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DEVELOPMENT OF A GAS-PROMOTED OIL AGGLOMERATION PROCESS

Technical Progress Report

October 1, 1993 - September 30, 1994

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ABSTRACT

During the first year of the project two model mixing systems, which differed in size but were similar in design, were constructed and tested. The systems were equipped for measuring agitator speed and torque and for measuring the turbidity of coal particle suspensions undergoing agglomeration. Preliminary measurements of aqueous suspensions of coal particles showed that the Beer-Lambert law applies to such suspensions at least for low concentrations. Therefore, the measured turbidity can be used as an indicator of particle concentration and a means for monitoring the progress of oil agglomeration. However, the method is not applicable for large particle concentrations so a different technique was tested for monitoring the agglomeration of large concentrations. This technique involves measuring agitator torque and observing changes in torque while agitator speed is held constant. The results of preliminary tests of the technique were encouraging. In these tests significant changes in agitator torque were observed when particle agglomeration took place as long as solids concentration of 25 w/v% or more were utilized.

A number of agglomeration tests were conducted using either one or the other of the two monitoring techniques. Both methods showed that even very small amounts of air can promote the oil agglomeration of coal particles suspended in water. Even the amount of air dissolved in water at room temperature and pressure can affect the process providing the air is displaced from the solution by a slightly soluble agglomerant such as heptane. The apparent rate of agglomeration was observed to increase as more air was introduced and also as agitator speed was increased.

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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

Previous research showed that having a gas present in an agitated system used for the agglomeration of an aqueous suspension of coal particles with oil would reduce greatly the required mixing shear rate and power input. To take advantage of this discovery, the present research project was initiated. The project involves building and testing several model mixing systems which differ in scale but are representative of standard industrial mixing systems used for mixing solid particles, liquid, and gas. Over the three year life of the project numerous batch agglomeration tests will be conducted with these systems to determine the nature of the gas promotion mechanism, to relate process performance and agitator power requirements to key parameters, and to find a suitable basis for scaling up the size of the mixing system.

During the first year of the project two laboratory mixing systems were designed, constructed, and tested. These systems were similar in design but differed in size and minor construction detail. Instruments were provided for measuring agitator speed and torque and for

measuring the turbidity of a coal particle suspension as the particles were being agglomerated. During a batch agglomeration test the progress of agglomeration was monitored either by measuring the turbidity of the suspension or by measuring agitator torque at constant speed. Previous work in our laboratory had shown that changes in the turbidity of a suspension undergoing agglomeration provided a reliable means for observing agglomeration of dilute suspensions (refs. 1-3), and a report in the literature suggested that changes in agitator torque could provide a means for tracking agglomeration of concentrated suspensions (ref. 4). However, the reliability of agitator torque as a method for monitoring agglomeration needed to be verified.

A number of agglomeration tests were conducted with these mixing systems using finely ground coal and carefully controlled conditions. Special attention was given to the amount of air present in the system as this proved to be a critical parameter. Even the air dissolved in the water proved important. Other important parameters which were studied included solids concentration and agitator speed. Although Pittsburgh No. 8 coal was used for most of the tests, Upper Freeport coal was used for some tests.

WORK PERFORMED

Mixing Systems

Two model mixing systems were designed and constructed for the investigation. One of the principal components of each system was a cylindrical tank which was fitted with a removable cover, four vertical baffles, and an agitator. Although the two tanks differed in size, they were geometrically similar with the scale of one tank being three-fourths (75%) the scale of the other tank. Also the tanks differed with respect to minor construction details.

Figure 1 is a cross-sectional view of the larger tank which had an inside diameter of 15.24 cm (6.00 in.) and height of 15.24 cm (6.00 in.). The measured net volume of this tank was 2870 cm^3 (0.101 ft^3) when it was fitted with baffles and an agitator. Each of the four vertical baffles projected inward a distance of 1.27 cm (0.50 in.). The walls of the tank and baffles were made of Plexiglas, whereas the top and bottom were made of stainless steel. The top and bottom were slightly concave to facilitate drainage of liquid from the bottom and venting of gas from the top. A cooling coil was attached to the bottom to remove heat generated by the agitator and thereby to control the temperature of the system. The top and bottom were easily removed to facilitate cleaning. Several openings were provided in the top of the tank for introducing material and for admitting the agitator shaft. An opening was provided in the bottom for draining the tank, and an opening was provided in the side for removing a stream of material needed for the measurement of turbidity. This opening was located 2.54 cm (1.00 in.) above the bottom.

Figure 2 is a cross-sectional view of the smaller tank which had an inside diameter of 11.43 cm (4.50 in.) and height of 11.43 cm (4.50 in.). The measured net volume of this tank was 1185 cm^3 (0.042 ft^3) when it was fitted with baffles and an agitator. The tank had four vertical baffles and each baffle projected inward a distance of 0.95 cm (0.375 in.). The tank and baffles were constructed completely of Plexiglas. The top was slightly concave to facilitate venting of gas, but the bottom was perfectly flat since it did not have a drain opening. Although the top could be removed easily, the bottom was attached permanently to the walls. Several openings in the top and one in the side were provided for the same reasons noted above for the

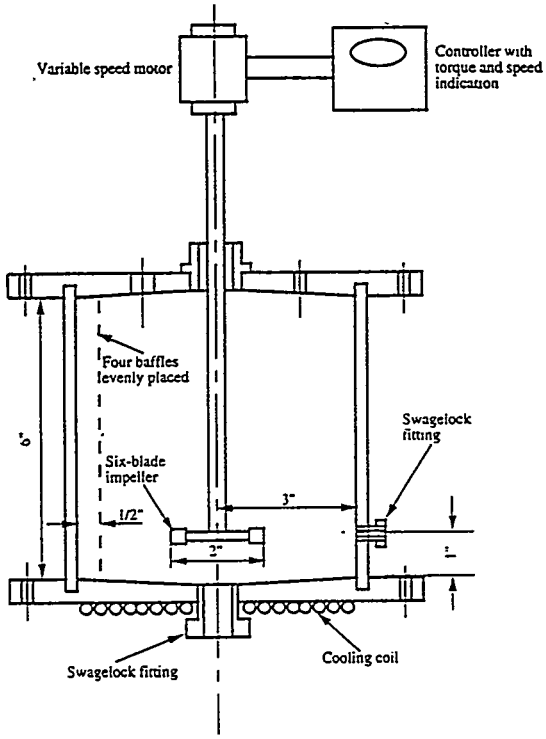

Figure 1. The model mixing system with the 15.24 cm (6.00 in.) diameter tank.

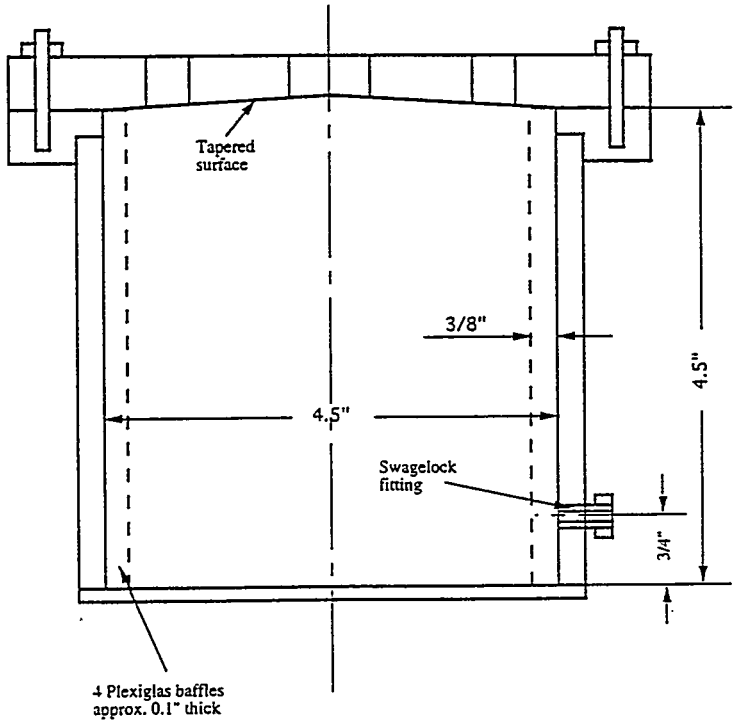

Figure 2. The 11.43 cm (4.50 in.) diameter mixing tank.

larger tank. The side opening was located 1.91 cm (0.75 in.) above the bottom. To reduce the adhesion of oil-coated particles on the walls and other Plexiglas surfaces, the tank was treated with a mixture of Nochromix and concentrated sulfuric acid for 30 sec. and then was rinsed thoroughly with deionized water. This is a strong oxidizing treatment which made the Plexiglas surface less oleophilic and more hydrophilic.

Two variable speed agitators were available for use with either mixing tank. Each of the agitators could be controlled over a speed range of 20 to 2500 rpm and each was designed to provide a continuous indication of drive shaft speed and torque. The power and torque ratings were 93 watts (1/8 hp) and 3600 g·cm (3.13 ft·lb), respectively, for one drive motor and 41 watts (1/18 hp) and 1600 g·cm (1.39 ft·lb), respectively, for the other motor. These were maximum ratings for continuous service. A single Rushton-type turbine impeller was attached to the vertical drive shaft of each agitator. This type of impeller has six, vertical flat blades mounted on a horizontal disk. Two impellers were available for use with either drive motor. One impeller had a diameter of 6.35 cm (2.50 in.) and was made of brass, while the other impeller had a diameter of 5.08 cm (2.00 in.) and was made of stainless steel.

The turbidity of a particle suspension was determined by continuously pumping a stream of material from either mixing tank to the measuring cell of a photometric dispersion analyzer where the light transmittance of the suspension was determined as it flowed through a tubular glass cell. The suspension was then returned to the mixing tank from where it came. A peristaltic pump was used for pumping the suspension, and a PDA 2000 instrument manufactured by Rank Brothers Ltd. was used for measuring the turbidity.

Applicability of the Beer-Lambert Law

The applicability of the Beer-Lambert law for characterizing coal particle suspensions was verified by measuring the apparent turbidity of such suspensions with a photometric dispersion analyzer. Small particles of anthracite coal were suspended in water using the larger mixing tank and the 5.08 cm (2.00 in.) diameter agitator impeller. A small stream of material was conducted from the mixing system to the photometric dispersion analyzer and back to the mixing system. The light transmissiveness of the suspension was determined by measuring the intensity of a narrow beam of light which passed through the suspension as it flowed through a glass tube having an inside diameter of 3.0 mm. Assuming the Beer-Lambert law to be applicable, the turbidity τ would be given by the following relation:

$$\tau = \frac{1}{L} \ln \frac{V_o}{V} \tag{1}$$

where L is the optical path length through the suspension (assumed to be 3.0 mm), V_o is the output signal voltage from the photometric dispersion analyzer when pure water is present in the measuring tube, and V is the output signal voltage when a particle suspension is present. The design of the measuring system is such that the output signal is proportional to the intensity of the transmitted light. For a suspension of uniformly sized particles, the turbidity would be related to particle concentration as follows:

$$\tau = NC \tag{2}$$

where N and C are the number concentration and scattering cross section, respectively, of the particles. For a spherical particle, its scattering cross-section would be given by the expression,

$$C = \frac{1}{4} Q \pi d^2 \tag{3}$$

where Q is a non-dimensional scattering coefficient for the particle of diameter d. For particles which are much larger than the wavelength of light, the scattering coefficient is equal to 2 (ref. 5). By combining the last two equations, the following relation is obtained:

$$\tau = \frac{1}{2} \pi \, d^2 \, N \tag{4}$$

It can be shown that if the particle size of a suspension of monosize, spherical particles is varied while holding the total mass of particles and system volume constant, the turbidity of the suspension will vary with particle size and with particle concentration as indicated below.

$$\tau = k_1 \, d^{-1} \tag{5}$$

$$\tau = k_2 \, N^{1/3} \tag{6}$$

In other words, the turbidity will vary inversely with particle size or directly with number concentration to the one-third power.

