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DEVELOPMENT OF A GAS-PROMOTED OIL AGGLOMERATION PROCESS

Quarterly Technical Progress Report

July 1, 1995 - September 30, 1995

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ABSTRACT

The preliminary laboratory-scale development of a gas-promoted, oil agglomeration process for cleaning coal advanced in three major research areas. One area of research resulted in the development of a method for measuring the rate of agglomeration of dilute particle suspensions and using the method to relate the rate of agglomeration of coal particles to various key parameters. A second area of research led to the development of a method for monitoring a batch agglomeration process by measuring changes in agitator torque. With this method it was possible to show that the agglomeration of a concentrated coal particle suspension is triggered by the introduction of a small amount of gas. The method was also used in conjunction with optical microscopy to study the mechanism of agglomeration. A third area of research led to the discovery that highly hydrophobic particles in an aqueous suspension can be agglomerated by air alone.

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PURPOSE AND OBJECTIVES

The overall purpose of this research project is to carry out the preliminary laboratory-scale development of a gas-promoted, oil agglomeration process for cleaning coal using model mixing systems. Specific objectives include determining the nature of the gas promotion mechanism, the effects of hydrodynamic factors and key parameters on process performance, and a suitable basis for size scale-up of the mixing system.

INTRODUCTION

Several scale model mixing systems have been built for use in achieving the specific objectives. These systems are similar in design to the type of industrial mixing system which would probably be used for a full-scale commercial operation. The model systems are provided with instruments for measuring agitator speed and torque and for measuring the turbidity of dilute particle suspensions undergoing agglomeration. Numerous batch agglomeration tests have been conducted with these systems to study the mechanism and kinetics of the process and to determine the effects of several key parameters on process performance. It has been established that the progress of agglomeration can be monitored by observing either changes in agitator torque in the case of concentrated particle suspensions or changes in turbidity in the case of dilute suspensions.

During the past year the research has focussed on three major areas. One areas has been the kinetics of the gas-promoted, oil agglomeration process. This area has been investigated by using a theoretical model to relate the rate of agglomeration to the rate of change of turbidity of a dilute particle suspension undergoing agglomeration. The relationship between the rate of agglomeration and several key parameters has been determined.

A second area has been an investigation of the agglomeration mechanism and characteristics of concentrated particle suspensions. Changes which take place during agglomeration have been observed with an optical microscope and related to changes in measured agitator torque. The foundation for a thorough study of the effects of key parameters on process performance has been laid.

A third area has been a study of the agglomeration characteristics of hydrophobic particles which are bonded by gas alone. This study has provided further insight into the agglomeration mechanism.

The results achieved in each of these areas are described below.

WORK PERFORMED

Agglomeration Kinetics of Dilute Suspensions

Technical Basis: For analyzing the kinetics of agglomeration of coal particles, it was assumed that a batch agglomeration test would be conducted starting with a dilute suspension of monosize, spherical particles and that the growth mechanism would involve binary collisions between particles of equal size at each stage of growth as indicated in Figure 1. In order words, it was assumed that all agglomerates would grow at the same rate, and, therefore, at any given instant the suspension would be composed of monosize agglomerates. Furthermore, it was

Figure 1. Preliminary stages of a proposed model for representing the formation and growth of agglomerates.

assumed that due to compaction the density of each agglomerate would be essentially the same as that of coal. Consequently, the volume fraction of solids ϕ would remain constant during the process of agglomeration. For a suspension of monosize spherical particles, ϕ would be related to the particle number concentration N and the radius r of an individual particle as follows:

$$\phi = (4/3) \pi r^3 N \quad (1)$$

For an agglomeration process which produces compact, monosize, spherical agglomerates so that ϕ remains constant, the number concentration N of agglomerates of radius r at any instant would be related to the initial concentration N_0 of particles of radius r_0 as indicated below

$$(4/3) \pi r^3 N = (4/3) \pi r_0^3 N_0 \quad (2)$$

This equation reduces to:

$$N/N_0 = (r_0/r)^3 \quad (3)$$

For a dilute suspension of monosize, spherical particles such that the size of the particles is many times the wavelength of light, the turbidity τ of the suspension is related to particle size and concentration as follows:

$$\tau = 2 \pi r^2 N \quad (4)$$

The last two equations are combined to obtain the expression,

$$N/N_0 = (\tau/\tau_0)^3 \quad (5)$$

which relates the particle concentration N and suspension turbidity τ at any time to the initial concentration N_0 and turbidity τ_0 . Equation 5 is used to determine N from measured values of τ and τ_0 and the value of N_0 calculated by means of the expression,

$$N_0 = 3 m/4 \rho \pi r^3 V \quad (6)$$

where m is the total mass of particles, ρ is the particle density, and V is the volume of suspension.

