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Development of a Gas-Promoted Oil Agglomeration Process.

Air-Promoted Oil Agglomeration of Moderately Hydrophobic Coals.
2. Effect of Air Dosage in a Model Mixing System

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Abstract

In Part I of this series of papers, it was shown that a definite amount of air had to be present in a laboratory mixing unit which produced a moderate shear rate in order to form compact, spherical agglomerates in an aqueous suspension of moderately hydrophobic coal using heptane or hexadecane as an agglomerant. In this paper, the effects of different amounts of air including dissolved air are discussed. The results indicate that a small amount of air will trigger the process of agglomeration, and even the air dissolved in water under equilibrium conditions at room temperature and pressure is sufficient to promote agglomeration provided it is released from solution.

Introduction

In a selective oil agglomeration process for cleaning coal, fine-size particles are suspended in water and treated with a water-immiscible hydrocarbon which can range from pentane to heavy fuel oil (1-3). Vigorous agitation is applied to disperse the oil and to produce frequent contacts between oil-coated particles. Under proper conditions compact, spherical agglomerates are produced which are held together by oil bridges between particles. The agglomerates can be

separated and recovered from the unagglomerated mineral matter by a simple screening operation.

The importance of having air present in such a process was reported in Part I of this series of papers (4). In that work moderately hydrophobic Colchester Seam coal from Illinois was agglomerated with either heptane or hexadecane in an improvised laboratory mixing unit which was not representative of standard industrial practice. Nevertheless it was shown that by adding a small amount of air to an agitated suspension of coal particles which had been dosed with heptane it became possible to produce compact, nearly spherical agglomerates in a reasonable time, whereas without added air only small flocs and flakes were produced in the same time frame.

In the work described below, another moderately hydrophobic coal (Pittsburgh No. 8 Seam from Ohio) was agglomerated in a small, scale model mixing system which was representative of a type of mixer that is widely used by industry. One of the principal components of the system was a cylindrical tank with a flat bottom and flat cover and it included an agitator with a Rushton-type turbine impeller and accurate means for controlling and indicating speed. The volume of the tank was 2870 cm^3 which was six times the volume of the mixing system used previously. Since suspensions with small particle concentrations were employed as before, it was possible to monitor the progress of agglomeration during a batch test by observing the change in turbidity of the suspension.

A number of batch agglomeration tests were conducted to determine the effects of air dosage and agitator speed on the apparent rate of agglomeration of Pittsburgh No. 8 coal. Some tests were conducted with degassed suspensions in order to establish the possible effect of dissolved air. For most tests heptane was employed as an agglomerant.

Materials and Experimental Methods

A sample of Pittsburgh No. 8 Seam coal from Belmont County, Ohio, was used for this study. The sample had an ash content of 27.8% and total sulfur content of 5.05% on a dry basis. The supplier characterized the coal rank as high volatile A bituminous. Probably because of its high ash content, the coal appeared only moderately hydrophobic. The coal was prepared by first crushing with a jaw crusher and roll mill. The material was then divided by riffling into small portions which were ground in a stirred ball mill so that more than 99% was finer than 37 μm. The ground material was partially dewatered to produce a wet paste containing about 56% solids, and the paste was stored until needed in a refrigerator set at 5°C. The particle size range of the ground coal was 1 to 10 μm as determined by computerized image analysis.

Pure n-heptane was used as an agglomerant in most tests. It was obtained from Burdick and Jackson Laboratories Inc. which indicated that the material had been distilled in glass and had a normal boiling point of 98-99°C. Hexadecane (99%) and squalane (99%) obtained from Aldrich Chemical were used as agglomerants in a few tests. According to the supplier, the hexadecane had a normal boiling point of 287°C and the squalane a boiling point of 176°C at a pressure of 0.05 mm Hg. For all agglomeration tests, coal particles were suspended in deionized water having a resistivity of 17.9 megohm·cm.