The applicability of equations 4, 5, and 6 for monosize, coal particle suspension was verified by conducting a series of measurements on suspensions of closely-sized anthracite particles. To prepare these particles, anthracite lumps were crushed and ground in the dry state, and the ground material was subsequently separated into a series of size fractions by dry screening using sieves which ranged from 100 to 400 mesh. The material retained on each screen was subsequently washed on the screen with water to remove fines.

To prepare a suspension for the turbidity measurement, 5.0 g of particles of a given size was mixed with deionized water. The suspension was degassed at room temperature by applying a vacuum equivalent to an absolute pressure of 13 kPa over a period of 30 min. The suspension was stirred during this operation. After degassing, the suspension was transferred to

the previously described 2.87 L mixing system fitted with a 5.08 cm (2.00 in.) diameter turbine impeller. After removing all of the air from the system, the suspension was conditioned by stirring the suspension for 2 min. at 1000 rpm. During this time, a stream of material was circulated through the turbidity measuring tube, and at the end of the conditioning period a measurement of the turbidity was made. The mixing system was then emptied and prepared for the next measurement.

For the first series of measurements, the number concentration of particles was kept constant (N = 7150 particles/ml) while the average particle size was varied over the range from 40.5 to 137 μm. To keep N constant, the corresponding mass of coal had to vary from 1.06 g for the smallest particle size to 40.89 g for the largest size. The results presented in Figure 3 indicate that the turbidity of the suspensions varied directly as the square of particle diameter based on screen opening size. This result was in general agreement with equation 4 except that the line determined by linear regression did not pass through the origin. The small discrepancy may have been due to back scattering of light or possibly particle coagulation. Another possibility is that the turbidity measuring cell may have become coated when the particle suspension was flowing through it.

For the second series of measurements the particle size was held constant (d = 115 μm) while the particle concentration was varied over a range from 739 to 5913 particles/ml. The total mass of particles had to increase from 2.50 g at the lowest particle concentration to 20.0 g at the highest particle concentration. To calculate the particle concentration, it was assumed that the particles were spherical and that the density ρ of an individual particle was 1.48 g/cm^3. Therefore, the particle concentration N was given by the following expression:

$$N = \frac{6\ M}{\pi\ \rho\ d^3\ V} \qquad (7)$$

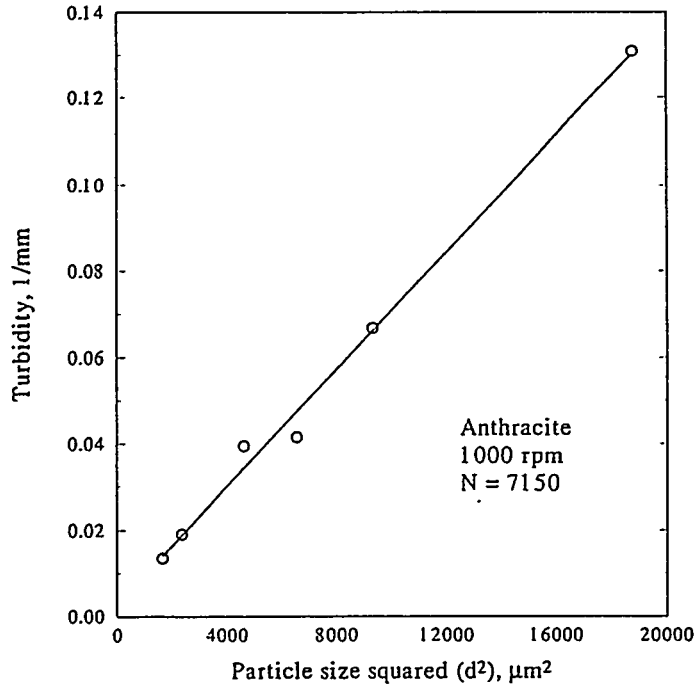

Figure 3. Effect of particle size on the turbidity of anthracite coal suspensions having the same particle concentration (7150 particles/ml).

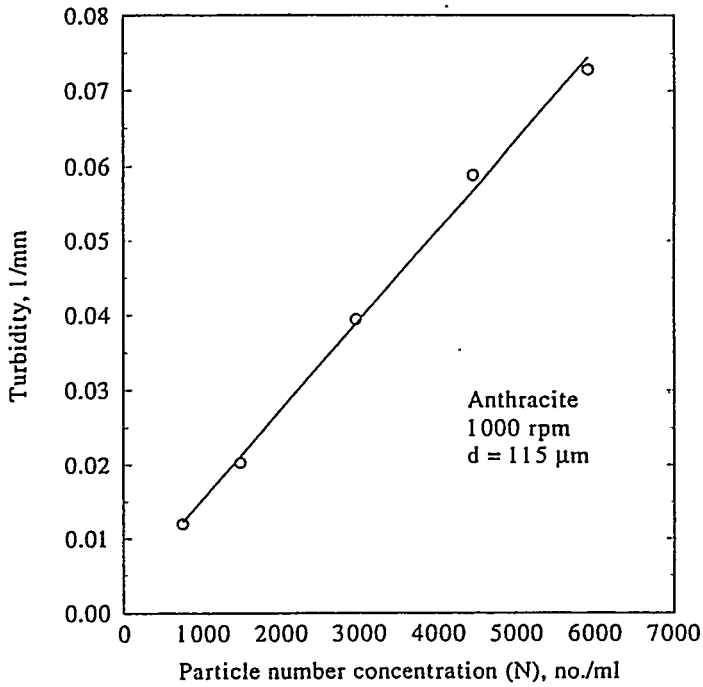

Figure 4. Effect of particle concentration on the turbidity of anthracite coal suspensions prepared with uniformly sized particles.

where M is the total mass of particles and V is the volume of the suspension. The results presented in Figure 4 show the turbidity varied directly with particle concentration as predicted by equation 4. However, again the line fitted by linear regression did not pass through the origin which again may have been due to one of the reasons suggested above.

For the third series of measurements, the total mass of particles was held constant at 5.0 g and the particle size was varied over the range from 40.5 to 137 μm. Since the total volume of the suspension was held constant at 2.87 L, the particle concentration had to vary from 874 particles/ml for the largest particles to 33,840 particles/ml for the smallest particles. The results which are presented in Figures 5 and 6 show that the turbidity varied directly with d^{-1} as predicted by equation 5 or directly with $N^{1/3}$ as predicted by equation 6.

The implication of the preceding results is that a particle agglomeration process can be monitored by observing the change in the turbidity of a particle suspension as it undergoes agglomeration at least for solids concentrations up to the maximum concentration used for the preceding measurements which was 1.4%. In a batch process a given mass of particles is agglomerated to form larger particles. As the agglomerates increase in size, the total number of particles decreases so the turbidity will decrease. By the end of the process the larger particles or agglomerates are composed of many smaller particles. Since there will always be some void space between the constituent particles of an agglomerate, equations 5 and 6 have to be modified by introducing the porosity ϵ of an agglomerate in order to have the equations apply to an agglomeration process. For a process in which small monosize particles are converted into large monosize agglomerates the turbidity would vary in accordance with the following expressions:

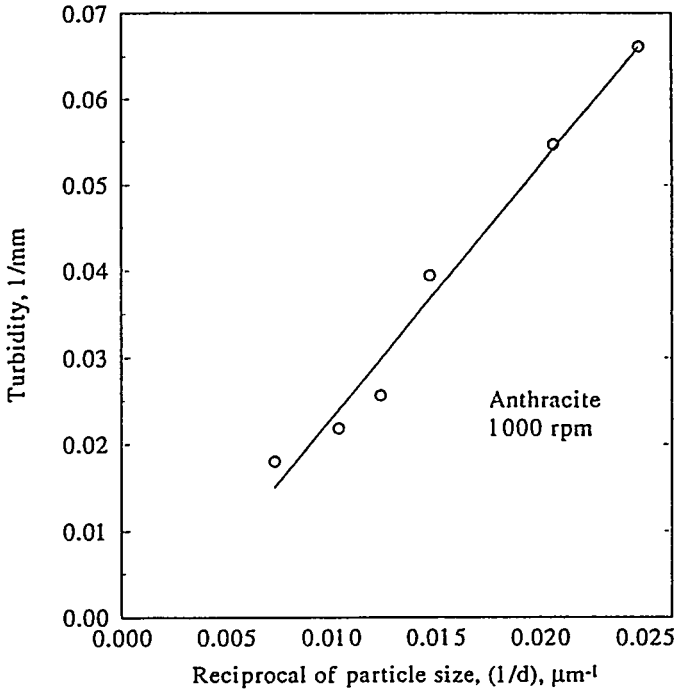

Figure 5. Correlation between turbidity and particle size for anthracite coal suspensions containing 5.0 g of solids.

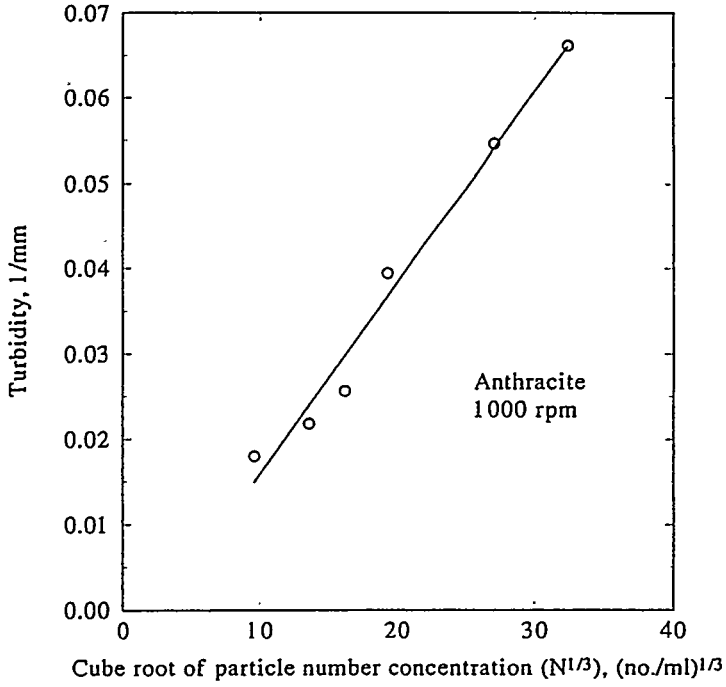

Figure 6. Correlation between turbidity and particle concentration for anthracite coal suspensions containing 5.0 g of solids.

$$\tau = k_1 d^{-1(1-\epsilon)} \quad (8)$$

$$\tau = k_2 N^{1/3(1-\epsilon)} \quad (9)$$

Further modification of the preceding equations is required for them to represent the more general case involving a distribution of particle sizes.

