% when 5% of the volume of the system was occupied by air, but the recovery of graphite was only 48% when no air was present. Microscopic examination of the agglomerates produced when air was present revealed the incorporation of air bubbles into the agglomerates. For another agglomeration test with a heptane dosage of 6 v/w %, graphite particles were prepared by dry grinding. After the particles were suspended in water and placed in the mixing unit, no air was visible and yet 100% of the graphite was recovered upon agglomeration. Therefore, it appeared that the particles retained a film of air which was as effective in promoting agglomeration as having a much larger volume of air present.

Further agglomeration tests were conducted with Illinois No. 6 coal which was much less hydrophobic than graphite (ref. 6). These tests showed that having air present in the agglomeration system increased coal recovery significantly when lower molecular weight alkanes such as pentane or heptane were employed, but not when higher molecular weight hydrocarbons such as hexadecane were used.

Somewhat different results were observed subsequently when highly hydrophobic No. 2 Gas Seam coal from West Virginia was agglomerated in a similar system operated at somewhat lower speed, i.e., 5500 rpm, resulting in an impeller tip speed of 13 m/s (ref. 1). Under such conditions, the presence of an air film on the surface of the particles increased both the rate and extent of agglomeration with a given amount of hexadecane. The difference between these results and those obtained with Illinois No. 6 coal could have been due either to a difference in coal properties or agitator speed or a combination of both.

Related Work Based on a Lower Shear Rate

Related work conducted with an agglomeration system which produced a lower shear rate than the system used for the preceding work also demonstrated the importance of having air present (refs. 22,23,30). For this work, a closed mixing system was used which had an agitator with a flat blade turbine impeller driven at 1800 rpm resulting in a tip speed of 5.4 m/s. Since the shear rate is proportional to tip speed, the shear rate produced by this system was only 11.5% of that produced by a kitchen blender operating at 20,000 rpm. Under the lower shear rate conditions, the presence of air in the system was essential for the agglomeration of moderately hydrophobic Colchester Seam coal from

Illinois with either heptane or hexadecane (refs. 22,23). Without air present, only loose assemblages of particles and flocs were produced by mixing the suspended coal with an agglomerant. However, with air present, compact, nearly spherical agglomerates were produced under otherwise similar conditions.

Photomicrographs made at different stages of the air-promoted process showed that aggregates composed of a few particles were formed first followed by the formation of larger, more extended assemblages of particles (ref. 23). Later these gave way to larger, compact, nearly spherical agglomerates. Midway during the process, a variety of particle structures was observed which ranged from loose, extended aggregations of particles to compact, nearly spherical agglomerates. At the mid point, numerous gas bubbles which were partly coated with particles and aggregates were also observed in the agglomeration milieu when heptane was used as an agglomerant. However, when hexadecane was used instead of heptane, no gas bubbles were observed among the recovered aggregates and agglomerates. Even though gas bubbles were not observed, having air present was as necessary for agglomerating Colchester coal with hexadecane as with heptane. With air present, the rate of agglomeration was proportional to oil dosage, and the rate appeared slightly higher with hexadecane than with heptane. When artificial mixtures of coal and kaolin were agglomerated, a good separation was achieved by using a relatively large oil dosage which resulted in a large coal recovery.

When the lower shear rate system was used for the agglomeration of highly hydrophobic No. 2 Gas Seam coal from West Virginia, it was found that air did not have to be present to produce compact, nearly spherical agglomerates (ref. 30). However, the rate of

agglomeration was much greater and larger agglomerates were produced with a given amount of oil when air was present. Also, having air present improved product quality and recovery. The effect of air was greater with small amounts of oil than with larger amounts.

These results indicate that by having air present it will be possible to greatly reduce the shear rate and power input to an agglomeration system and thereby improve the economics of the process.