Equation 5 is differentiated with respect to time to provide a means for obtaining the rate of change of particle concentration which is a measure of the rate of agglomeration.

$$\frac{dN}{dt} = \frac{3 N_0}{\tau_0^3} \tau^2 \frac{d\tau}{dt} \quad (7)$$

Equations 5 and 7 were modified to account for the fact that only the organic fraction of the coal particles tend to agglomerate. This required assuming that the initial number concentration of organic particles N_0' is related to the initial total number concentration of particles N_0 as follows:

$$N_0' = N_0 (1-X) \quad (8)$$

where X is the coal ash content. The modified expressions for determining the number concentration of agglomerates N' consisting only of organic particles and the rate of agglomeration of organic particles dN'/dt are shown below.

$$N' = (1-X) N_0 [(\tau - X\tau_0)/(1-X) \tau_0]^3 \quad (9)$$

$$\frac{dN'}{dt} = \frac{3 N_o (\tau - X\tau_o)^2}{(1-X)^2 \tau_o^3} \frac{d\tau}{dt} \quad (10)$$

Equation 9 was used for estimating the concentration of agglomerates and equation 10 for estimating the rate of agglomeration based on the measured turbidity.

The agglomeration model described above does not differ greatly from the modified Smoluchowski model for orthokinetic flocculation of spherical particles discussed by Gregory (ref. 1). According to classical Smoluchowski theory, the rate of flocculation of particles in a uniform shear field is controlled by the rate of collision between particles moving along parallel streamlines. The rate of flocculation was shown to depend on particle size and concentration as indicated below.

$$-\frac{dN}{dt} = \frac{16}{3} \alpha G r^3 N^2 \quad (11)$$

In this expression α is the collision efficiency and G is the uniform shear rate. If the volume fraction of particles ϕ remains constant during the process, the preceding equation reduces to,

$$-\frac{dN}{dt} = \frac{4}{\pi} \alpha \phi G N \quad (12)$$

Under such conditions flocculation appears to be a first order rate process with respect to particle concentration. For systems not having a uniform shear field and for turbulent flow conditions, G is replaced by a mean shear rate $\bar{G}$.

Since an actual agglomeration system would not be likely to satisfy all of the assumptions underlying the model described above, the more general and less restrictive rate equation shown below was used to represent the kinetics of agglomeration.

$$-\frac{dN'}{dt} = k(N')^\beta \quad (13)$$

In this equation k and β are empirical constants which are likely to depend on coal properties, oil properties and concentration, gas concentration, and the mean shear rate.

To determine k and β and how well equation 13 fit the results of an individual experiment, measured values of τ were first correlated with the corresponding values of t by employing a polynomial equation, usually 10th order. This equation was subsequently differentiated to obtain the rate of change of turbidity for various values of N , and equations 9 and 10 were then used to determine corresponding values of N' and dN'/dt . These values were used in turn to find k and β by applying linear regression analysis to the data. For this analysis equation 13 was converted to the following form:

$$\ln \left(-\frac{dN'}{dt} \right) = \ln k + \beta \ln N' \quad (14)$$

Experimental Method. Coal from the Pittsburgh No. 8 seam in Belmont County, Ohio, and coal from the Upper Freeport seam in Indiana County, Pennsylvania, were used for studying the kinetics of agglomeration. The first coal had an ash content of 28% and total sulfur content of 5% while the second coal had an ash content of 14% and total sulfur content of 2%, both on a dry basis. The first coal was much less hydrophobic than the second coal. After crushing, the coals were wet ground in a stirred ball mill and then stored as a wet paste until used. The weight mean particle size was $14.4 \mu\text{m}$ for the first coal and $12.7 \mu\text{m}$ for the second coal.

Agglomeration tests were carried out in a covered cylindrical tank with a flat bottom. The tank had an inside diameter of 15.24 cm (6.0 in.) and height of 15.24 cm (6.0 in.), and it was fitted with four vertical baffles and an agitator. The variable speed agitator was fitted with a 5.08 cm (2.0 in.) diameter, Rushton-type impeller which had six, vertical flat blades mounted on a horizontal disk located 2.54 cm (1.0 in.) above the bottom of the tank. An agitator control unit indicated both shaft speed and torque. The measured net volume of the tank fitted with baffles and an agitator was 2870 cm³ (0.101 ft³). The turbidity of a particle suspension was determined by continuously pumping a stream of material from the mixing tank through the measuring cell of a photometric dispersion analyzer (PDA 2000 built by Rank Brothers Ltd.) and back to the tank. Additional system details are provided in the previous annual report (ref. 2).