Oil Agglomeration Materials and Methods

A number of oil agglomeration experiments were conducted with Pittsburgh No. 8 Seam coal from Belmont County, Ohio, and with Upper Freeport Seam coal from Indiana County, Pennsylvania. The Pittsburgh No. 8 coal is regarded as high volatile A bituminous coal whereas the Upper Freeport coal is probably a medium volatile bituminous coal. After drying the coal, the ash and total sulfur contents were 27.8% and 5.05% for the Pittsburgh coal and 13.9% and 2.02% for the Upper Freeport coal, respectively.

Relatively pure n-heptane and i-octane obtained from Burdick and Jackson Laboratories Inc. were used as agglomerants in most cases. According to the supplier, these materials had been distilled in glass with the normal boiling point being 98-99°C for the n-heptane and 99-100°C for the i-octane. Hexadecane (99%) with a normal boiling point of 287°C and squalane (99%) with a boiling point of 176°C at a pressure of 0.05 mm Hg were obtained from Aldrich Chemical and were used as agglomerants in a few experiments. For all agglomeration tests, coal particles were suspended in deionized water having a resistivity of 17.9 megohm·cm.

Other materials were used in a few experiments. These materials included floated silica powder and washed sea sand which were obtained from Fisher Scientific and low density polyethylene pellets supplied by Quantum Chemical Co. The size distributions of the silica powder and sea sand were determined by screening and are indicated below.

Particulate Material	Screen Mesh U.S. Standard	Weight %
Sand	-25/+45	13.9
	-45/+70	49.3
	-70/+140	36.0
	-140	0.8
Silica	-140/+270	16.9
	-270/+400	23.4
	-400	59.7

The polyethylene pellets were approximately 3 mm (1/8 in.) in diameter, untreated by any chemicals or additives, and naturally hydrophobic.

To prepare coal for agglomeration tests the material was first crushed with a jaw crusher and roll mill, and the material was then divided into small portions by riffling. The small portions were stored under Argon until needed. Shortly before being used, one or more individual portions were reground with a roll mill to pass a No. 14 U.S. Standard screen. The material was ground further in a stirred ball mill so that more than 99% was finer than 37 μm, and the average particle size appeared to be about 10 μm when a sample was examined with a scanning electron microscope. The ball mill charge consisted of 250 g coal, 250 g water, and 1200 g stainless steel balls (3 mm or 1/8 in. diameter). The mill was operated for 20 min. at a speed of 540 rpm. The product was partially dewatered with a Büchner filter funnel and then stored as a paste containing 56% solids in a refrigerator set at 5°C.

The agglomeration experiments were conducted with the previously described mixing systems. Before conducting a typical agglomeration experiment the selected mixing system was partly filled with deionized water, and a measured quantity of coal paste was added and

dispersed in the water. Initial experiments were conducted without degassing the water. For later experiments the water and sometimes the coal paste were first degassed. The most frequently used method of degassing involved applying a partial vacuum to the partly filled mixing system at room temperature. The partial vacuum corresponded to an absolute pressure of 5-6 kPa, and it was applied for about 20 min. Afterwards the mixing system was topped off with degassed water. Any remaining gas bubbles were removed from the system.

Before conducting an oil agglomeration experiment, the amount of air present in the mixing system had to be set. This was usually accomplished by completely filling the system with water and coal, and before the coal was dispersed, a specific amount of air was introduced either by injecting a measured amount of air or by removing a measured volume of water which was replaced by an equal volume of air. Small volumes of air, as for example 2.5 ml, were introduced with a syringe. Larger volumes were introduced by withdrawing water.

After air had been introduced, the coal suspension was stirred at a given speed for 3 min. whereupon a measured quantity of an agglomerant such as heptane was introduced with a syringe, usually in a single dose. As stirring was continued at the same rate, the progress of agglomeration was monitored in most cases by observing the change in turbidity of the suspension. This was accomplished by circulating a small stream of the suspension through the optical cell or measuring tube of a photometric dispersion analyzer. As the particles combined to form agglomerates the particle concentration decreased which reduced the turbidity of the suspension. The reduction in turbidity was reflected by an increase in the output signal from the photometric dispersion analyzer. Therefore, by plotting the output signal against mixing time it was possible to observe both the apparent rate of agglomeration and the extent of agglomeration.

While this technique worked well for small particle concentrations, it could not be used for large concentrations. Therefore, when large particle concentrations were employed, the progress of agglomeration was monitored by measuring the agitator torque which changed as agglomeration took place.

Initial Oil Agglomeration Experiments

An initial series of agglomeration experiments was conducted in which Pittsburgh No. 8 coal was suspended in water which had not been degassed. These experiments were conducted with the 15.24 cm (6.0 in.) diameter mixing tank which held 2870 ml (0.101 ft^3). An agitator impeller having a diameter of 5.08 cm (2.00 in.) was also employed. Also in each experiment the coal was agglomerated with 20 v/w% heptane, and the progress of agglomeration was determined by observing the change in turbidity of the suspension.

For the first set of experiments, the amount of air introduced was varied among experiments, whereas the initial coal particle concentration (1.00 w/v%) and agitator speed (1500 rpm) were kept constant. The results presented in Figure 7 indicate that in each experiment the output signal from the photometric dispersion analyzer increased greatly over time which would have been the result of particle agglomeration. The results also indicate that as the amount of air was increased from one experiment to the next, the output signal also increased markedly. Therefore, both the rate and extent of agglomeration increased with increasing amounts of air.

Similar results were achieved when a solids concentration of 4.00 w/v% was employed in another set of experiments (see Figure 8). Again it can be seen that particle agglomeration took place when 10 cm^3 of air or more was present in the mixing system, and the rate or extent of

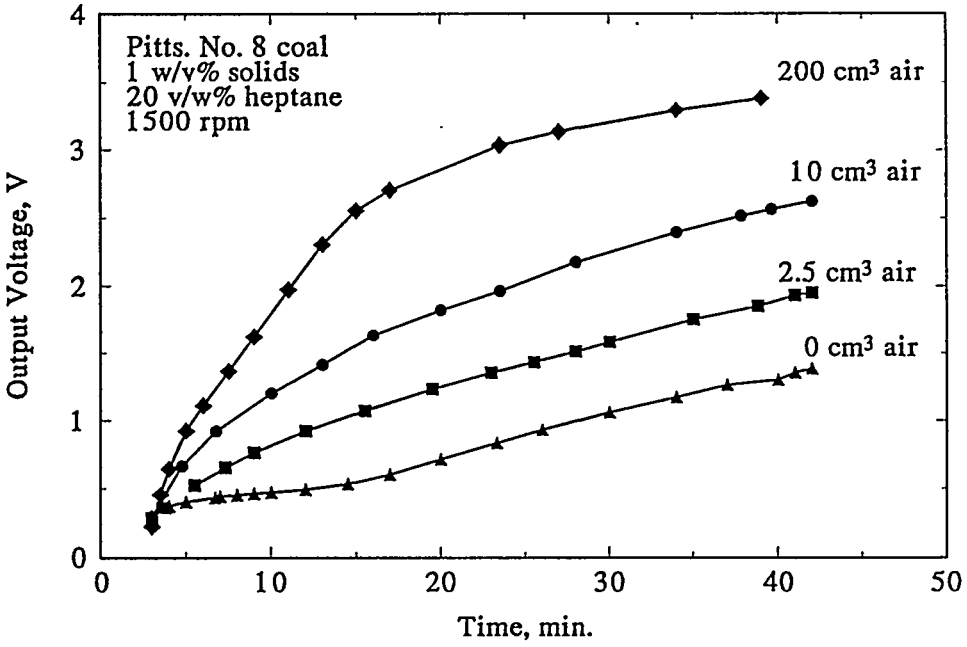

Figure 7. Results of agglomeration tests with Pittsburgh coal suspended in water which had not been degassed followed by the introduction of the indicated amount of air.

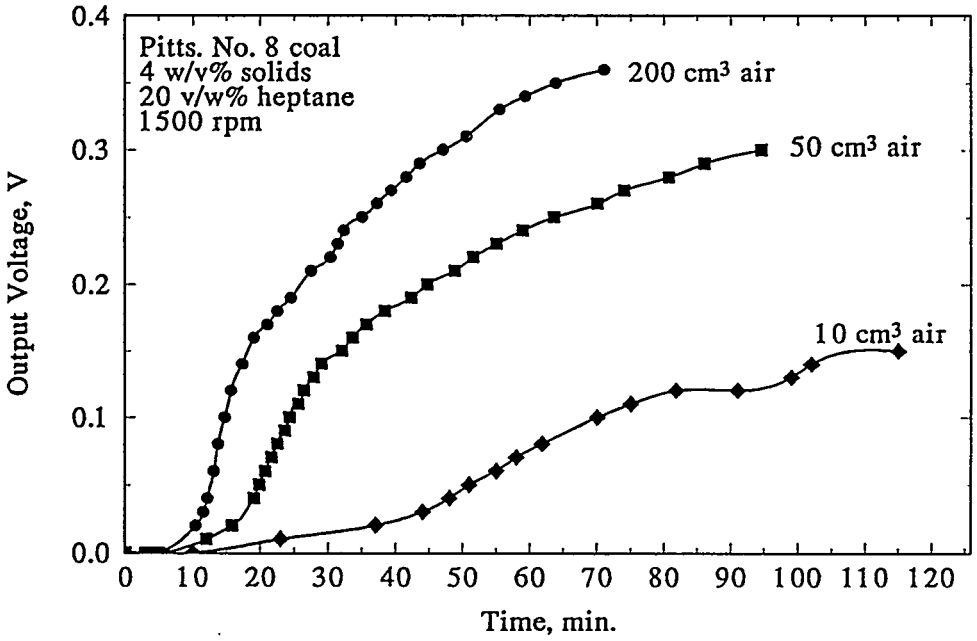

Figure 8. Results of agglomeration tests with a higher concentration of Pittsburgh coal suspended in water which had not been degassed followed by the introduction of the indicated amount of air.

agglomeration increased with increasing amounts of air. However, at the higher solids concentration the rate of agglomeration appeared slow at first after heptane was added, and with the smallest amount of air present in the system, the rate of agglomeration did not appear to increase significantly until more than 40 min. had elapsed. These results may be deceptive because at the higher solids concentration the turbidity measuring technique was less sensitive to changes in particle concentration. Therefore, considerable agglomeration may have taken place before a noticeable change in turbidity was observed. This is an area which needs further study.

The effect of solids concentration on the air-promoted agglomeration process is illustrated further by the results presented in Figures 9 and 10 which were obtained by adding 50 cm^3 of air to the system and using an agitator speed of 1500 rpm. It can be seen that as the initial solids concentration increased, the change in output signal and, therefore, the change in turbidity over a given time interval decreased. Although the results seem to suggest that the rate and extent of agglomeration decreased with increasing solids concentration, that was probably not the case. Since the Pittsburgh No. 8 coal had a large mineral matter content and the mineral matter was unlikely to have been agglomerated, there would have been a large number of unagglomerated mineral particles remaining in suspension after all the coal particles were agglomerated. Furthermore, the amount of residual unagglomerated mineral matter would have increased as the initial solids concentration increased which would have caused the final turbidity of the suspension to increase.