SEPARATION OF COAL AND PYRITE

Separation Difficulty

To lay the foundation for the separation of coal and pyrite by selective agglomeration, an initial study was made of the separation of artificial mixtures of graphite and mineral pyrite (ref. 5). The results of agglomeration tests conducted with the individual materials showed that the agglomerability of the two materials differed greatly. When graphite was agglomerated with 3 v/w % heptane, the recovery was nearly 100%, but when pyrite was treated under similar conditions, the recovery was only 17%. This difference in agglomerability seemed related to the difference in the hydrophobic and/or oleophilic properties of the two materials as indicated by contact angle measurements on freshly polished flat surfaces. The equilibrium air-water-solid contact angle measured through the water phase was 60° for graphite and 46° for pyrite which indicated that the graphite was somewhat more hydrophobic than the pyrite. In addition, the receding oil-water-solid contact angle measured through the oil phase was 50° for graphite and 107° for pyrite, which showed that the graphite was considerably more oleophilic than the

pyrite. When mixtures of the two materials were agglomerated with small amounts of heptane, bulky graphite flocs were formed which entrapped pyrite. However, with larger amounts of heptane, compact spherical agglomerates of graphite were produced which were largely free of pyrite. Therefore, an excellent separation was achieved with 15 v/w % heptane.

In contrast to the ease with which graphite and pyrite were separated, the separation of coal and pyrite by selective agglomeration proved quite troublesome. An initial attempt to separate an artificial mixture of hydrophobic Upper Freeport coal and mineral pyrite by agglomeration with heptane was unsuccessful because both materials were recovered in large measure (ref. 27). Also, two different attempts to separate artificial mixtures of weakly hydrophobic Illinois No. 6 coal and mineral pyrite by agglomeration with heptane resulted in only partial separation with a higher recovery of pyrite than coal being realized (refs. 16,27). Eventually a good separation of an artificial mixture of Upper Freeport coal and mineral pyrite was achieved by suspending the mixture in a salt solution for agglomeration with heptane (refs. 14,16). This achievement has been discussed above in the section on Properties of the Suspending Medium.

To determine other conditions which favor the separation of coal and pyrite, additional agglomeration tests were conducted with artificial mixtures of Upper Freeport coal and mineral pyrite (ref. 17). Further tests were also conducted with mixtures of graphite and pyrite for comparison. In both cases, the surface of the pyrite particles had been oxidized by exposure to ambient air for several weeks. With both types of mixtures, the recovery of coal or graphite by agglomeration with heptane was generally large, while the

recovery of pyrite and, therefore, the separation efficiency varied with the pH of the suspension and the heptane dosage. The separation of graphite and pyrite was least affected by these parameters, probably because the surface properties of pyrite and graphite were greatly different under most conditions. Achieving a good separation of coal and pyrite required both suspending the particles in a basic solution and limiting the heptane dosage. Similar requirements also had to be met in order to separate graphite from acid-cleaned pyrite. Apparently, the hydrophobicity and/or oleophilicity of the acid-cleaned pyrite was sufficiently greater than that of the oxidized pyrite to limit the separation conditions. Therefore, it appeared that the surface properties of two materials had to differ appreciably in order to achieve a good separation.

To further evaluate the effect of the relative hydrophobicity of coal and pyrite on the separation of these materials, additional agglomeration tests were conducted with artificial mixtures of Colchester Seam coal from Illinois and mineral pyrite (ref. 13). As before, the surface of the pyrite had been oxidized by exposure to ambient air. The surface properties of the coal were varied by oxidizing the material with air at 150°C for either 8, 20, or 72 hr. When mixtures of the coal and pyrite were agglomerated with heptane, the relative recovery of the two components varied greatly, depending on the heptane dosage and the difference in hydrophobicity of the two components. Thus, when a mixture of unoxidized coal and pyrite was agglomerated, a good separation was achieved because the recovery of coal was much greater than the recovery of pyrite, apparently because the hydrophobicity of coal was much greater than that of the pyrite. However, as the coal surface became more heavily oxidized and less hydrophobic, the recovery of coal relative

to the recovery of pyrite decreased. Therefore, after the coal had been oxidized for 20 hr, the recovery of coal by agglomeration was nearly the same as the recovery of pyrite, and after the coal had been oxidized for 72 hr, the recovery of coal by agglomeration was less than the recovery of pyrite. Hence, which ever component was most hydrophobic was recovered in greatest amount.