The mixing system used for conducting agglomeration tests consisted of a covered cylindrical tank with an agitator and an instrument for measuring the turbidity of the suspension being agglomerated. The tank which had an inside diameter of 15.24 cm and height of 15.24 cm was fitted with four vertical baffles. Each baffle projected inward a distance of 1.27 cm from the wall. The top and bottom of the tank were slightly concave to facilitate drainage and/or venting of material. The net volume of the tank after it was fitted with baffles and an agitator was 2870 cm^3. The walls of the tank and baffles were made of Plexiglas while the top and bottom were made of stainless steel. The variable speed agitator was operated by a motor control unit which indicated shaft speed, and it was fitted with a 5.08 cm diameter, Rushton-type turbine impeller that had six, vertical flat blades mounted on a horizontal disk. The impeller was mounted 2.54 cm above the bottom of the tank on a vertical shaft located at the tank centerline.

The turbidity of a suspension undergoing agglomeration was determined with a photometric dispersion analyzer which was built by Rank Brothers Ltd. and designated as a PDA 2000 instrument. For this determination a stream of material was drawn continuously from the mixing tank through a port located in the same horizontal plane as the impeller and conducted to the measuring cell of the analyzer. The stream was returned via a peristaltic pump to the mixing tank where it was introduced through an opening in the top of the tank.

To prepare for an agglomeration test, the mixing tank was partly filled with deionized water, and a measured amount of coal paste was dispersed in the water. For some tests the water was partially degassed first which usually involved subjecting the partly filled system to a reduced pressure (5-6 kPa absolute) for 20 min. at room temperature. After adding the coal paste, the mixing system was topped off with degassed water. Any remaining gas bubbles were removed from the system.

For some agglomeration tests a specific amount of air was introduced before oil was added, whereas for other tests air was introduced after oil was added. Two different methods were employed for adding air to a slurry-filled system. When the volume of air was small (e.g., 2.5 cm^3), the air was injected near the impeller by using a syringe with a long needle, whereas larger volumes were introduced by withdrawing a measured amount of slurry which was replaced by an equal volume of air.

When air was introduced before oil, the coal suspension was agitated for 3 min. at a given speed after air was introduced. A measured quantity of oil was then injected with a syringe, usually in a single dose. As agitation was continued at the same rate, the progress of agglomeration was monitored by observing the change in turbidity of the suspension. As the particle combined to form agglomerates, the particle concentration decreased which reduced the turbidity of the suspension. Since the reduction in turbidity was reflected by an increase in the output signal from the photometric dispersion analyzer, the rate of increase of the output signal was indicative of the apparent rate of agglomeration (4,5).

When oil was introduced before air, the coal suspension was stirred for 9 min. at a given speed after oil was introduced. A measured quantity of air was then added and the test was continued as described above.

At the start of an agglomeration test, the system was at room temperature. Since no attempt was made to control the system temperature, the temperature rose gradually because of the agitator power input. For an agitator speed of 1500 rpm, the rate of temperature increase was 2.5°C/hr and for an agitator speed of 2400 rpm it was 13°C/hr.

Experimental Results

Preliminary Agglomeration Tests

A preliminary series of agglomeration tests was conducted in which the previously prepared paste of ground coal was first mixed with water which had been partially degassed by applying a reduced pressure. To achieve the results presented in Figure 1, the following conditions were employed in each test: 1 wt.% solids concentration, 20 v/w% heptane (20 ml heptane/100 g coal) concentration, and 1500 rpm agitator speed. In one test no air was added to the partially degassed suspension, and after heptane was introduced the suspension was stirred for almost 2.0 hr. without evidence of agglomeration because throughout this interval the output voltage of the photometric dispersion analyzer remained almost constant. Similar results were observed in another test in which the water used for preparing the coal suspension was degassed first by boiling for 30 min. The water was cooled quickly and used immediately for an agglomeration test. The results were almost identical to those obtained by vacuum degassing. In sharp contrast to these results were the results achieved when a small amount of air was added to a degassed suspension which had been conditioned with heptane for 9 min. As soon as air was introduced, the analyzer output voltage started to rise indicating the onset of agglomeration. Since the slope of the output voltage curve was indicative of the rate of agglomeration, it can be seen that with only 7 cm^3 of added air the rate was fairly rapid. When the volume of air was increased to 15 cm^3, the rate more than doubled. However, increasing the volume of air from 15 to 25 cm^3 had only a slight effect on the rate. It is noteworthy that when another experiment was conducted by agglomerating coal in water which had not been degassed, the results, which are also reported in Figure 1, were similar to those achieved when 7 cm^3 air was added to the degassed system. Therefore, it appeared that even the air dissolved in the water was sufficient to promote agglomeration under some conditions.