To determine the effect of agitator speed on the rate of particle agglomeration, one set of experiments was conducted with an initial solids concentration of 1.00 w/v% and another set with an initial solids concentration of 4.00 w/v%. Within each set the agitator speed was

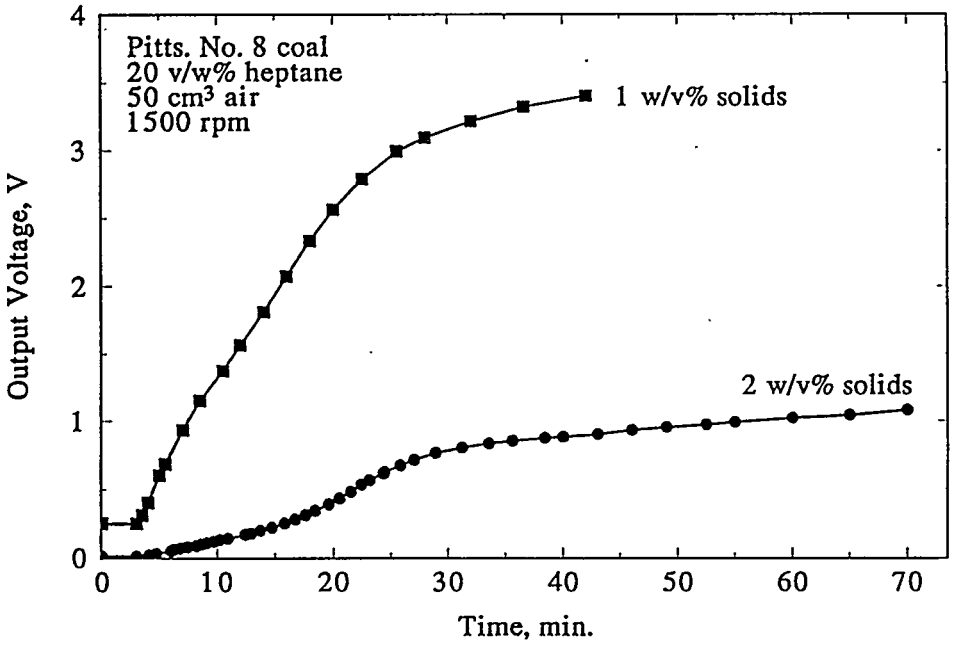

Figure 9. Agglomeration of small concentrations of Pittsburgh coal suspended in water which had not been degassed and with 50 cm^3 of air added.

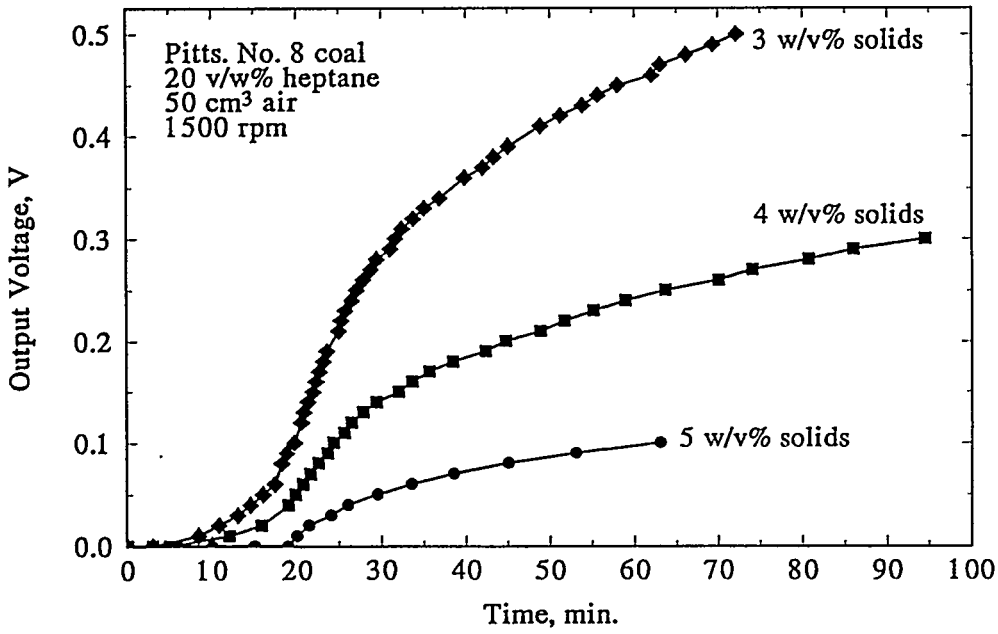

Figure 10. Agglomeration of larger concentrations of Pittsburgh coal suspended in water which had not been degassed and with 50 cm^3 of air added.

varied among experiments while the amount of air introduced was kept at 50 cm^3. The results presented in Figures 11 and 12 show that for an agitator speed of 1250 rpm or more the rate of agglomeration was relatively high and that the rate of agglomeration increased with increasing stirring rate. Figure 11 also indicates that the greatest increase in agglomeration rate was produced by an increase in agitator speed from 1000 to 1500 rpm. Further increases in agitator speed produced progressively smaller increases in agglomeration rate so that an increase in speed from 2000 rpm to 2400 rpm caused only a slight increase in agglomeration rate. In addition Figure 11 indicates that for an initial solids concentration of 1.00 w/v% the rate of agglomeration at 1000 rpm was very slow, and Figure 12 suggests that for an initial solids concentration of 4.00 w/v% the rate of agglomeration at 1000 rpm was nil. But the apparently nonexistent rate of agglomeration at the larger solids concentration may have been a reflection of the insensitivity of the measurement technique rather than to a complete lack of agglomeration.

A final set of experiments in this series was carried out to compare the effect of adding various types of solids to the coal agglomeration system with the effect of adding air or not adding anything. In one experiment 50 g of sand was added while in another 50 g of polyethylene pellets was added. Since these solids were relatively coarse compared to the coal particles, the addition of these materials was expected to have some effect on the hydrodynamics of the system. The results are compared in Figure 13 with the results of experiments in which nothing was added and in which 50 cm^3 of air was added. In all cases a 1.00 w/v% coal suspension was agglomerated with 20 v/w% heptane by using an agitator speed of 1500 rpm. Interestingly, almost identical results were obtained with sand and polyethylene beads even

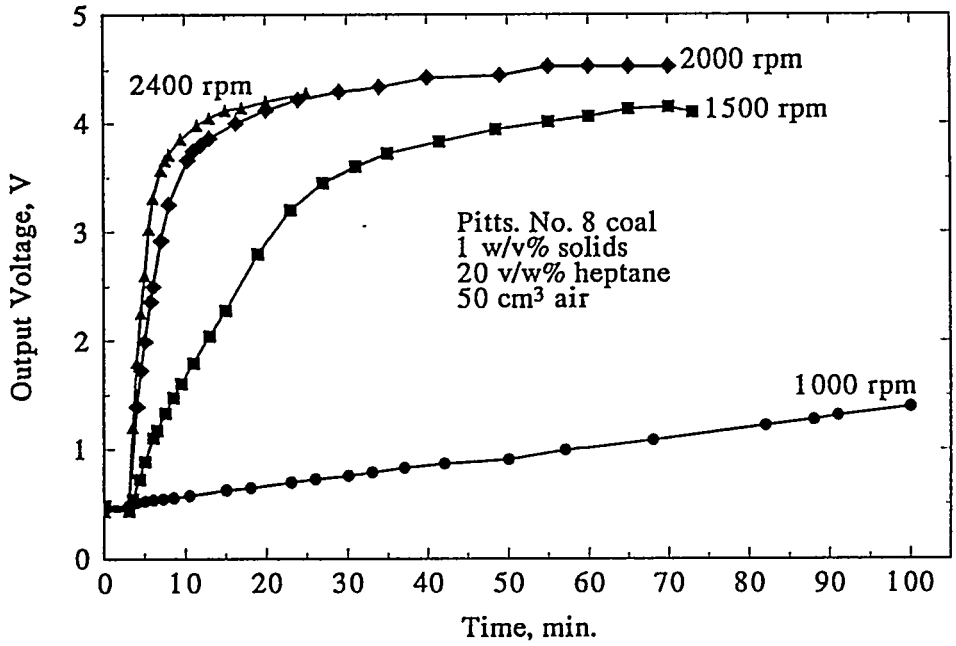

Figure 11. Effect of agitator speed on agglomeration of 1 w/v% concentration of Pittsburgh coal suspended in water which had not been degassed and which had 50 cm^3 of air added.

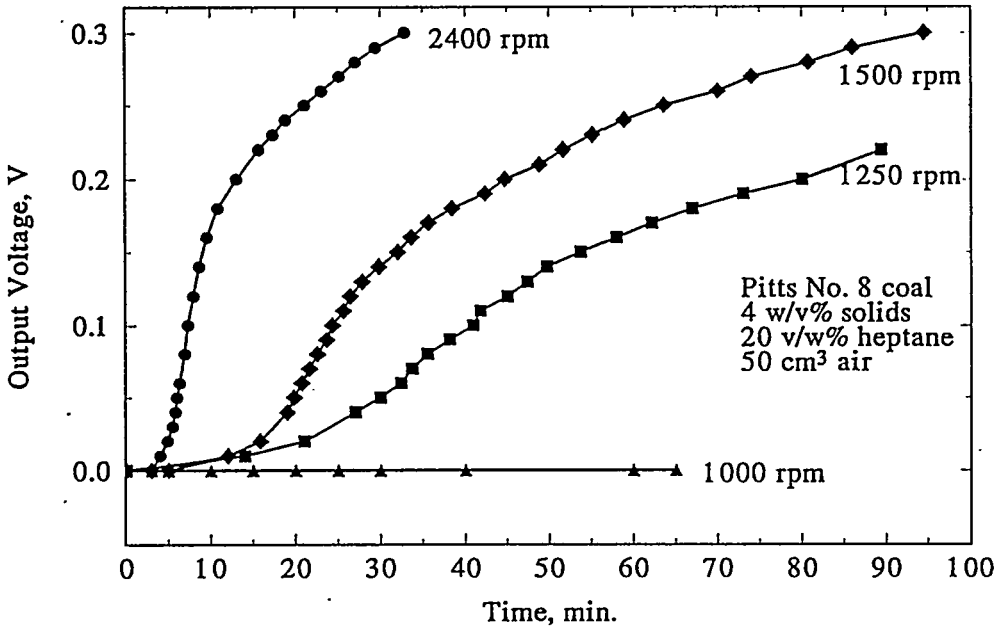

Figure 12. Effect of agitator speed on agglomeration of 4 w/v% concentration of Pittsburgh coal suspended in water which had not been degassed and which had 50 cm^3 of air added.