Pyrite Surface Properties

From the preceding discussion it is apparent that mild oxidation can greatly reduce the hydrophobicity of coal. Oxidation can also affect the surface properties of pyrite greatly, but the results will vary depending on the balance between hydrophobic and hydrophilic oxidation products. While there has been considerable debate in the literature as to whether a pristine pyrite surface is hydrophobic, it is very doubtful that a pristine surface will ever be encountered in practice because a pyrite surface is oxidized so rapidly. Electrochemical measurements conducted with a pyrite electrode showed that the surface of freshly cleaved pyrite was oxidized in a deoxygenated, aqueous solution within a few minutes (ref. 3). Also, exposure of freshly ground pyrite particles to ambient air for a few hours produced a thin layer of iron sulfate on the surface of the particles (ref. 21).

Yoon et al.^c observed both hydrophobic and hydrophilic oxidation products on pyrite surfaces which had been oxidized in aqueous suspensions. The products believed

^c R.-H. Yoon, M. L. Lagno, G. H. Luttrell, and J. A. Mielczarski, "On the Hydrophobicity of Coal Pyrite," in: *Processing and Utilization of High-Sulfur Coals IV*, P. R. Dugan, D. R. Quigley, and Y. A. Attia (eds.), Elsevier, Amsterdam, 1991, pp. 241-253.

responsible for increasing the hydrophobicity of the pyrite were iron polysulfides, with the amount increasing as the pH decreased. The products believed responsible for making the pyrite more hydrophilic were iron oxides and hydroxides which increased with increasing pH.

In a review of previous work by others, Hayes *et al.*^f stated that in general, sulfide minerals can oxidize to produce a continuum of metal deficient sulfides with decreasing metal content which can range all the way to elemental sulfur. Of course, elemental sulfur is strongly hydrophobic. Additional oxidation beyond this state can produce thiosalts and ultimately sulfate ions and metal ions. The latter can readsorb on the mineral surface as hydrolysis products.

The results, which are the subject of the present report, are consistent with the preceding observations made by others. Thus, the surface of mineral pyrite which had been oxidized by prolonged exposure to air at ambient temperature appeared to be coated with a hydrophilic layer of oxidized material which was soluble in hydrochloric acid but only sparingly soluble in hot water (ref. 17). Subsequent FTIR measurements indicated that the oxidized material was probably iron sulfate (ref. 21). Zeta potential measurements indicated that the oxidized material was converted to ferric hydroxide when the pyrite was suspended in an aqueous solution of $\text{pH} \geq 4$ (ref. 17). When the oxidized pyrite was treated with hot hydrochloric acid, the hydrophilic layer was removed, and the pyrite became highly oleophilic since it was readily agglomerated with heptane. The acid-

^f R. A. Hayes, D. M. Price, J. Ralston, and R. W. Smith, "Collectorless Flotation of Sulphide Minerals," *Mineral Processing and Extractive Metallurgy Review*, 2, 203-234 (1987).

cleaned pyrite seemed to be coated with elemental sulfur since the coating appeared to be removed by acetone, a known solvent for sulfur. Furthermore, the zeta potential of acid-cleaned pyrite was nearly the same as that of sublimed sulfur over a wide range of pH. Since a fresh pyrite surface was observed to oxidize very rapidly in water (ref. 3), it is quite possible that a film of elemental sulfur was produced on the surface of the pyrite as the hydrophilic oxidation products were removed by acid.

Pyrite Depressants

Since it appeared that a film or coating of elemental sulfur probably accounts for the hydrophobicity which pyrite exhibits under certain conditions, a search was conducted for a material which would suppress the agglomeration of sulfur-coated pyrite. In order to test a number of potential pyrite depressants, a form of pyrite was required which is consistently hydrophobic and/or oleophilic. Such a form was obtained by treating pyrite particles with an acidified solution of sodium sulfide which seemed to deposit a coating of elemental sulfur (ref. 9). The presence of elemental sulfur was indicated by the appearance of colloidal particles of elemental sulfur in the treatment mixture, the strong agglomerability of the treated material in both basic and acid solutions, and the stability of the treated material. Thus, it was possible to dry and store the treated material for up to three weeks without affecting the agglomerability of the material noticeably. Also, the agglomerability of the treated pyrite was large enough so that it readily formed compact, spherical agglomerates which increased in size in proportion to the amount of heptane employed. This result indicated a highly oleophilic material, since it had been shown

previously that only the more oleophilic materials produced spherical agglomerates (ref. 7).

