DEVELOPMENT OF A GAS-PROMOTED OIL AGGLOMERATION PROCESS

Technical Progress Report

April 1, 1995 - June 30, 1995

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PURPOSE

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.

INTRODUCTION

Several scale model mixing systems have been built and are being utilized to study the gas-promoted, oil agglomeration process for cleaning coal. Numerous batch agglomeration tests have been conducted with these systems. During an individual test the progress of agglomeration has been 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. A mathematical model has been developed for relating the rate of agglomeration of coal particles to the rate of change of turbidity of a dilute particle suspension undergoing agglomeration. The model has been utilized for analyzing and interpreting the results of a number of oil agglomeration tests in which several different system parameters were varied.

During the most recent quarter further agglomeration experiments were conducted to obtain a better and more complete understanding of the relationship between the rate of agglomeration and different system parameters. Whereas earlier experiments had been confined

to Pittsburgh No. 8 seam coal, the latest round of experiments also involved Upper Freeport seam coal. Again the results obtained with dilute suspensions were analyzed by fitting a mathematical model to the data. Several experiments were also conducted with concentrated suspensions using observed agitator torque to monitor agglomeration. In addition, the agglomeration of hydrophobic solids by air alone was investigated.

WORK PERFORMED

Agglomeration Kinetics of Dilute Suspensions

The apparatus, experimental technique, and materials described previously (ref. 1,2) were used for measuring the rate of agglomeration of coal particles suspended in water. The apparatus included an enclosed mixing tank having a diameter of 15.24 cm (6.00 in.) and net volume of 2870 cm³ (0.101 ft³). The tank was fitted with four vertical baffles and a variable speed agitator that included a 5.08 cm (2.00 in.) diameter, Rushton-type turbine impeller. Instrumentation was provided for measuring agitator speed and torque and for determining the turbidity of the suspension.

Two types of coal were utilized. The first type was from the Pittsburgh No. 8 Seam in Belmont County, Ohio, and it had an ash content of 27-28% and sulfur content of 5%. The second type was from the Upper Freeport Seam in Indiana County, Pennsylvania, and it had an ash content of 14% and sulfur content of 2%. The most likely rank classification for these coals was high volatile A bituminous for the first coal and medium volatile bituminous for the second coal. Each type of coal was prepared by first crushing and then grinding in a stirred ball mill as a slurry. The ground material was partially dewatered and stored as a wet paste until utilized.

The weight mean particle size determined by automatic image analysis was 14.4 μm for the first coal and 12.7 μm for the second coal.

To prepare for an agglomeration test, a small amount of paste was weighed out and mixed with deionized water. The resulting slurry was transferred to the enclosed mixing tank which was then filled completely by adding more water. After any remaining pockets of air were eliminated by operating the agitator, a specific amount of air was introduced by withdrawing a measured volume of liquid with a syringe. The slurry was then conditioned by operating the agitator for 2 min. at the same speed which was to be used for the ensuing run. During the conditioning period most of the air which had been introduced was dispersed as small bubbles. At the end of the conditioning period, a measured quantity of heptane was introduced near the impeller by using a syringe fitted with a long needle. The progress of agglomeration was monitored subsequently by observing changes in the turbidity of the suspension. The rate of agglomeration was determined by employing the method of analysis described previously (ref. 2,3), and the results were used for evaluating the constants which appear in the mathematical model shown below to represent the kinetics of agglomeration.

$$-\frac{dN}{dt} = k N^a \quad (1)$$

This expression was converted to the following form in order to use linear regression to evaluate the constants:

$$\ln\left(-\frac{dN}{dt}\right) = a \ln N + \ln k \quad (2)$$

In this expression N represents the particle number concentration, and, therefore, dN/dt represents the rate of agglomeration. The constants " a " and " k " represent the kinetic order and specific agglomeration rate, respectively.