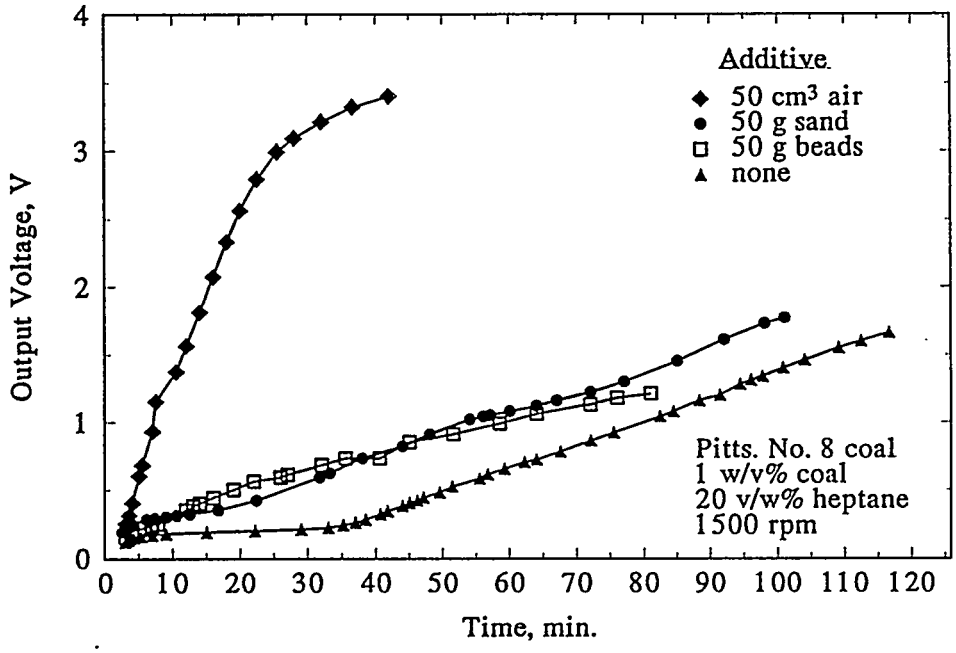

Figure 13. Effect of adding air or different solids on the agglomeration of a suspension of Pittsburgh coal in water which had not been degassed.

though these materials differed considerably in size and surface properties. While the results with these materials seemed to be slightly better than the results achieved when nothing was added, the difference may not have been significant. Therefore, it was concluded that the addition of either type of solids had little effect. In contrast, the addition of 50 cm^3 of air to the system had a very large effect. Although the presence of air in the system would have had some effect on the hydrodynamics of the system, the magnitude of the effect produced by air suggested that its influence was greater than a change in hydrodynamics was likely to produce.

Oil Agglomeration with Minimal Amounts of Air

Although the previous series of experiments showed that air played an important role in the oil agglomeration of coal particles, it remained to be seen whether the air dissolved in the water

in which the particles was suspended had any influence on the process. To investigate this aspect, another series of experiments was conducted with Pittsburgh No. 8 coal which had been prepared as before including grinding in a stirred ball mill as a concentrated suspension in water. The agglomeration experiments were conducted with the 15.24 cm (6.0 in.) diameter mixing tank using a 5.08 cm (2.00 in.) diameter impeller. The experimental procedure was similar to that used before except that the water was degassed for most experiments.

For the first set of experiments the prepared coal paste was mixed with water which had been degassed previously by applying a partial vacuum as described above. After heptane was introduced, a suspension was stirred for 9 min. before a measured quantity of air was added. The amount of air was varied among tests, whereas the following parameters were kept constant: 1.00 w/v% solids, 20 v/w% heptane, and 1500 rpm stirring speed. The results presented in Figure 14 indicate that when no air was added to the mixing system, the output signal from the photometric dispersion analyzer remained flat for up to 2 hr showing that no agglomeration occurred. However, when only 7 ml of air was added 9 min after heptane was introduced, the output signal immediately started to rise and continued to rise steadily showing that agglomeration took place. The addition of larger amounts of air produced even larger and more rapid increases in the output signal indicating higher rates of agglomeration. Interestingly, when an experiment was conducted by agglomerating coal in water which had not been degassed, the results, which are also reported in Figure 14, were similar to those achieved when 7 ml air was added to the degassed system. Therefore, it appeared that air dissolved in the water was sufficient to promote agglomeration. But did the air have to come out of solution to promote agglomeration?

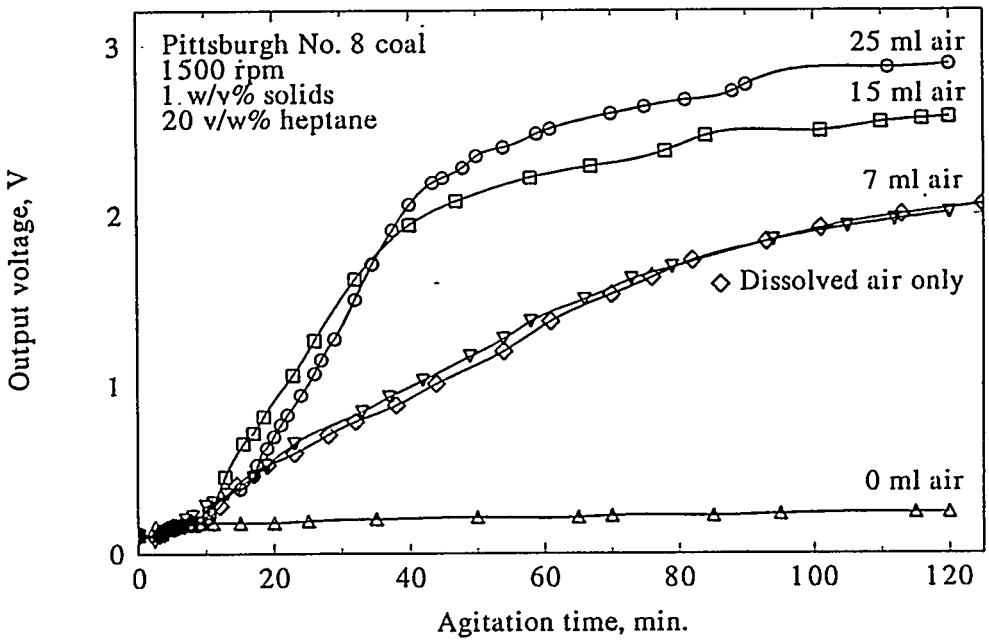

Figure 14. Results of agglomeration tests with Pittsburgh coal suspended in water which had been degassed followed by the introduction of different amounts of air.

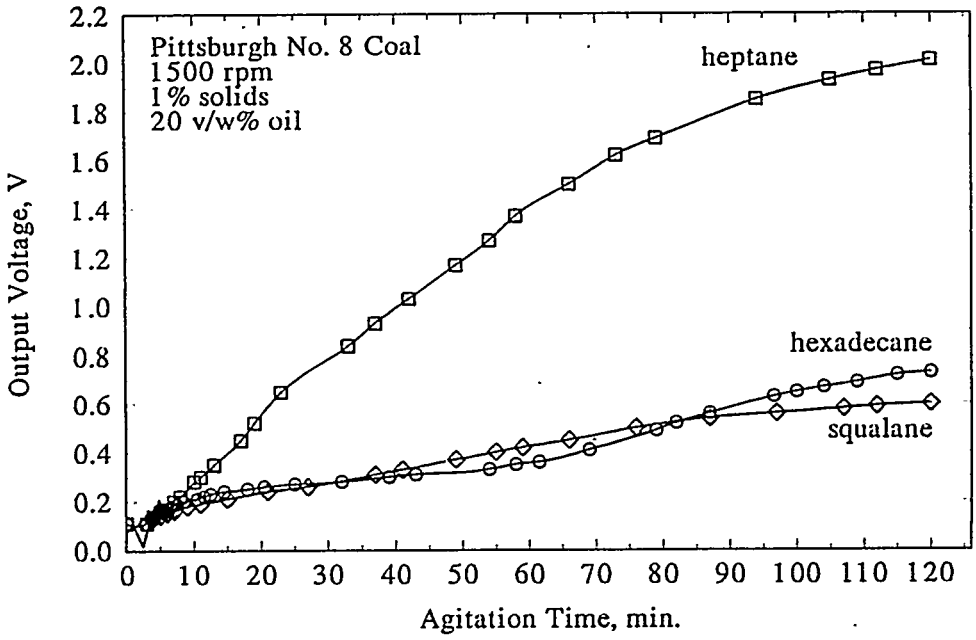

Figure 15. Results of agglomeration tests with Pittsburgh coal suspended in water which had not been degassed.

To answer this question additional experiments were conducted using water which had not been degassed and hexadecane and squalane as agglomerants. No air was added to the system other than the air dissolved in the water. The results achieved with the different agglomerants and shown in Figure 15 indicate that the rate of agglomeration with either hexadecane or squalane was much smaller than with heptane. Although the solubility of heptane in water is small, it is still appreciably greater than that of hexadecane or squalane. The results suggest that when heptane is used as an agglomerant some heptane dissolves in the water and displaces enough air from the water to promote agglomeration. Hexadecane and squalane being much less soluble displace less air, and, therefore, have much less effect. This hypothesis was tested further by first saturating water with heptane and then using the water to suspend coal for a test of agglomeration. The water was not degassed otherwise and any excess heptane was removed by evaporation at room temperature before conducting the agglomeration test. The results of the agglomeration test which are reported in Figure 16 show that virtually no agglomeration took place during the first 35 min, and then agglomeration proceeded very slowly. The results were in sharp contrast to those observed when an agglomeration test was conducted using water which had not been degassed. Also the results obtained with heptane saturated water were very similar to those observed with water which had been degassed by applying a partial vacuum. Therefore, it seems very likely that the displacement of air from water by heptane is sufficient to promote the agglomeration of Pittsburgh No. 8 coal.

Another method of degassing water used for agglomeration was also tested. This method involved boiling the water for 30 min to remove dissolved air. The water was then cooled rather quickly and used immediately for an agglomeration test. The results of this test which

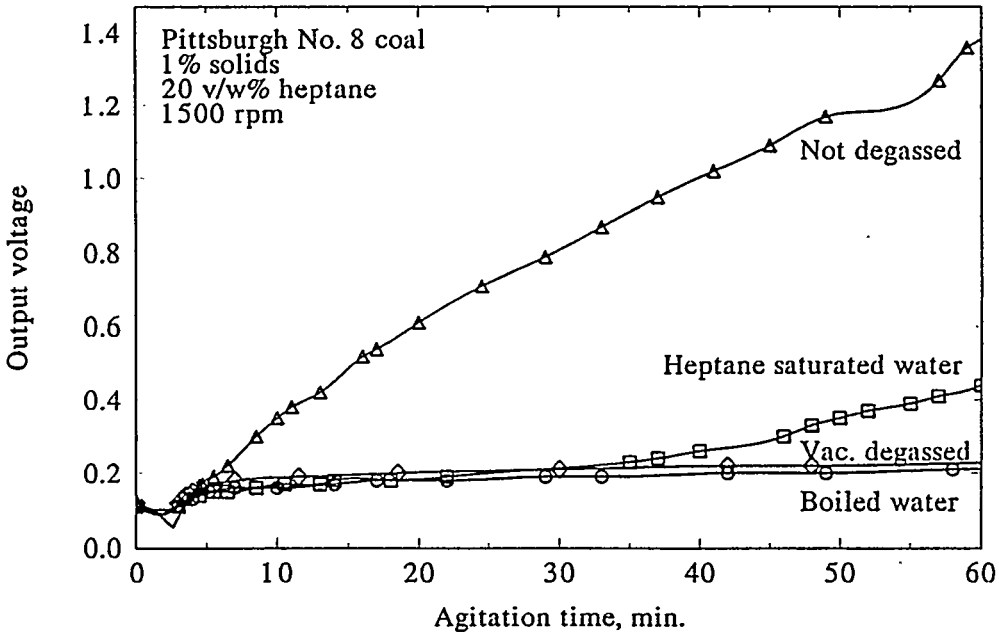

Figure 16. Results of agglomeration tests with Pittsburgh coal suspended in water which had received different treatments.