Further evidence that the treated pyrite was coated with elemental sulfur was obtained by subjecting the pyrite to microflotation tests (ref. 11). These tests were conducted without a collector or frother in a modified Hallimond tube, and they showed that the floatability of the treated pyrite was similar to that of elemental sulfur particles. Additional evidence of a sulfur coating on the treated pyrite was obtained by electrochemical measurements (ref. 4).

A number of potential pyrite depressants were tested using sulfurized pyrite prepared as described above. One of the materials tested was sodium sulfide applied in low concentrations (ref. 9). In a slightly acidic solution ($\text{pH} = 5.7$), a concentration of 0.01 M was required to suppress pyrite agglomeration. However, in a basic solution ($\text{pH} = 10$), a concentration of only 0.001 M was required to achieve the same effect. Other materials tested included a wide variety of oxidizing and reducing agents (refs. 10,28). Oxidizing agents which proved to be effective depressants included 0.003 M ferric chloride at $\text{pH} 2.6$, 0.10 M hydrogen peroxide at $\text{pH} 3.6$ to 8, and 0.003 M potassium monopersulfate at $\text{pH} 7.5$. Reducing agents which proved to be effective depressants included 0.01 M ferrous sulfate at $\text{pH} 6.5$, 0.003 M sodium dithionite at $\text{pH} 7.2$, 0.003 M sodium thiosulfate at $\text{pH} 9.2$, 0.003 M titanous chloride at $\text{pH} 1.7$, and 0.003 M pyrogallol at $\text{pH} 4.3$ to 8.1. Other materials which were found to be effective depressants included 5 mg/liter of quebracho at $\text{pH} 4.6$ to 7.9 and milk whey. Because such a small concentration was effective, quebracho seemed to be the most powerful depressant among the materials tested.

Among the preceding materials, ferric chloride was chosen for additional evaluation as a pyrite depressant by conducting a series of agglomeration tests involving the separation of artificial mixtures of Upper Freeport coal and sulfurized pyrite (ref. 10). In the absence of a depressant, both materials were highly hydrophobic and largely agglomerated by heptane so little separation was realized. However, by suspending the mixture in 0.002 M ferric chloride and applying a heptane dosage of 12.5 v/w %, a coal recovery of 94 % was achieved while rejecting 87% of the pyrite.

A search for additional pyrite depressants revealed a series of bifunctional organo-sulfur compounds which were very effective in suppressing the agglomeration of sulfurized pyrite with heptane (ref. 12). This series of compounds included thioglycolic acid, thiolactic acid, mercaptosuccinic acid, 3-mercaptopropionic acid, and 2-mercaptoethanesulfonic acid. Each of these materials contains both a sulfhydryl group ($-SH$) and either a carboxyl or sulfonic acid group. Each material applied in concentration of 0.003 M suppressed the agglomeration of sulfurized pyrite. Additional testing with thioglycolic acid showed that it was more effective in a basic solution than in an acidic solution and that it would suppress the agglomeration of sulfurized coal pyrite as well as sulfurized mineral pyrite. All of the materials improved the separation of artificial mixtures of Illinois No. 6 coal and sulfurized mineral pyrite, although the best separation was achieved when thioglycolic acid was used. Without a pyrite depressant, pyrite and coal were recovered equally well by agglomeration with heptane.

Supporting microflotation tests also showed that thioglycolic acid was a good pyrite depressant (ref. 4). These tests showed that mineral pyrite, which was nonfloatable in a

somewhat oxidized state, was readily floated by using diesel oil as a collector of after applying the sulfurizing treatment. With either approach, thioglycolic acid in concentrations of 0.001 M or greater was an effective pyrite depressant. When used with sulfurized pyrite, thioglycolic acid was a more effective depressant at pH 9.3 than at pH 4.6 and under oxidizing rather than reducing conditions.

Since thioglycolic acid showed exceptional promise as a pyrite depressant, additional research was conducted to acquire a better understanding of the interaction of thioglycolic acid with coal and pyrite (ref. 21). Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS) was used to study the adsorption of thioglycolic acid by freshly ground mineral pyrite, oxidized pyrite, sulfurized pyrite, elemental sulfur, and a low-ash coal from New Zealand. While freshly ground pyrite and coal adsorbed thioglycolic acid at pH 3, sulfur adsorbed thioglycolic acid only at pH 4.6 or higher. The adsorption of thioglycolic acid by either pyrite or sulfur seemed to involve the formation of a metal thioglycolate. Therefore, it was probably necessary for sodium ions to first be adsorbed by sulfur in order to form sodium thioglycolate. The adsorption of thioglycolic acid by coal involved a different mechanism, probably hydrogen bonding of the C=O group of thioglycolic acid to an -OH group on the coal surface or hydrogen bonding between the carboxyl group of thioglycolic acid and a carboxyl group on the surface.