To prepare for an agglomeration test, a measured quantity of the previously prepared coal paste was combined with sufficient deionized water to completely fill the mixing tank. Next the agitator and peristaltic pump were operated to eliminate any air pockets. For conducting a run with a known amount of air present, a measured amount of water was withdrawn from the tank while a corresponding amount of air was admitted. The slurry was conditioned to produce a homogeneous state by operating the agitator for 3 min. at the planned operating speed. As agitation was continued, a measured amount of heptane or hexadecane was introduced quickly with a syringe. This marked the beginning of a run. As the run was continued, measurements of the turbidity were made at frequent intervals, and after 20 to 30 min. the run was discontinued.

Experimental Results. A number of batch agglomeration runs were made to study the effects of various parameters on the kinetics of agglomeration of the different types of coal. To demonstrate the importance of having some gas present in the system, several runs were conducted using suspensions of Pittsburgh coal particles which had been degassed first by subjecting the suspensions to a reduced pressure (50-100 mmHg absolute) for 20 min. The suspensions were then treated with no gas present in the mixing tank. The results of such a run are shown in Figure 2 together with the results of a run made with a suspension of coal which had not been degassed and to which had been added 20 cm³ of air. It can be seen that the turbidity of the degassed suspension decreased very slowly after heptane was introduced which indicated that the rate of agglomeration was very slow. In contrast the turbidity of the suspension which had not been degassed and which contained added air decreased rapidly indicating rapid agglomeration.

To determine the effects of added air dosage and particle concentration on the actual rate of agglomeration, two series of runs were conducted with suspensions of Pittsburgh coal which had not been degassed. For one series of five runs in which the initial particle concentration varied between 0.1% and 0.5% among runs, 20 cm³ of air was added to each suspension. For another series of three runs in which the initial particle concentration varied between 0.1% and 0.3% among runs, 50 cm³ of air was added. For each series the results were fitted by equation 14 to determine the empirical coefficients and the goodness of fit. Figure 3 indicates that in each case most of the data points fell on or close to the straight line determined by linear regression. For 20 cm³ of added air the line is represented by the equation,

$$\ln \left(- \frac{dN'}{dt} \right) = -2.17 + 1.37 \ln N' \quad (15)$$

Figure 2. Effect of air on rate of agglomeration of Pittsburgh coal. Conditions: 0.1 w/w% coal, 20 v/w% heptane, 1500 rpm.

Figure 3. Effects of varying initial particle concentration and added air on rate of agglomeration of Pittsburgh coal. Conditions: 0.1 - 0.5 w/w% coal, 20 v/w% heptane, 1500 rpm.

and for 50 cm³ of added air by,

$$\ln \left(-\frac{dN'}{dt} \right) = -0.40 + 1.28 \ln N' \quad (16)$$

Since the correlation coefficient R was 0.997 in the first case and 0.984 in the second case, an excellent correlation was achieved and the kinetics seemed to be well represented by a rate equation of the form of equation 13. A comparison of the results at the midrange of particle concentration showed that the rate of agglomeration was twice as great with 50 cm³ of air as with 20 cm³ of air.

To show the effect of heptane dosage on the rate of agglomeration of Pittsburgh coal, the results of runs made with 10 and 20 v/w% heptane are presented in Figure 4. Again the proposed rate equation fit the results well since a correlation coefficient greater than 0.99 was obtained in each case. The kinetic order was similar for the two cases, whereas the specific rate constant k was 1.69 times greater for the run made with 20 v/w% heptane as for the run made with 10 v/w%. While the rate of agglomeration between runs was affected by heptane concentration, the rate was apparently not affected significantly during a run because of changing heptane concentration. This result together with the apparent independence of the kinetic order on heptane concentration indicates that the rate of agglomeration was not controlled by the rate of collision between oil droplets and coal particles but more likely by the rate of collision between oil-coated particles or between coal aggregates and that the collision efficiency was increased by an increase in heptane dosage.