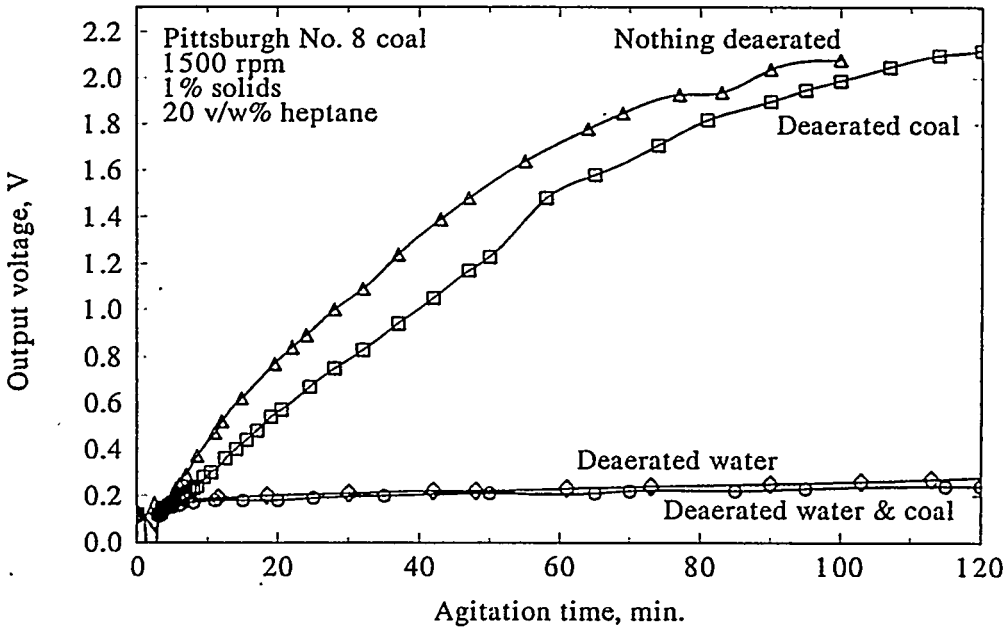

Figure 17. Results of agglomeration tests with Pittsburgh coal in suspensions prepared by different methods.

are shown in Figure 16 were almost identical to the results which had been obtained by vacuum degassing.

To complete the picture on the effects of deaeration, two additional experiments were conducted. For one of these experiments the coal and water were first mixed together and then the suspension was deaerated by applying a partial vacuum as described above. The results which are shown in Figure 17 were almost identical to those obtained in an earlier but similar experiment in which only the water had been degassed. Therefore, it appeared that any air introduced by the coal paste in the earlier experiment was negligible. For another experiment the coal paste amounting to 52.5 g was first mixed with 100 ml of water. This mixture was degassed by applying a partial vacuum. Water which had not been degassed was added to the mixture and an agglomeration test was conducted. The results reported in Figure 17 were similar to those obtained previously in which neither the water nor the coal paste were degassed. Therefore, these experiments indicate that any air introduced by the coal paste was negligible.

While the preceding experiments showed that even small amounts of air can promote the oil agglomeration of Pittsburgh No. 8 coal, the air had to be present as a separate phase. Apparently heptane is capable of displacing enough air dissolved in water at normal temperature and pressure to promote agglomeration. To test this theory additional experiments were conducted using water which had not been degassed. Furthermore, no air was introduced during the experiments.

The results of one set of experiments are indicated by Figure 18. In this set the solids concentration was varied among experiments while the heptane concentration and stirring speed were kept constant. The results indicate that the material was agglomerated in each case, and

the effect of particle concentration was similar to that noted previously when 50 cm^3 air was introduced (see Figures 9 and 10). However, the rate of agglomeration was much slower when the only air present was that which was initially dissolved in the water.

The results of another set of experiments in which no air was added are shown in Figure 19. In this set the stirring speed was varied while the solids concentration and heptane concentration were kept constant. Again it appeared that agglomeration was promoted by air which was initially dissolved in the water. Moreover the rate of agglomeration increased with stirring speed as had been observed previously when 50 cm^3 of air had been added (Figure 12). A comparison of Figures 12 and 19 shows that for a given stirring speed the rate of agglomeration was slower when no air was added. The difference in results caused by the addition of 50 cm^3 of air was especially great for an agitator speed of 1500 rpm. In addition, the difference in results caused by an increase in agitator speed from 1500 rpm to 2400 rpm was much greater for the system without added air. However, the difference was so much greater that the results need to be verified. There is a possibility that at the higher agitator speeds some air may have been drawn into the system inadvertently because the system was difficult to seal. Also at the higher agitator speeds, cavitation produced by the impeller may have had an effect similar to that of dispersed air bubbles. Therefore, further consideration needs to be given to these potential problems.

Oil Agglomeration of Concentrated Suspensions

Since changes in turbidity during agglomeration were only measurable for dilute particle suspensions, another technique was required to monitor the progress of agglomeration of concentrated suspensions. Therefore, consideration was given to the measurement of agitator

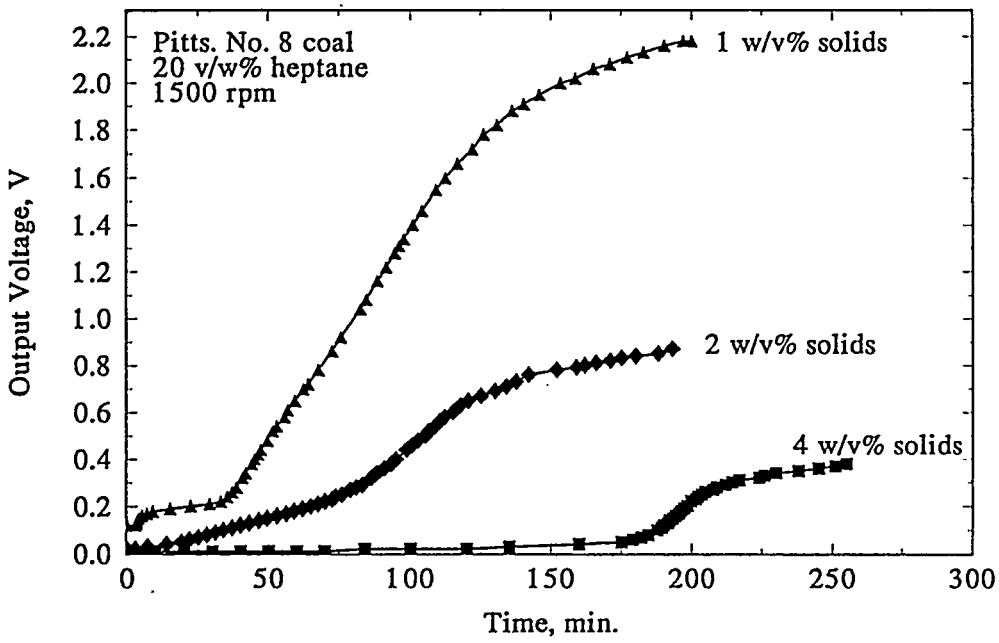

Figure 18. Effect of solids concentration on agglomeration of Pittsburgh coal suspended in water which had not been degassed.

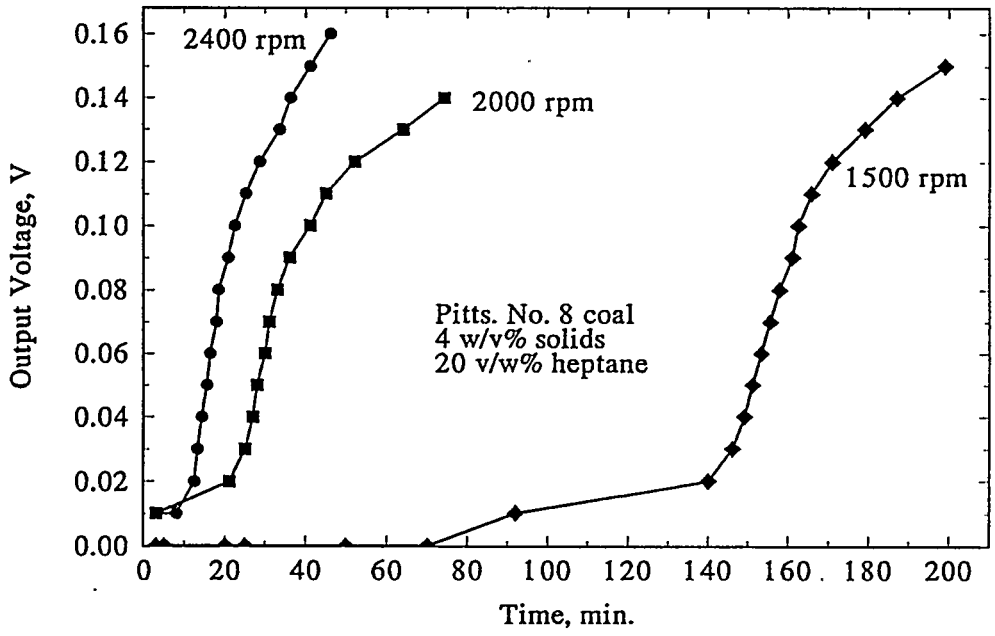

Figure 19. Effect of agitator speed on agglomeration of Pittsburgh coal suspended in water which had not been degassed.

torque as a procedure for monitoring agglomeration. For this part of the investigation the 11.4 cm (4.50 in.) diameter mixing tank and 5.08 cm (2.00 in.) diameter agitator impeller were employed for most experiments. The measured volume of this tank was 1185 cm^3 when it was fitted with baffles and an agitator. Both Pittsburgh No. 8 coal and Upper Freeport coal were utilized, and these materials were prepared as before. For most of the agglomeration tests the wet-ground coal was suspended in water which had first been degassed by applying a vacuum corresponding to -95 kPa for 20 min. In some tests a known quantity of air was introduced by withdrawing a measured amount of water from the mixing tank after it had been filled completely with coal and water. The procedure used for an agglomeration test was similar to that described above except that indicated (uncalibrated) agitator torque was monitored instead of the turbidity of the suspension. Also i-octane was used as an agglomerant for Pittsburgh No. 8 coal in place of n-heptane.

An initial experiment was conducted to see how agitator torque would be affected by the introduction of a known amount of i-octane into a particle suspension which was unlikely to agglomerate. A suspension of silica particles was utilized, since the material was hydrophilic and, therefore, unlikely to agglomerate. The results are presented in Figure 20. Since there was considerable variation in the indicated torque, the range and mean value of the indicated torque at each instant are shown. It can be seen that as soon as i-octane was introduced there was a significant drop in agitator torque. For extended periods both before and after the point of addition, the torque fluctuated around fixed average values which indicated that the drop in torque due to adding i-octane was by about 20 g·cm.