FURTHER CONSIDERATION OF SURFACE PROPERTIES

Due to the importance of particle surface properties in the oil agglomeration process, further consideration was given to factors which predict and/or determine coal hydrophobicity. A statistical analysis of both published and unpublished data collected elsewhere

showed that there is a strong association between hydrophobicity and inherent coal moisture content (refs. 19,20). It was found that coal hydrophobicity correlates better with moisture content than with carbon content, and better with the moisture/carbon molar ratio than with the hydrogen/carbon or oxygen/carbon atomic ratios.

A review of the technical literature showed that hydrophobicity plays an important role in filtration and dewatering of coal particles (ref. 29). Generally, the greater the hydrophobicity of the coal, the easier it is to dewater. Since the presence of a film of oil on the surface of coal enhances the hydrophobicity of the material, it would also improve the dewaterability of the material. Consequently, coal which is recovered by an oil agglomeration process will be easier to dewater than it would have been otherwise.

For an oil-water-solid system, the contact angle has been expressed in the past as either the angle measured through the oil phase or the angle measured through the water phase. To avoid confusion and to facilitate communication in studies of oil agglomeration processes, Yang and Drzymala (ref. 31) recommended that the contact angle should always be expressed as the angle measured through the oil phase. In this way, the smaller the angle, the greater the tendency for oil to displace water from the surface of the solid. A contact angle of zero would correspond to complete displacement of water by oil and such a surface would be called "aqua-oleophilic" (meaning oleophilic in water). A contact angle of 180° would correspond to no displacement of water by oil and such a surface would be "aqua-oleophobic" (meaning oleophobic in water). Intermediate contact angles would correspond to various levels of "aqua-oleophilicity."

CONCLUSIONS

Improved laboratory equipment and procedures were developed for studying particle agglomeration with oil in aqueous suspensions. The equipment included a small high-speed mixing unit which was operated as a closed system to control air access, making it possible to admit or exclude air. The mixing unit was connected to a photometric dispersion analyzer so that the turbidity of a suspension undergoing agglomeration could be monitored continuously, which made it possible to obtain an indication of the rate of agglomeration as well as an indication of the extent of agglomeration over a given time interval or for a complete run. A lower speed mixing unit was also developed for a closely related project, and it was used to study agglomeration at a lower shear rate where the presence of air in the system had a very large effect.

An assessment of various methods for characterizing the surface of particles showed that the properties measured by several different methods correlated well with each other as well as with different measures of agglomeration performance. Thus, the extent of particle agglomeration achieved during an agglomeration test seemed to correlate equally well with either induction time, heat of immersion, hydrophilicity index, or the three-phase contact angle measured by a modified suction potential method.

A study of agglomerate structures produced by oil agglomeration showed that the structure of any given agglomerate depends on particle surface characteristics and oil dosage and in some cases on the ionic strength of the suspending medium, presence of air in the system, and shear rate. Agglomeration of coal or graphite suspensions at high shear rates with small amounts of oil produced open, bulky flocs which became more compact

when more oil was added. However, under such conditions, only the more hydrophobic materials were converted to compact spherical agglomerates with higher oil dosages. Also, an increase in ionic strength of the suspending medium resulted in greater compactness. In addition, the presence of air in the system facilitated the process of agglomeration, particularly at a lower shear rate. Thus, by having air present it was possible to produce compact, spherical agglomerates from a moderately hydrophobic coal at a moderate shear rate, whereas without air, only loose particle aggregations were produced.

Although mineral particles were agglomerated to some extent at high shear rates, the particles tended to collect around individual oil droplets and form bridges between droplets. Except for pyrite agglomerates, these structures were relatively weak and did not withstand screening.