To show the effect of agitator speed on the rate of agglomeration of Pittsburgh coal, the results of runs made with different agitator speeds are presented in Figure 5. The results

Figure 4. Effect of heptane concentration on rate of agglomeration of Pittsburgh coal. Conditions: 0.1 w/w% coal, 20 v/w% heptane, 20 cm³ air, 1500 rpm.

Figure 5. Effect of agitator speed on rate of agglomeration of Pittsburgh coal. Conditions: 0.1 w/w% coal, 20 v/w% heptane, 20 cm³ air.

indicate that an increase in agitator speed from 1500 to 2100 rpm produced about a six fold increase in agglomeration rate. Since this is a much larger increase in the rate than the Smoluchowski theory would predict, an increase in shear rate must have had other beneficial effects besides increasing the collision rate between particles.

A number of runs were also made with Upper Freeport coal. The agglomeration of this material was also found to be promoted by a gas as can be seen by the results presented in Figure 6 for two series of runs made with 20 cm³ of added air and 50 cm³ of added air, respectively. The first series included eight runs with an initial particle concentration varying between 0.05 and 0.4% among runs, and the second series included three runs with an initial particle concentration varying between 0.1 and 0.24%. Application of linear regression analysis produced the following two equations for the first and second cases, respectively:

For 20 cm³ air:

$$\ln\left(-\frac{dN'}{dt}\right) = 0.78 + 1.23 \ln N' \quad (17)$$

For 50 cm³ of air:

$$\ln\left(-\frac{dN'}{dt}\right) = 1.00 + 1.24 \ln N' \quad (18)$$

Since the correlation coefficient R was 0.988 in the first case and 0.997 in the second case, the correlation was excellent. A comparison of the results at the midrange of particle concentration showed that the rate of agglomeration was increased approximately 40% by increasing the amount of air from 20 cm³ to 50 cm³. While this increase was not as large as that observed with the less hydrophobic Pittsburgh coal, it was still significant. It is noteworthy that the

Figure 6. Effects of varying initial particle concentration and added air on rate of agglomeration of Upper Freeport coal. Conditions: 0.05 - 0.4 w/w% coal, 20 v/w% heptane, 1500 rpm.

Figure 7. Effect of coal type on rate of agglomeration. Conditions: 0.1 - 0.3 w/w% coal, 20 v/w% heptane, 1500 rpm.

kinetic order was virtually the same for the two cases and very similar to that observed for Pittsburgh coal with 50 cm³ of air (see equation 16).

A comparison of the results achieved with the two types of coal is presented in Figure 7 for the case involving 50 cm³ of air to promote agglomeration. The lines on this graph correspond to equations 16 and 18 for Pittsburgh coal and Upper Freeport coal, respectively. The rate of agglomeration of Upper Freeport coal was about 2.5 times greater than that of Pittsburgh coal for a particle number concentration corresponding to $\ln N' = 12$. The difference in the rate of agglomeration was due most likely to the difference in the hydrophobicity of the two types of coal.

To see how the rate of agglomeration of Upper Freeport coal was affected by the properties of the agglomerant, the results of runs made with heptane and hexadecane are compared in Figure 8. For the given conditions the rate of agglomeration with hexadecane was approximately half that with heptane at a particle number concentration corresponding to $\ln N' = 12$. This difference may have been due to the larger viscosity of the hexadecane which made it more difficult to disperse. This possibility was supported by another run in which the hexadecane was emulsified first by treating a mixture of the hydrocarbon and water with a high-speed blender before adding it to the coal suspension. The results are shown in Figure 9 together with the results obtained without first emulsifying the hexadecane. As a consequence of emulsification, the rate of agglomeration was increased almost fourfold for $\ln N' = 12$. Since emulsification was carried out in an open blender, it is quite likely that some air was incorporated in the oil in water emulsion which also enhanced the rate of agglomeration.

Figure 8. Effect of oil type on rate of agglomeration of Upper Freeport coal. Conditions: 0.1 w/w% coal, 20 v/w% oil, 20 cm³ air, 1500 rpm.

Figure 9. Effect of emulsifying hexadecane before use on rate of agglomeration of Upper Freeport coal. Conditions: 0.1 w/w% coal, 20 v/w% oil, 20 cm³ air, 1500 rpm.