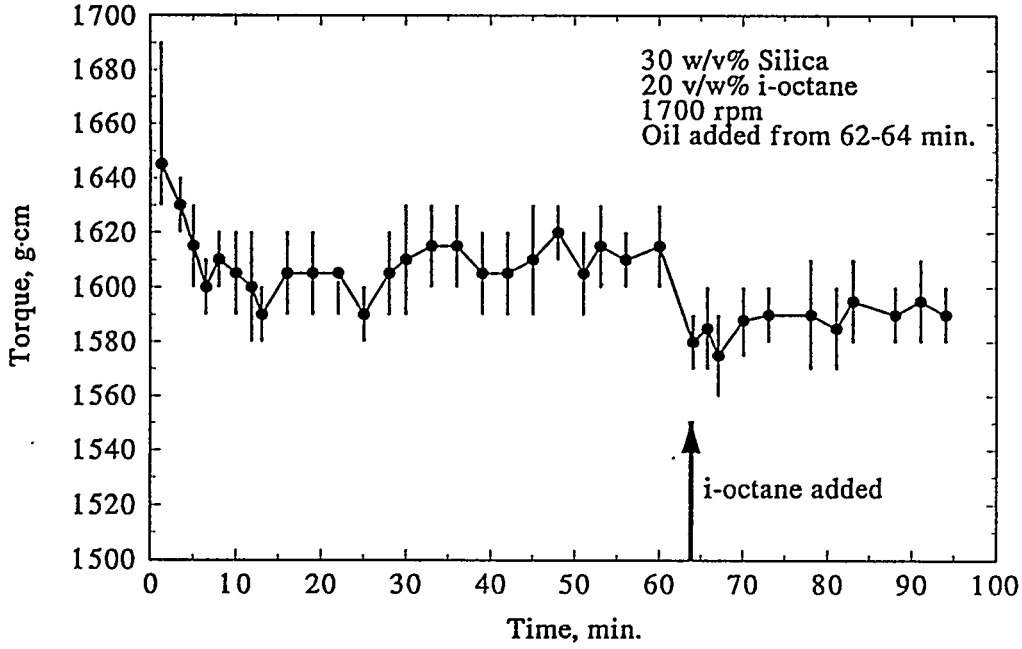

Figure 20. Effect on agitator torque of adding i-octane to a suspension of silica particles in degassed water.

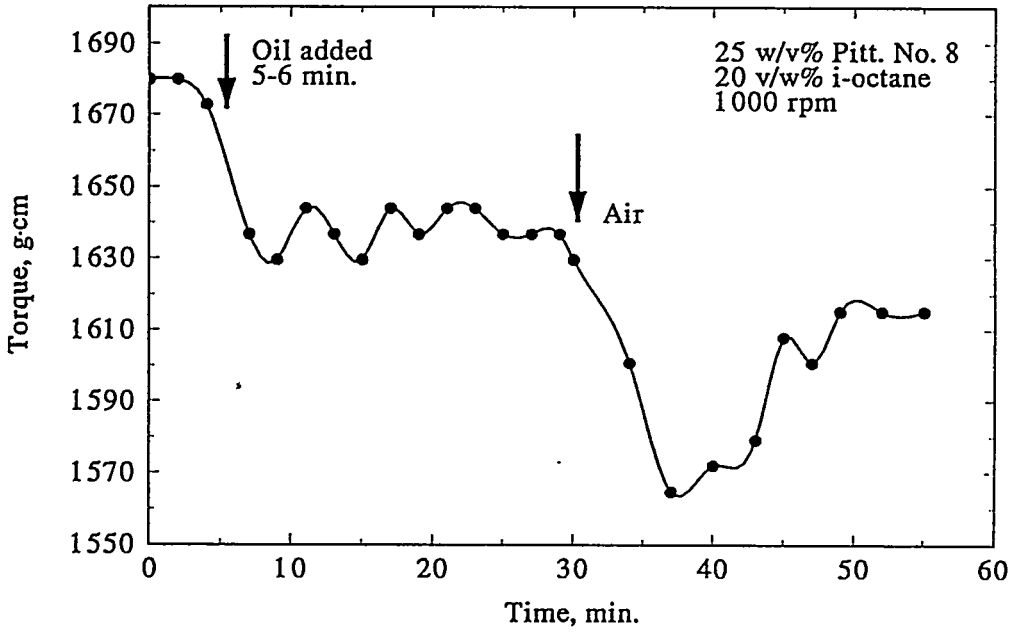

Figure 21. Observed changes in agitator torque caused by introducing i-octane and air into a suspension of Pittsburgh coal in degassed water and by the resulting agglomeration of coal particles.

In the next experiment, a suspension of Pittsburgh No. 8 coal containing 25 w/v% solids was prepared using degassed water. For an agglomeration test the material was agitated at 1000 rpm, and after 5-6 min. i-octane was introduced at a rate of 20 v/w%. The agitator torque dropped immediately and then remained relatively steady until air was introduced (see Figure 21). As soon as air was added, the torque dropped again. Within 7 min. the torque was a minimum and then began to increase due to particle agglomeration. After 20 min. from the time air was introduced, the torque appeared to approach a constant value indicating completion of the agglomeration process. Interestingly, the final torque value was less than the value of the torque before air was introduced.

For the next two experiments a greater solids concentration and larger stirring rate were employed to see if these changes would result in a greater increase in agitator torque when the particles were agglomerated. Pittsburgh No. 8 coal in a solids concentration of 50 w/v% and a stirring rate of 1700 rpm were used for both tests. Also the coal was suspended in degassed water and the particles were agglomerated with 20 v/w% i-octane in both tests. However, in the first test no air was added to the system whereas in the second test 25 cm^3 of air was introduced. The results of these tests, which are given in Figures 22 and 23, indicate a much greater increase in agitator torque resulting from particle agglomeration than recorded in Figure 21. Therefore, the combination of a larger solids concentration and higher stirring speed did have the desired effect. The results of the two tests at the higher solids concentration differed from each other with respect to the onset of agglomeration. In the first test when no air was added to the system, agglomeration was delayed 15 min. after i-octane was introduced. In the second test agglomeration started within 3-4 min. after air was introduced.

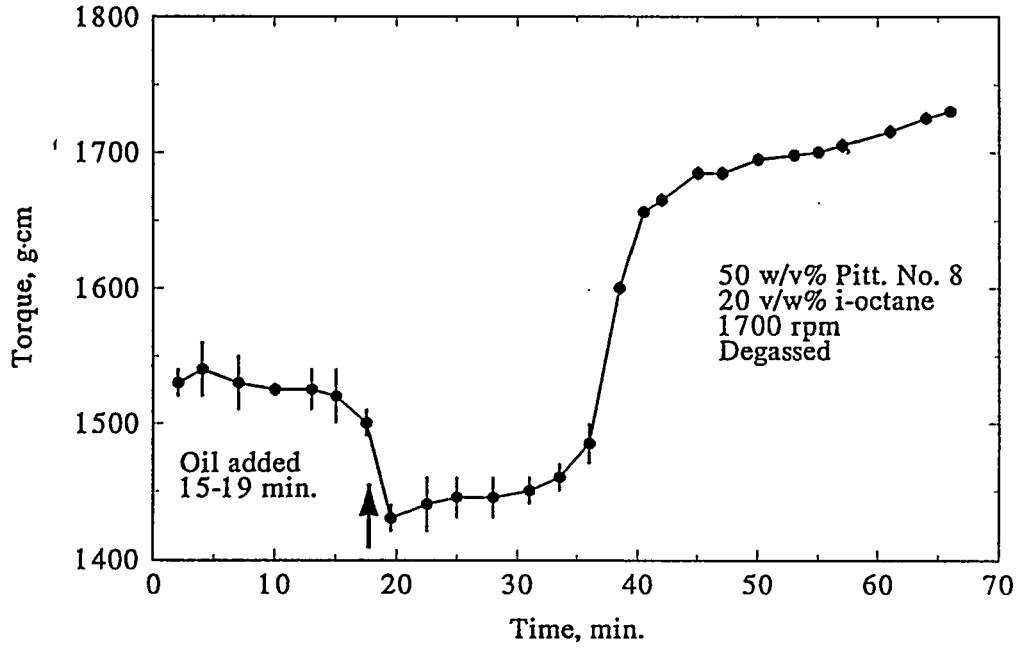

Figure 22. Change in agitator torque produced by oil agglomeration of a large concentration of Pittsburgh coal in degassed water.

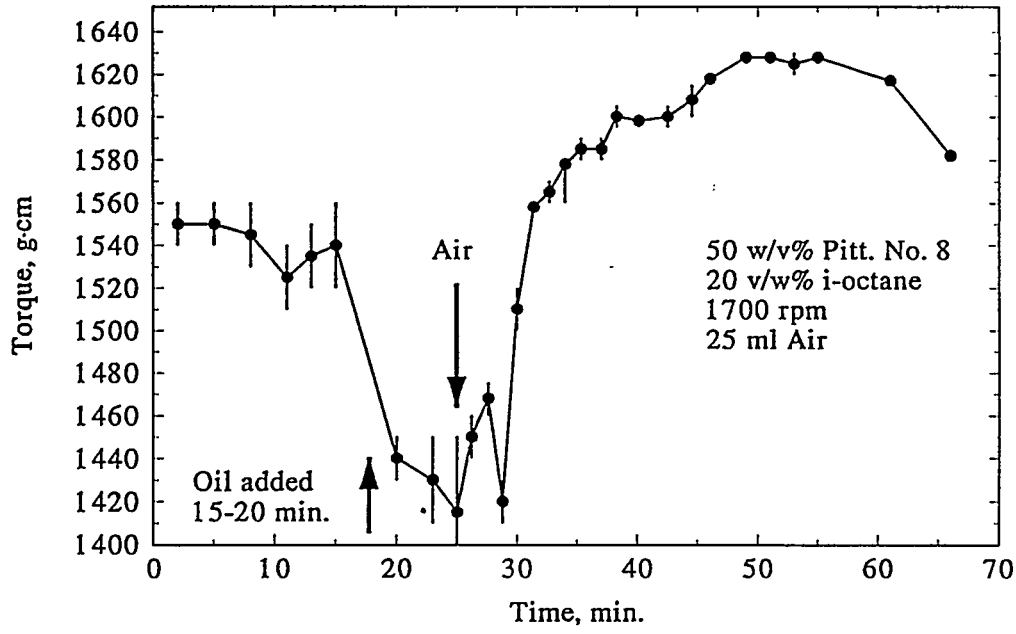

Figure 23. Effect of adding air on oil agglomeration of a large concentration of Pittsburgh coal in degassed water.

In the next two experiments the i-octane concentration was reduced to 10 v/w%, but otherwise the conditions were the same as for the last two tests. In the first test no air was added to the system, and although the agitator torque dropped following the addition of i-octane, further change indicating particle agglomeration did not appear (see Figure 24). In contrast after 25 cm^3 of air was introduced in the second test, there was a fairly rapid rise in agitator torque signifying agglomeration (see Figure 25). However, in comparison to the results shown in Figure 23 which were obtained with 20 v/w% i-octane, the overall increase in agitator torque produced by 10 v/w% i-octane was considerably smaller.