The recovery of coal particles from a suspension by oil agglomeration and screening was highly dependent on the surface properties of the material, the oil dosage, and the screen aperture size. For materials having similar particle size distributions but differing in hydrophobicity, the recovery achieved with a given oil dosage increased with increasing particle hydrophobicity. This principle was demonstrated with graphite, pyrite, and different types of coal. It was also demonstrated by altering the hydrophobicity of particular types of coal through oxidation and then determining the response of the treated coal to oil agglomeration.

Particle recovery by oil agglomeration was also dependent on the properties of the suspending medium. For highly hydrophobic coals, the recovery was affected only

slightly by pH, whereas for oxidized and weakly hydrophobic coals, the recovery declined noticeably at higher pH levels. The recovery of strongly hydrophobic coals with a given oil dosage was enhanced considerably by increasing the ionic strength of the suspending medium. Conversely, the recovery of weakly hydrophobic coals and pyrite was reduced by increasing the ionic strength. These effects appeared to be due to compression of the electrical double layer surrounding individual particles in the case of strongly hydrophobic coals and to adsorption of hydrated cations in the case of weakly hydrophobic coals and pyrite.

Agglomeration of different types of coal and pyrite was suppressed by the presence in the suspending medium of certain multivalent cations which form metal hydroxy complexes at specific pH levels. Since coal agglomeration was suppressed at the specific pH levels where the complexes were most stable, there was a strong indication that suppression was due to adsorption of the complexes. In the case of pyrite, agglomeration was suppressed over a wide pH range, and the degree of suppression increased with increasing pH. Suppression appeared to be due to adsorption of other species in addition to the metal hydroxy complexes.

The presence of air in the mixing system promoted the oil agglomeration of coal and graphite particles, and even small amounts of air were effective. Thus even a thin film of air remaining on the surface of particles which had been prepared by dry grinding was sufficient to improve coal recovery. While air had a favorable effect on particle agglomeration over a wide range of shear rates, it proved absolutely essential for

agglomeration of moderately hydrophobic coal at a lower shear rate. This was demonstrated in a related project.

The rate of agglomeration of coal particles was observed to depend on the surface properties of the solids, oil dosage, properties of the aqueous medium, and presence of air. Strongly hydrophobic particles agglomerated much more rapidly than moderately hydrophobic particles, and the rate of agglomeration was proportional to the oil dosage. While the rate of agglomeration was affected only slightly by changes in pH over a wide range, the rate did decline noticeably between pH 11 and 12 for a moderately hydrophobic coal. An increase in the ionic strength of the aqueous medium produced a marked increase in the rate of agglomeration of highly hydrophobic coal but only a slight increase in the rate of agglomeration of a moderately hydrophobic coal. In a related project it was shown that at a lower shear rate the presence of air greatly increased the rate of agglomeration of a highly hydrophobic coal.

The separation of coal and pyrite particles by selective agglomeration was shown to depend on the relative hydrophobicity of the materials, the oil dosage, and the pH and ionic strength of the aqueous medium. The surface of pyrite was observed to oxidize rapidly at ambient temperature, producing oxidation products which ranged from hydrophobic to hydrophilic depending on the oxidation environment. In acidic solutions, oxidation seemed to leave a hydrophobic coating of elemental sulfur on the surface of pyrite which promoted agglomeration. Therefore, when pyrite was suspended in an acidic medium, it was likely to be recovered by oil agglomeration. Successful separation of artificial mixtures of coal and pyrite was achieved with hydrophobic coals, providing the

materials were suspended in a basic solution and agglomerated with a limited amount of oil. An increase in ionic strength of the solution also enhanced the separation. When mixtures of pyrite and an oxidized or weakly hydrophobic coal were agglomerated, both materials were agglomerated to some extent, and the recovery of pyrite generally exceeded the recovery of coal.

A number of pyrite depressants were identified which suppressed the oil agglomeration of sulfur coated or sulfurized pyrite. Several of these materials including ferric chloride and thioglycolic acid were also shown to improve the separation of artificial mixtures of coal and sulfurized pyrite. While thioglycolic acid adsorbed on both coal and pyrite, the adsorption mechanism differed for the two cases. Adsorption on pyrite seemed to involve the formation of a metal thioglycolate, whereas adsorption on coal probably involves hydrogen bonding.

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APPENDIX

Reprints of papers which are discussed in the main body of the report.

*Reprints and preprints
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