Conclusions. The semiempirical rate equation which was used for correlating and analyzing the results of batch agglomeration tests provided an adequate representation of the kinetic data collected during most individual runs or a series of runs made with different initial particle concentrations. In most cases the kinetic order with respect to particle concentration was between 1.0 and 1.3 which was fairly consistent with the assumptions underlying the proposed mechanism and measurement technique. The rate of agglomeration seemed to be controlled by the rate of collision between oil-coated particles or between coal aggregates rather than between oil droplets and coal particles. The rate of agglomeration increased as more air was added to the system or as the agglomerant concentration or agitator speed was increased. The rate was also greater for the more hydrophobic Upper Freeport coal than for the less hydrophobic Pittsburgh No. 8 coal. In addition, a greater rate was achieved with heptane than with hexadecane. The rate achieved with hexadecane was enhanced considerably by first emulsifying the material.

Agglomeration of Concentrated Suspensions

A number of batch experiments were conducted in which the agglomeration of concentrated particle suspensions of Pittsburgh No. 8 coal was monitored by continuous measurement of agitator torque. Two different mixing tanks were employed which were smaller but similar in design to the one described above. One tank had an inside diameter of 7.62 cm (3.00 in.) while another tank had an inside diameter of 11.4 cm (4.50 in.). In each case the inside height of the tank was equal to the diameter of the tank. Also each tank was fitted with four vertical baffles which projected inward a distance equal to 0.083 times the diameter of the tank. Each tank was constructed entirely of Plexiglas and each tank was fitted with an agitator which employed a

standard Rushton-type turbine impeller. A variable speed, agitator drive system was used which provided an indication of both speed and torque. Additional details are provided in a previous report (ref. 2).

The coal was prepared as described above by grinding a concentrated slurry of the material with a stirred ball mill and then removing most of the water to form a thick paste. For each agglomeration experiment one of the mixing tanks was half filled with previously degassed water and a measured quantity of coal paste was introduced. The mixture was stirred slowly by hand to expel any trapped air bubbles. Degassed water was then added to completely fill the tank, and the agitator was operated slowly for several minutes to fully disperse the coal. All of the water used for preparing the coal slurry was degassed first by applying a vacuum corresponding to -95 kPa for approximately 20 min. When the speed was increased to a predetermined value, the measurement of agitator torque started. Values of agitator torque indicated by the uncalibrated instrument were recorded and are presented below. After about 15 min., the agglomerant was added slowly using a syringe fitted with a long needle so that the material was introduced just above the rotating impeller. After a predetermined interval, a known amount of air was introduced just above the impeller with a long needle attached to a syringe. The measurement of agitator torque was continued until the greatest changes in torque had taken place.

For an initial agglomeration experiment, a mixing tank having a diameter of 11.4 cm (4.50 in.) was filled with a coal suspension having a solids concentration of 32 wt.%, and the suspension was stirred at 1700 rpm with a 5.08 cm (2.00 in.) diameter impeller located 1.9 cm (0.75 in.) above the bottom of the tank. Sufficient heptane was introduced to provide a

concentration of 30 v/w% based on the weight of dry solids. About 10 min. later, 20 ml of air was introduced. As the run progressed the agitator torque varied as shown in Figure 10. Before the heptane was introduced the agitator torque was 1450 g·cm, and after heptane was added the torque decreased quickly to about 1300 g·cm. The torque then varied only slightly until 20 ml of air was introduced just above the impeller. At this point the torque decreased quickly to 1225 g·cm and then increased rapidly at first and then more gradually. The torque peaked at 1525 g·cm and then decreased slightly. The rapid changes which occurred following the introduction of air seemed to be a manifestation of particle agglomeration. Subsequent examination of the product with an optical microscope revealed mainly uniform, compact spherical agglomerates having a diameter of 2.0 - 2.7 mm.

For another experiment the mixing tank was filled with degassed water, and while the water was agitated at 1700 rpm, the same amounts of heptane and air were introduced as before. Following the additions of heptane and air, the torque decreased as before (Figure 10). However, after the second drop in torque, the torque recovered only slightly with continued stirring. Therefore, it was apparent that with no coal present and no particle agglomeration, the change in agitator torque was minor. Consequently the large increase in agitator torque following the addition of air in the previous experiment had to be due to agglomerate building.

To see whether the addition of air to the system triggered the process of agglomeration, additional experiments were conducted in which the time between the addition of heptane and the addition of air was varied from 2.5 to 15 min. The results shown in Figure 11 indicate that the large and pronounced increase in agitator torque due to agglomerate building did not take

Figure 10. Changes in agitator torque resulting from the addition of heptane and air to a concentrated Pittsburgh No. 8 coal slurry and to pure water.