Since the preceding results indicated that agglomeration was actually triggered by the introduction of air, further tests were conducted to verify this supposition. The tests were conducted under similar conditions starting with suspensions prepared from degassed water. In each test the suspension was stirred for 5 min. before introducing heptane. After adding heptane, stirring was continued, and after a measured time interval, 50 cm^3 of air was introduced. This interval varied from 5 to 35 min. among the three tests in the series. From the results presented in Figure 2 it can be seen that agglomeration did not take place until air was added, but as soon as it was introduced, agglomeration was rapid. Therefore, air does indeed trigger agglomeration.

Although the results in Figure 1 suggest that even dissolved air could trigger agglomeration, it remained to be seen in what form the air had to be present to initiate agglomeration. There was a possibility that some of the dissolved air would come out of solution due to cavitation when a suspension was agitated vigorously, and indeed when nondegassed water by itself was stirred at 1500 rpm or higher speeds, small gas bubbles appeared. Also it was possible that adding heptane to air-saturated water would force enough air out of solution to promote agglomeration since heptane is slightly soluble in water. Because it was very difficult to detect the presence of small gas bubbles in a coal suspension, an indirect method was used to investigate this possibility. Water which had not been degassed was saturated with heptane, and then the heptane-saturated water was used for an agglomeration test. The results are shown in Figure 3 together with the results of previous tests made either with water which had been degassed or with water which had not been degassed. It can be seen that in the test with heptane-saturated water virtually no agglomeration took place during the first 35 min., and then agglomeration proceeded very slowly. Therefore, the results were similar to those obtained with water which had been degassed by applying a vacuum. Apparently, heptane is capable of displacing enough air from solution to affect the process of agglomeration.

A further indication that the displacement of air from solution was involved in triggering agglomeration resulted from agglomeration tests with other hydrocarbons including hexadecane and squalane. Water which had not been degassed was used for these tests, and no additional air was added to the system. The results presented in Figure 4 indicate that the rate of agglomeration with either hexadecane or squalane was very slow compared to that with heptane under the same conditions. Since the solubility of hexadecane and squalane in water is much lower than that of heptane in water, it seems likely that these hydrocarbons would displace less air from water. Consequently, in tests with the higher molecular weight hydrocarbons less air came out of solution to promote agglomeration than in the test with heptane.

The preceding experiments showed that enough air was dissolved in water at room temperature and pressure to promote the agglomeration of a moderately hydrophobic coal in low concentration with heptane. Additional experiments were conducted to see whether the same amount of air was sufficient to promote the agglomeration of larger solids concentrations. The results in Figure 5 indicate that with an agitator speed of 1500 rpm the onset of agglomeration was delayed greatly when the solids concentration was increased from 1 to 4 wt.%. Therefore, an increase in solids concentration seemed to require a corresponding increase in the amount of air present. However, the need for more air became less apparent when a higher agitator speed was employed (see Figure 6). With a speed of 2000 rpm or more the agglomeration of a suspension with 4 wt.% solids started within 10-20 min. after heptane was introduced compared to a delay of 140 min. or longer at 1500 rpm.

Effects of Air Dosage and Agitator Speed

Since air seemed to play a key role in the agglomeration process, further experiments were conducted to determine the effect of air dosage on the apparent rate of agglomeration. For these experiments water which had not been degassed was used, and in most cases a measured amount of air was added to the system initially. The coal suspension was stirred subsequently for 3 min. whereupon a known volume of heptane was added. The results of a series of experiments in which the air dosage was varied while employing a solids concentration of 1 wt.% and stirring speed of 1500 rpm are shown in Figure 7. It can be seen that the apparent rate of agglomeration increased with increasing air dosage. However, the effect of air dosage was nonlinear since the rate did not increase in direct proportion to the volume of air added.

Another series of experiments carried out with a solids concentration of 4 wt.% and a stirring speed of 1500 rpm produced similar results (see Figure 8). It is noteworthy that with only 10 cm^3 of added air, agglomeration started much sooner than was observed before (Figure 6) when only dissolved air was present initially. Also it is apparent that the agglomeration rate increased markedly when the air dosage was increased from 50 to 200 cm^3. Therefore, with a solids concentration of 4 wt.% the system was capable of utilizing a larger quantity of air effectively than with a solids concentration of 1 wt.% where a similar increase in air dosage had little effect on the apparent rate.