The results of a number of runs made to determine the effects of different parameters on the rate of agglomeration are presented in Table 1 and in Figures 1-4. Although the results shown in Figure 1 for Pittsburgh No. 8 coal were presented previously (ref. 2), they have been recalculated and are included here for comparison with the results shown in Figure 2 for Upper Freeport coal. The data shown in these two figures represent the results of a number of runs made with different initial particle concentrations and with different amounts of added air, either 20 ml or 50 ml. It can be seen that for a given type of coal and a given amount of air the data fit a straight line representing equation 2 very well. In each case the correlation coefficient r exceeded 0.97. Also for three out of the four cases shown, the kinetic order was nearly 1.25. Although the agglomeration rate increased when more air was added to the system, the kinetic order did not appear to be affected by the increase in concentration of air. Therefore, the principal effect of adding air was to increase the specific agglomeration rate. Furthermore, a comparison of Figures 1 and 2 shows that for any given particle concentration and amount of air, the rate of agglomeration of Upper Freeport coal was greater than the rate of agglomeration of Pittsburgh No. 8 coal. The difference in agglomeration rate was due very likely to the difference in hydrophobicity of the two types of coal since Upper Freeport coal is known to be more hydrophobic than Pittsburgh No. 8 coal.

Table 1. Agglomeration runs made with finely ground coal in a dilute aqueous suspension.

Run No.	Coal		Oil			Air, ml	Speed, rpm	N _o 10 ⁻⁶ /cm ³	τ _o mm ⁻¹	Order "a"	ln k
	Type	wt., g	Type	ml	v/w%						
Figure 1											
20	Pitt.	3.03	C ₇ H ₁₆	0.55	20	50	1500	0.522	0.253	1.336	-0.851
21	Pitt.	6.07	C ₇ H ₁₆	1.10	20	50	1500	1.045	0.483	1.446	-2.379
22	Pitt.	9.15	C ₇ H ₁₆	1.65	20	50	1500	1.585	0.795	1.396	-2.032
24	Pitt.	2.68	C ₇ H ₁₆	0.55	20	20	1500	0.462	0.260	1.346	-1.577
25	Pitt.	5.37	C ₇ H ₁₆	1.10	20	20	1500	0.924	0.490	1.478	-3.342
26	Pitt.	8.37	C ₇ H ₁₆	1.65	20	20	1500	1.441	0.768	1.452	-3.196
27	Pitt.	10.46	C ₇ H ₁₆	2.20	20	20	1500	1.802	0.973	1.472	-3.483
28	Pitt.	13.86	C ₇ H ₁₆	2.75	20	20	1500	2.387	1.272	1.419	-2.954
Figure 2											
114	UFP	1.39	C ₇ H ₁₆	0.28	20	20	1500	0.240	0.163	1.419	-1.326
115	UFP	5.57	C ₇ H ₁₆	1.10	20	20	1500	0.958	0.562	1.225	1.139
116	UFP	8.35	C ₇ H ₁₆	1.65	20	20	1500	1.438	0.842	1.343	-0.583
117	UFP	11.13	C ₇ H ₁₆	2.20	20	20	1500	1.917	1.049	1.268	0.220
132	UFP	2.78	C ₇ H ₁₆	0.55	20	20	1500	0.479	0.317	1.182	1.488
133	UFP	4.17	C ₇ H ₁₆	0.83	20	20	1500	0.719	0.462	1.241	0.692

Run No.	Coal		Oil			Air, ml	Speed, rpm	N_o $10^{-6}/\text{cm}^3$	τ_o mm^{-1}	Order "a"	ln k
	Type	wt., g	Type	ml	v/w%						
134	UFP	5.57	C ₇ H ₁₆	1.10	20	20	1500	0.958	0.603	1.218	0.850
135	UFP	6.96	C ₇ H ₁₆	1.39	20	20	1500	1.198	0.748	1.150	1.858
136	UFP	2.78	C ₇ H ₁₆	0.55	20	50	1500	0.479	0.317	1.249	1.047
137	UFP	4.17	C ₇ H ₁₆	0.83	20	50	1500	0.719	0.477	1.265	0.697
138	UFP	5.57	C ₇ H ₁₆	1.10	20	50	1500	0.958	0.619	1.239	1.009