Figure 11. Effect of delaying the time of air introduction into a concentrated Pittsburgh No. 8 coal slurry which had been dosed with heptane.

place until after air was injected. Therefore, the process of agglomeration had to be triggered by air.

Further experiments were conducted to study the effects of mixing tank size and impeller size and speed on the kinetics of agglomeration. For these experiments the impeller was located at midheight of the tank. Ground Pittsburgh No. 8 coal in 30 wt.% concentration was used together with i-octane in 20 v/w% concentration as an agglomerant.

For one set of runs the same mixing tank (i.e., 11.4 cm diameter) and same impeller (i.e., 5.08 cm diameter) were used as in the previous experiments, but the amount of air introduced in each run was somewhat greater, being 34.2 ml, and i-octane was used as an agglomerant. Three runs were conducted using agitator speeds of 1300, 1750, and 2400 rpm, respectively. Since agitator torque was affected greatly by speed, it was necessary to plot the logarithm of torque (T) in order to present the results of the three runs on the same graph (Figure 12). Because the vertical scale is compressed, the changes in torque which accompanied agglomeration are not so obvious as for the previous experiments. Nevertheless, it can be seen that the torque decreased immediately following the addition of air and later increased as agglomerate building took place. The time between those two events increased markedly as agitator speed was reduced. Consequently, at 1300 rpm the torque did not increase significantly until 135 min. had elapsed following the injection of air. Even at 1750 rpm there was a delay of about 10 min. before torque increased. This delay was noticeably longer than that indicated by Figures 10 and 11 for the experiments conducted at 1700 rpm with a larger concentration of agglomerant (i.e., 30 v/w% heptane). However, part of the delay may have been due to the

Figure 12. Results of agglomerating 30 wt.% Pittsburgh coal with 20 v/w% i-octane and 34.2 ml air in 11.4 cm diameter tank with 5.08 cm diameter impeller.

Figure 13. Results of agglomerating 30 wt.% Pittsburgh coal with 20 v/w% i-octane and 10 ml air in 7.62 cm diameter tank with 5.08 cm diameter impeller.

method of introducing air in this particular run. For this run alone, air was introduced by withdrawing a measured amount of slurry and allowing air to enter the mixing tank around the agitator shaft. Therefore, it probably took longer for the air to be dispersed than for the other runs in which air was injected just above the impeller.

The results presented in Figure 12 are also noteworthy because in each case the final torque was similar to the initial torque before air was introduced. This was in contrast to the results presented in Figures 10 and 11 where the final torque was noticeably greater than the initial torque. The difference could have been due to the difference in agglomerant concentration which caused larger agglomerates to be produced in the earlier experiments than in the later runs.

For another set of runs a smaller mixing tank (i.e., 7.62 cm diameter) and the same size impeller (i.e., 5.08 cm) were used as for the preceding runs. While the coal and agglomerant concentrations were the same as for the last set, the amount of air was reduced to 10 ml for each run in this set to keep the air:coal ratio constant. Although the results presented in Figure 13 were generally similar to those observed previously, the increase in torque due to agglomerate building was somewhat larger than indicated by the last set. Also for a speed of 1750 rpm the interval between the time of air addition and agglomerate building was 5 min. instead of the 10 min. noted in the last set.

For the final set of runs a smaller impeller (i.e., 3.81 cm diameter) was used in the smaller mixing tank. The amount of air and other conditions were the same as for the preceding set. Again the results (Figure 14) were generally similar to the previous results. However, the increase in agitator torque due to agglomerate building was greater on a relative scale at both

Figure 14. Results of agglomerating 30 wt.% Pittsburgh coal with 20 v/w% i-octane and 10 ml air in 7.62 diameter tank with 3.81 cm diameter impeller.

2000 and 2400 rpm than indicated by the preceding set. Also at these speeds the interval between the time of air addition and agglomerate building was longer than for the preceding set.

Subsequent examination of the coal particle suspensions with an optical microscope at various stages of the agglomeration process showed that after air was introduced and during the initial stage of agglomeration, microagglomerates and flocs were produced while agitator torque remained relatively constant. By the time the torque started to increase markedly, all of the individual coal particles appeared to have been incorporated into large flocs and unconsolidated agglomerates. As these particle aggregations were converted into more consolidated and nearly spherical agglomerates, the torque rose rapidly.