To determine the effect of agitator speed on the rate of agglomeration when air is present, two series of agglomeration tests were carried out, one with 1 wt.% solids and another with 4 wt.% solids. In both cases 50 cm^3 of air was introduced initially. The results presented in Figures 9 and 10, respectively, show that for an agitator speed of 1250 rpm or higher the apparent rate of agglomeration increased with increasing agitator speed. However, the increase in rate produced by increasing the speed from 2000 to 2400 rpm was very small, at least for a solids concentration of 1 wt.%. It can also be seen that for an agitator speed of 1000 rpm the rate of agglomeration was very low. At this speed little if any air was drawn from the surface into a suspension by stirring. Consequently, the quantity of air present in the suspension was insufficient to promote agglomeration.

The preceding results indicate that both agitator speed and the amount of air influence the onset and rate of agglomeration in a complex way. Also while it would be tempting to compare the results of Figures 7 and 8 or of Figures 9 and 10 to infer something about the effect of solids concentration on the rate of agglomeration, the inference would be invalid because the slope of the curves shown in these diagrams is only an approximate indication of the rate, and it does not account fully for the complex relationship between the rate of agglomeration and the rate of change of turbidity. These complex issues and a more detailed discussion of the kinetics of agglomeration which accounts for the effect of particle concentration on the rate of agglomeration will be the subject of future papers.

Conclusions

The process of agglomeration of a moderately hydrophobic coal with heptane in an aqueous suspension is triggered by a small amount of air present as a separate phase. The quantity of air required to trigger agglomeration depends on solids concentration and the rate of agitation. More air is required for a higher solids concentration than for a lower concentration, and less air is required with a higher agitator speed than for a lower speed. The rate of agglomeration also depends on the quantity of air present as well as agitator speed. While the rate of agglomeration at first increases with increasing levels of either parameter, it eventually stops increasing and is unaffected by further increases in either parameter.