Upper Freeport coal was used for the last two experiments. Since this material was more hydrophobic than the Pittsburgh No. 8 coal, there was a noticeable difference in the results. Whereas only small agglomerates and bulky flocs were produced in the previous tests, relatively large spherical agglomerates were produced with Upper Freeport coal. Also the change in agitator torque due to the production of spherical agglomerates was relatively large even for a solids concentration of 25 w/v% (see Figures 26 and 27). In the first test when no air was added to the system which had been degassed, there was a 10 min. delay after i-octane was introduced before the agitator torque started increasing as a result of agglomeration. For the second test the system was not degassed. After introducing i-octane, the agitator torque dropped as noted in previous tests, but almost immediately the torque rose again indicating the onset of agglomeration. Therefore, the presence of dissolved air in the system again seemed to be an important factor in promoting agglomeration.

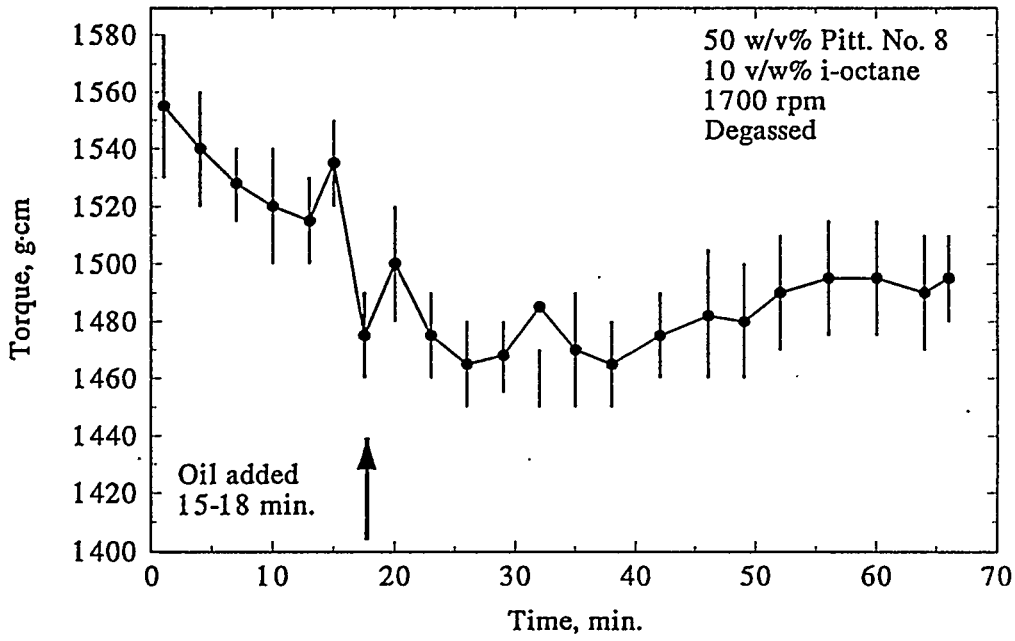

Figure 24. Results of adding 10 v/w% i-octane to a 50 w/v% suspension of Pittsburgh coal in degassed water.

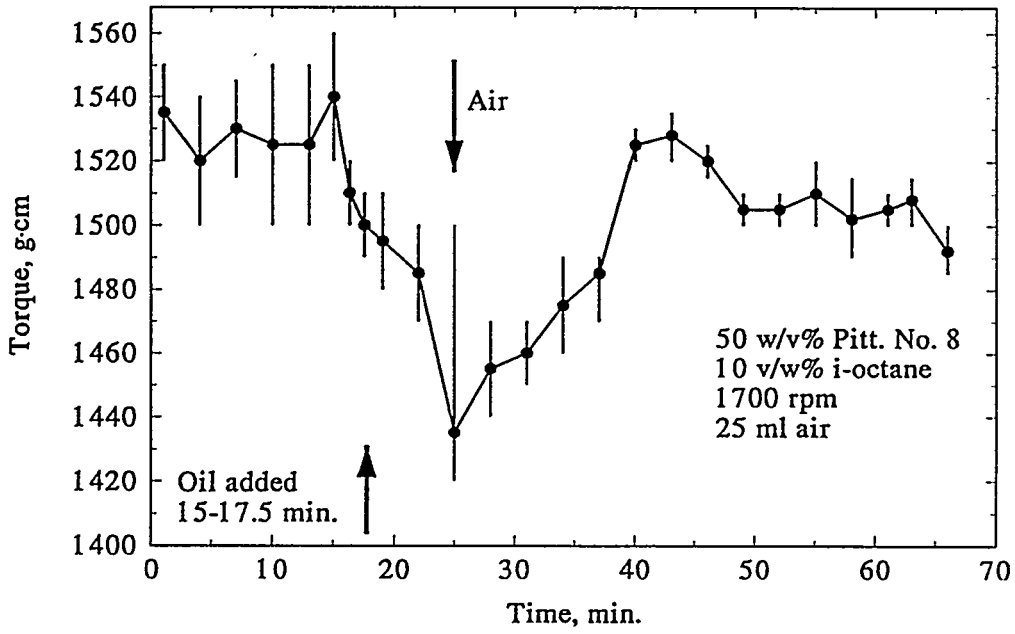

Figure 25. Results of introducing air following the introduction of 10 v/w% i-octane into a 50 w/v% suspension of Pittsburgh coal in degassed water.

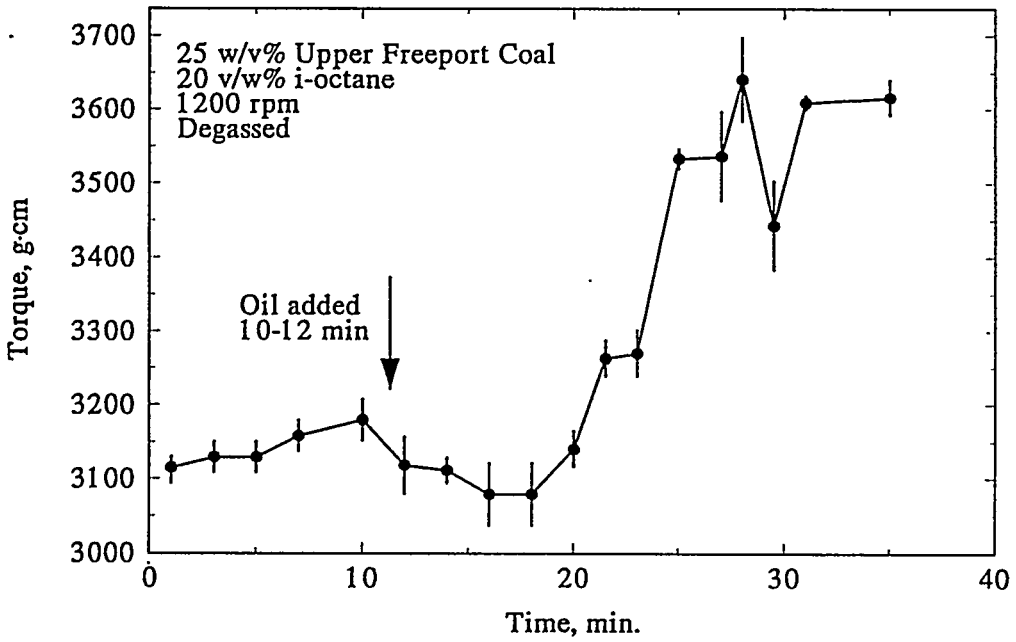

Figure 26. Change in agitator torque caused by spherical agglomeration of Upper Freeport coal suspended in degassed water.

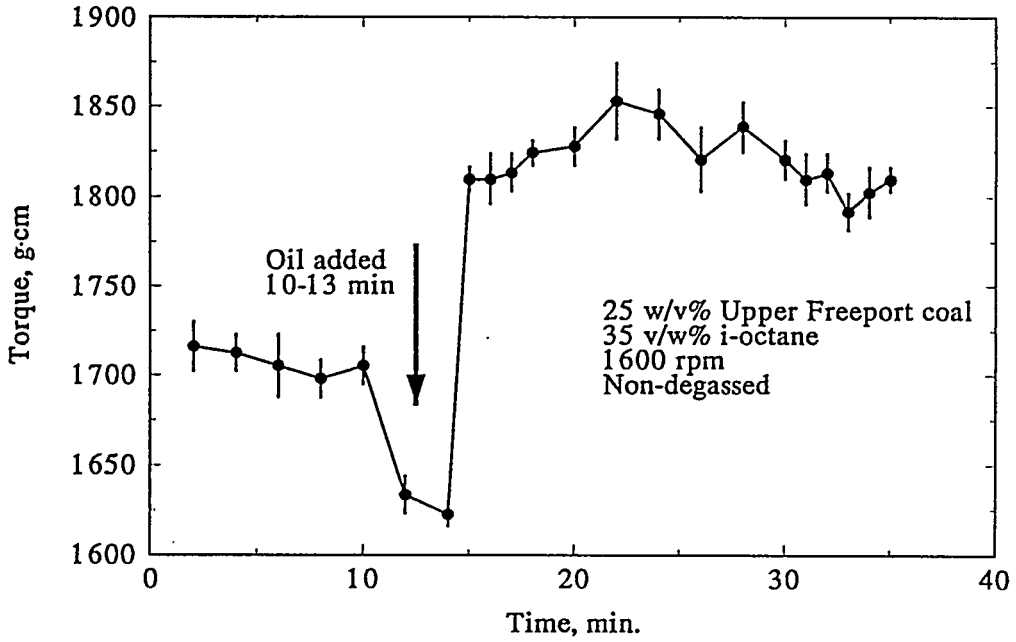

Figure 27. Change in agitator torque caused by spherical agglomeration of Upper Freeport coal suspended in water which had not been degassed.

CONCLUSIONS

The most remarkable result of the preceding series of experiments was the discovery that even a small amount of air can promote the oil agglomeration of coal suspended in water. Apparently even the air which is dissolved in water in equilibrium with the atmosphere at room temperature and pressure is sufficient to affect the agglomeration process. However, it appears that the air must be present as a separate phase. Using a light hydrocarbon such as heptane as an agglomerant seems to displace air dissolved in water so that the air becomes available to promote agglomeration. Adding additional amounts of air to the system increases the effect. Consequently the agglomeration rate is proportional to the quantity of air added up to some limit which has not been established. The agglomeration rate also increases with increasing agitator speed up to some limit.

For small concentrations of suspended solids the progress of agglomeration can be monitored by measuring the turbidity of a suspension because the turbidity provides a measure of particle concentration, and as a batch agglomeration experiment proceeds the concentration decreases. However, the method is not applicable for solids concentrations which exceed a few percent. Another technique which provides an indication of changes that take place during a batch agglomeration test involves measuring agitator torque. This method was shown to be applicable for monitoring particle agglomeration providing the solids concentration is 25 w/v% or more. The method is also dependent on agitator speed.

FUTURE PLANS

While it has been shown that only small amounts of air are required to promote oil agglomeration of coal particles, the mechanism is not well understood which inhibits the development of a mechanistic model for analyzing the kinetics of the process. Therefore, further consideration will be given to possible mechanisms. At the same time consideration will also be given to the development of a semiempirical model for representing and analyzing the kinetics. A suitable mathematical model is needed in order to understand and correlate the effects of particle concentration and other parameters on the rate of agglomeration.

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