Except for the highest agitator speed (i.e., 2400 rpm), the time required for the initial stage of agglomeration was greater than the time required for converting the large flocs and unconsolidated agglomerates into compact, spherical agglomerates. Furthermore, the initial agglomeration time appeared to depend strongly on agglomerant concentration and impeller diameter and speed. It was apparent that the time was reduced by an increase in agglomerant concentration or an increase in agitator speed, but the exact nature of these relationships remain to be worked out. Nevertheless a procedure has been developed for measuring the time required for the initial stage of agglomeration and relating this time to key parameters.

Air Agglomeration of Hydrophobic Solids

While attempting to wet and disperse dry particles of highly hydrophobic materials in water, it was discovered that the process of wetting was facilitated greatly by vacuum degassing of the mixture of particles and water. Therefore, it was reasoned that once dispersed in water, such particles would have a tendency to collect at an air-water interface, if a gas were dispersed in the liquid, which could in turn lead to the formation of air bridges between particles similar to the oil bridges between particles in oil agglomeration.

To investigate this concept a series of experiments was carried out in which aqueous suspensions of various hydrophobic solids were prepared by degassing and agitation, and then air was introduced in a series of small increments into the agitated suspensions. Evidence of particle agglomeration was obtained by observing the change in turbidity of a given suspension and by examining the product with an optical microscope.

Hydrophobic Materials. The hydrophobic solids included Teflon powder, flowers of sulfur, and finely ground gilsonite, Ceylon graphite, and Pittsburgh No. 8 coal. The source, type of

preparation, and particle size of each material are indicated in Table 1. The Teflon powder was designated by the manufacturer as No. 8 compression molding resin, and it consisted of potato-shaped pellets which ranged from 0.1 to 1.0 mm in size.

The hydrophobicity of the different materials was evaluated by measuring the three-phase, air/water/solid contact angle using the captive bubble measurement technique. A small air bubble was brought in contact with a flat, polished surface of the material under water, and both the water advancing and water receding contact angles were measured with a goniometer. The results of these measurements are shown in Table 2. Since Teflon exhibited the largest contact angle, it was the most hydrophobic material and, therefore, the most difficult to wet. The hydrophobicity of graphite was found to depend on whether it was prepared by dry polishing or wet polishing. The dry polished material may have been more hydrophobic than the wet polished material because of the presence of air in pores, cracks, and crevices. Although clean, wet polished Pittsburgh No. 8 coal was moderately hydrophobic with an average contact angle of 41° , it became completely hydrophilic when the polished surface was exposed first to a suspension of finely ground coal which apparently left a slime coating on the surface.

Agglomeration Tests. To prepare a suspension for agglomeration, a measured quantity of dry particles and 2800 cm^3 of water were placed in the 15.24 cm (6.00 in.) diameter mixing tank described above. The tank was sealed and connected to a vacuum pump. The suspension was degassed by applying a vacuum corresponding to -95 kPa for 20 min., and then the tank was topped off with previously degassed water. The suspension containing 1-2% solids was conditioned for 2 min. by operating the agitator at 2400 rpm. As agitation was continued, air was introduced in a series of measured increments, and the progress of agglomeration was

Table 1. Materials used for air agglomeration

Material	Source	Preparation	Size, mm
Teflon	Dupont Co.	None	0.575
Gilsonite	Uinta Basin	Dry grinding	<0.180
Sulfur	Fisher Scientific	None	<0.038
Graphite	Ceylon	Dry grinding	<0.038
Coal*	Pitts. No. 8 Seam	Wet grinding	0.010

*hvAB, 27% ash, 5% S

Table 2. The three-phase contact angle of different materials

Material	Contact Angle			Remarks
	θ_A	θ_R	θ_{AV}	
Teflon	109°	86°	98°	Cleaned/Not polished
Gilsonite	89°	43°	66°	Wet Polished
Sulfur	85°	45°	65°	Wet Polished
Graphite	81°	42°	61°	Dry Polished
Graphite	13°	13°	13°	Wet Polished
Pitts. Coal	58°	25°	41°	Wet Polished
Pitts. Coal	0	0	0	Slime Coated

Figure 15. Results of air agglomeration tests of different hydrophobic materials.

monitored by observing changes in the turbidity of the system. The relative turbidity change ($\Delta\tau_r$) in percent defined below was used as a measure of the extent of particle agglomeration.

$$\Delta\tau_r = \left[\frac{(\tau_o - \tau)}{\tau_o} \right] 100 \quad (19)$$

In this expression τ_o represents the initial turbidity of the unagglomerated suspension and τ represents the turbidity after agglomeration has taken place. It is apparent that as agglomeration takes place the relative turbidity change will increase while the absolute turbidity decreases.