Acknowledgement

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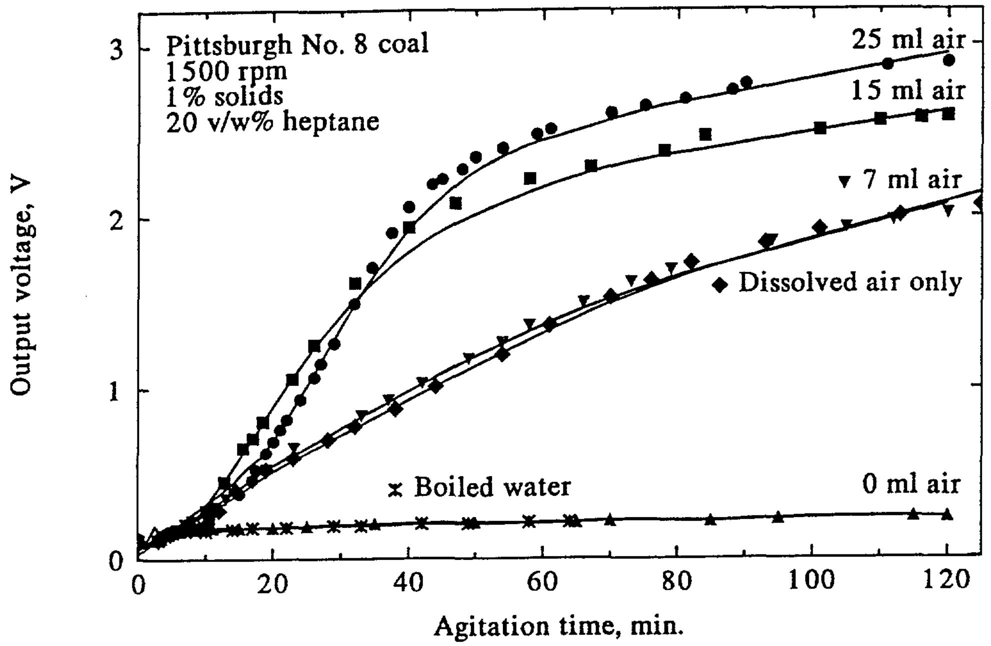
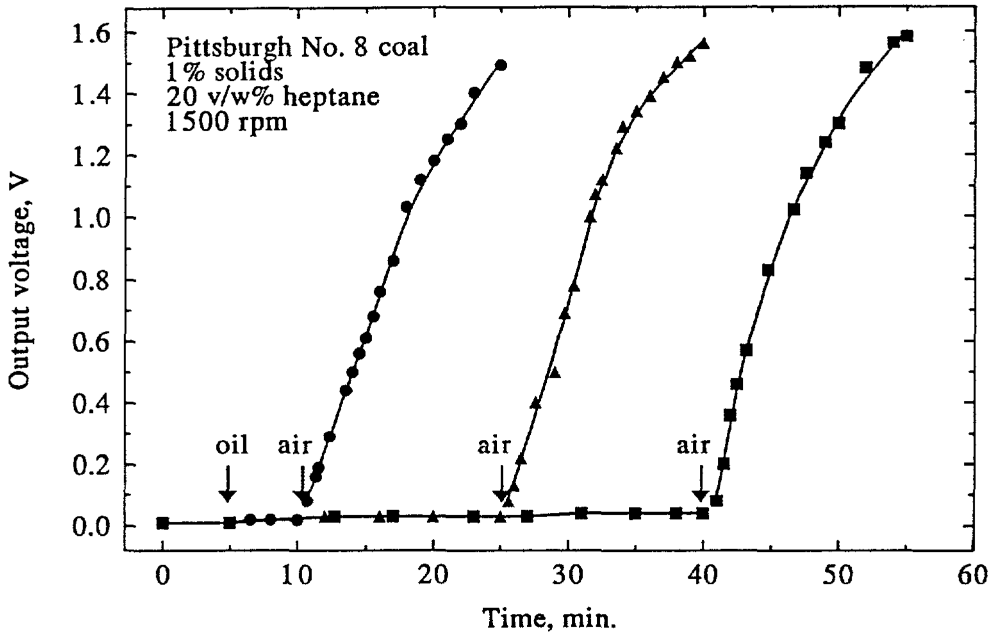
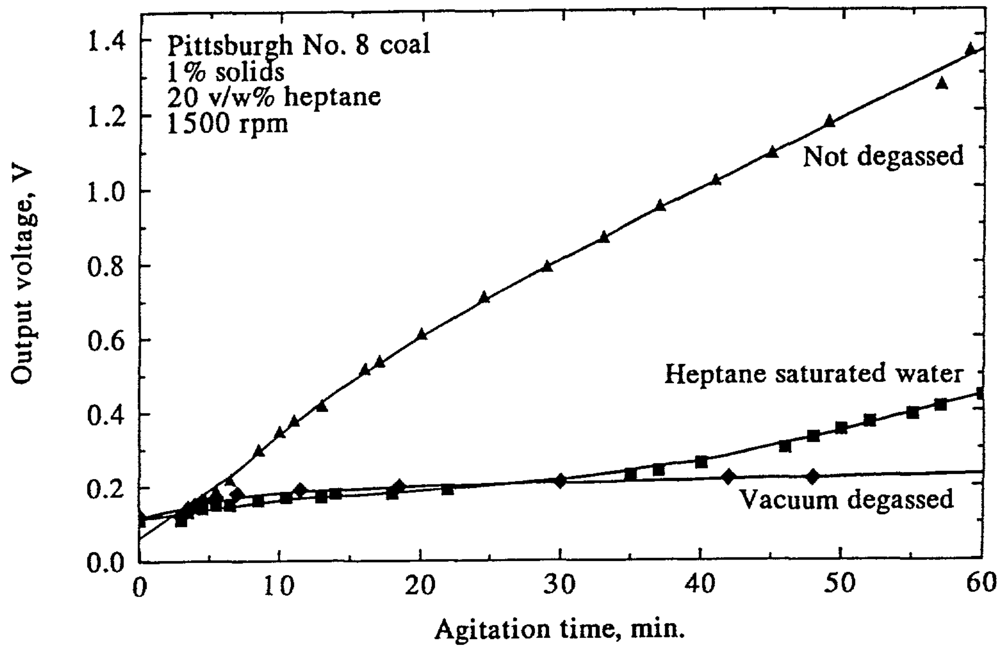