Figure 3

89	Pitt.	1.36	C ₇ H ₁₆	0.27	20	20	1400	0.235	0.135	1.753	-6.491
91	Pitt.	1.36	C ₇ H ₁₆	0.27	20	20	1600	0.235	0.137	1.487	-2.570
94	Pitt.	1.36	C ₇ H ₁₆	0.27	20	20	1900	0.235	0.140	1.503	-1.469
97	Pitt.	1.36	C ₇ H ₁₆	0.27	20	20	2100	0.235	0.142	1.534	-1.684

Figure 4

104	UFP	2.78	C ₇ H ₁₆	0.55	20	20	1500	0.479	0.283	1.097	1.888
119	UFP	2.78	C ₇ H ₁₆	0.83	30	20	1500	0.479	0.310	1.171	1.835
120	UFP	2.78	C ₇ H ₁₆	1.10	40	20	1500	0.479	0.309	0.984	4.255
121	UFP	2.78	C ₇ H ₁₆	1.39	50	20	1500	0.479	0.307	0.993	4.181

Figure 3. Effect of agitator speed on the rate of agglomeration of Pittsburgh No. 8 coal in a nondegassed suspension with 20 ml of added air.

Figure 4. Effect of heptane dosage on the rate of agglomeration of Upper Freeport coal in a nondegassed suspension with 20 ml of added air.

To study the effect of agitator speed on the agglomeration rate of Pittsburgh No. 8 coal under conditions not reported previously, a set of runs was conducted which provided the results shown in Figure 3. Except for run 89 made with an agitator speed of 1400 rpm, the kinetic order was approximately 1.5 in each case. Therefore, the principal effect of increasing agitator speed was to increase the specific agglomeration rate. However, an increase in agitator speed above 1900 rpm appeared to be counterproductive since it did not cause a commensurate increase in agglomeration rate.

To investigate the effect of heptane dosage on the agglomeration rate of Upper Freeport coal, a set of runs was carried out which produced the runs shown in Figure 4. For this set of runs the kinetic order was 1.0-1.2, and the specific agglomeration rate increased greatly as the heptane dosage was raised from 20 to 40 v/w%. Increasing the heptane dosage above 40 v/w% did not increase the agglomeration rate and actually may have reduced the rate slightly.

Agglomeration of Concentrated Suspensions

The results of several preliminary agglomeration experiments involving concentrated suspensions of coal were reported previously (ref. 1). These experiments showed that the continuous measurement of agitator torque could provide a means for monitoring a batch agglomeration process. Further agglomeration experiments were conducted more recently to refine the technique. An enclosed mixing tank having a diameter of 11.4 cm (4.50 in.) and a net volume of 1185 cm³ (0.042 ft³) was used for this purpose. The tank was fitted with four vertical baffles and an agitator which included a 5.08 cm (2.00 in.) diameter, Rushton-type turbine impeller. For the experimental work described below, the agitator was driven at a constant speed of 1700 rpm while the agitator torque was measured and recorded. Pittsburgh

No. 8 coal was prepared as before 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.

To prepare for an agglomeration experiment, approximately 400 ml of previously degassed water was added to the mixing tank and sufficient coal paste was introduced so that when the tank was subsequently filled with water the resulting slurry would have a solids concentration of approximately 30 w/v%. The amount of paste actually used corresponded to 382 g coal on a dry basis which resulted in a solids concentration of 32 w/v%. 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. After introducing the coal paste, 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. The agitator speed was increased subsequently to 1700 rpm, and the measurement of agitator torque was begun. After agitating the suspension for 15 min., 114 ml of heptane was added slowly using a syringe fitted with a long needle so that the heptane was introduced just above the rotating impeller. The heptane dosage corresponded to 30 v/w% based on the weight of dry solids.