The results of the series of agglomeration experiments conducted with different hydrophobic solids are shown in Figure 15. It can be seen that for each material except untreated Pittsburgh

No. 8 coal the relative turbidity change of the corresponding suspension increased as more air was introduced. Therefore, except for the untreated coal, air promoted the agglomeration of the various materials. Apparently the hydrophobicity of the untreated coal was insufficient to cause agglomeration. However, it was found that by preconditioning the coal with a small amount of heptane, the material responded to air agglomeration in the same way as the other hydrophobic solids responded. The slope of each line plotted in Figure 15 seemed to be proportional to the hydrophobicity of the corresponding material as indicated by its three-phase contact angle.

When samples of the Teflon particle suspension which had been treated with air were examined with an optical microscope, numerous particle aggregates or agglomerates were observed. The nature of the particle bonding was not apparent because there were no obvious air bubbles or air bridges between particles. However, when the sample was warmed gently by the light applied to view the sample with the microscope, air was expelled from within the agglomerates causes gas bubbles to appear on the surface of the agglomerates.

The treatment of gilsonite particles, which were considerably smaller and less hydrophobic than the Teflon particles, produced aggregates of particles which differed from those observed with Teflon. The gilsonite particles either tended to coat the surface and stabilize the somewhat larger gas bubbles or to form small and rather loose clusters or flocs which often appeared to be associated with smaller gas bubbles.

The treatment of even less hydrophobic materials such as graphite did not produce particle aggregations which were sufficiently stable to recover and view later with a microscope.

Bonding Mechanism. While the nature of the bonding mechanism which holds hydrophobic particles together in water has not been established with certainty, one of the possible binding

Figure 16. An idealized bridge formed by an air bubble confined between two flat particles immersed in water.

forces may be due to the interfacial tension between air and water. If an air bubble is introduced between two parallel flat plates which are made of a hydrophobic material and are submerged in water as shown in Figure 16, the force f due to interfacial tension which pulls the plates towards each other is given by the equation,

$$f = 2 \gamma p \sin \theta \quad (20)$$

where γ is the air-water interfacial tension, p is the perimeter of the circle of contact of the three phases on the solid surface, and θ is the three-phase contact angle. The same expression has been proposed to account for bonding of two hydrophobic coal particles by an oil bridge (ref. 3). Substitution of typical values for γ and θ in equation 20 indicates that the bonding force (f/p) would be similar in magnitude for an air bridge as for an oil bridge.

Conclusions. By treating degassed suspensions of various types of hydrophobic particles in water with increasing amounts of air while employing vigorous agitation, it was shown that

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Conclusions. By treating degassed suspensions of various types of hydrophobic particles in water with increasing amounts of air while employing vigorous agitation, it was shown that

particle aggregation or agglomeration was promoted by the addition of air. The extent of aggregation was proportional to the amount of air introduced per gram of solids, and it was also proportional to the hydrophobicity of the solids as indicated by the air/water/solid contact angle. In the case of coarse Teflon particles, relatively large agglomerates were produced which may have been held together by air bridges between particles. A model for this type of bonding is presented which is similar to a model proposed previously for explaining the bonding of oil agglomerated coal particles. In the case of other hydrophobic materials which were small in size compared to the size of gas bubbles, the particles tended to coat the surface of the gas bubbles and to form loose clusters or flocs which were associated with small gas bubbles.

OVERALL CONCLUSIONS

Detailed conclusions resulting from the main areas of research discussed above have been listed at the end of each section. It is apparent that the research produced several major achievements. One important achievement was the development of a method for measuring the rate of agglomeration of dilute particle suspensions and using this method to relate the rate of agglomeration of coal particles to various key parameters such as particle concentration, oil dosage, agitator speed, and the amount of gas present. Another important achievement was showing that agitator torque can be used to monitor the agglomeration of concentrated suspensions and then showing that the process of agglomeration is triggered by introducing a small amount of gas. A third important achievement was showing that highly hydrophobic particles can be agglomerated by air alone and that the mechanism of air agglomeration may be similar to that of oil agglomeration.

FUTURE PLANS

Further research will be conducted with concentrated particle suspensions to establish the relationship between process performance and key system parameters. Performance will include measurement of the time required to achieve a specific level of agglomeration and measurement of recovery-grade curves to show process selectivity. The performance will be related to parameters such as air dosage, oil concentration, and agitator speed. Various scale-up rules will be tested to see which may apply for predicting the performance of large-scale systems.

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