The results of an initial agglomeration experiment are shown in Figure 5. It can be seen that before oil (heptane) was introduced the agitator torque was 1450 g·cm and that after oil 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 with a long needle attached to a syringe. At this point the torque decreased quickly to 1225 g·cm and then started increasing rapidly. The rapid rise in agitator torque following the addition of air was an indication of

Figure 5. Changes in agitator torque resulting from the addition of heptane and air to a concentrated coal slurry and to pure water.

Figure 6. Effect of delaying the time of air introduction into a concentrated coal slurry which had been dosed with heptane.

particle agglomeration, and when the torque peaked, the process of agglomeration seemed to be complete. Subsequent examination of the material recovered at the end of the experiment with an optical microscope showed that most of the material was in the form of uniform, compact spherical agglomerates having a diameter of 2.0-2.7 mm.

To help interpret the preceding results, another experiment was conducted in which no coal was used. The mixing tank was filled with degassed water, and while the water was agitated at 1700 rpm, the same amounts of oil (heptane) and air were introduced as before. The results which are also presented in Figure 5 show that the initial agitator torque was lower than for the coal slurry. When either oil or air was introduced, the torque decreased quickly as the fluids were dispersed in the water. However, when oil was added to pure water, the drop in torque was less than that recorded when oil was added to the coal slurry. Following the drop in torque after the addition of air there was only a slow and relatively slight increase in torque as the three-phase mixture of air, oil, and water underwent some kind of change. What was absent was the large and rapid increase in torque which accompanied the process of particle agglomeration.

The initial agglomeration experiment indicated that air may have triggered the process of agglomeration. To see if that was the case additional agglomeration experiments were conducted in which the time between the addition of oil and the addition of air was varied. The results shown in Figure 6 indicate that the addition of air did indeed trigger the process of agglomeration because the very pronounced, rapid increase in agitator torque marking the onset of agglomeration did not occur until air was injected. This finding provides an indication of the

important role played by a gas in the process of agglomeration, but it does not explain the actual mechanism. Further study is needed to determine that aspect of the process.

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.

The hydrophobic solids included Teflon powder, flowers of sulfur, and finely ground gilsonite, Ceylon graphite, and Pittsburgh No. 8 coal. To prepare a suspension for agglomeration, a measured quantity of dry particles and 2800 cm³ 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 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.

$$\Delta\tau_r = [(\tau_o - \tau)/\tau_o] 100 \quad (3)$$

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 7. It can be seen that for each material except untreated

Figure 7. Results of air agglomeration tests of different hydrophobic materials.

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 7 seemed to be proportional to the hydrophobicity of the corresponding material as indicated by its three-phase contact angle.

Many of the details of the air agglomeration process will be presented at a technical conference in the near future (ref. 4).

CONCLUSIONS

The research which was been conducted from the inception of this project to date has produced the following achievements and conclusions:

1. Small amounts of air promote and even trigger the oil agglomeration of coal particles suspended in water.
2. Particles composed of highly hydrophobic materials such as Teflon or gilsonite can be agglomerated in an aqueous suspension by air alone.
3. A batch agglomeration process involving a dilute particle suspension can be monitored by measuring the turbidity of the suspension.
4. A batch agglomeration process involving a concentrated particle suspension can be monitored by measuring agitator torque.

5. A mathematical expression has been developed for relating the rate of agglomeration to the rate of change of turbidity of a dilute suspension.
6. A mathematical model has been proposed and tested for representing the kinetics of agglomeration of dilute suspensions.
7. The rate of agglomeration of dilute suspensions has been found to increase with increasing particle concentration, oil dosage, air dosage, agitator speed, and material hydrophobicity. However, at least in the case of either oil dosage, air dosage or agitator speed there is an upper limit beyond which an increase in the parameter does not produce a corresponding increase in agglomeration rate.

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