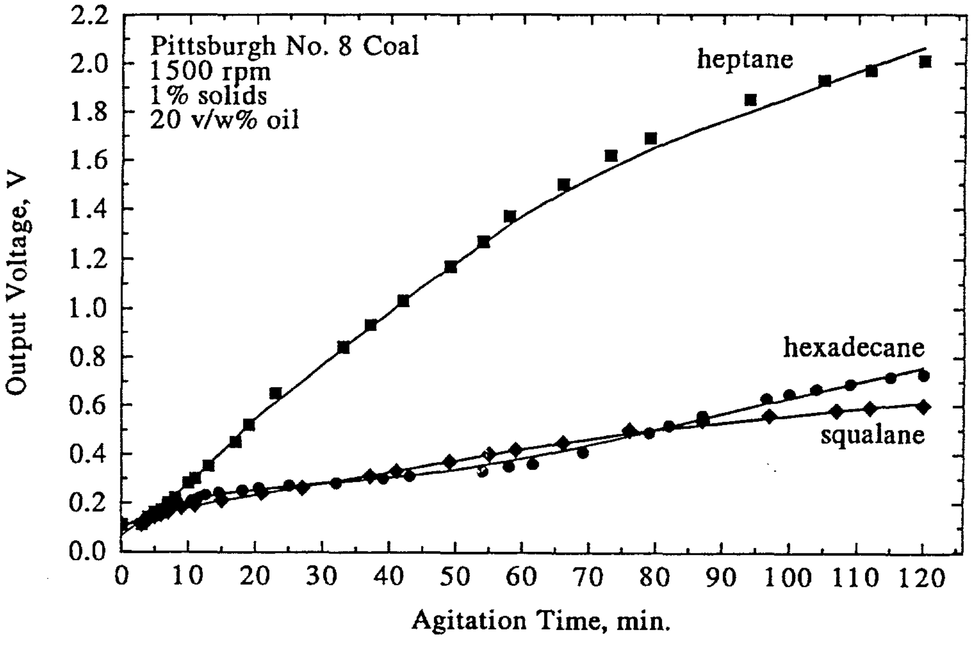
1. Results of agglomeration tests with coal suspended in water which had been degassed followed by the introduction of the indicated amount of air. Also shown are the results of a test made with water containing only dissolved air and a test made with boiled water.



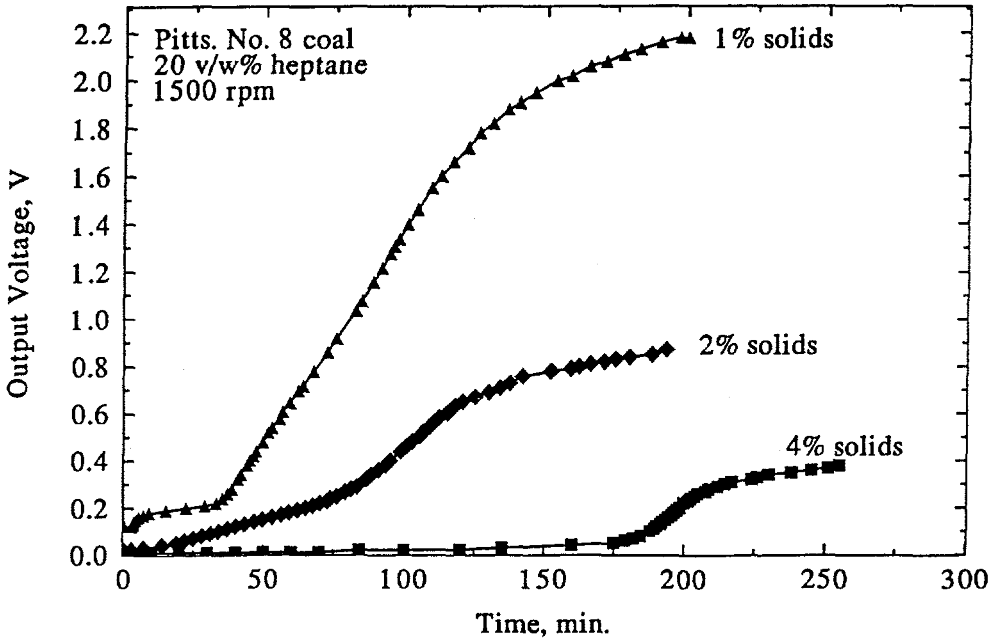
2. Results of three agglomeration tests in which 50 cm^3 of air was added at either 5, 20, or 35 min. after introducing heptane.



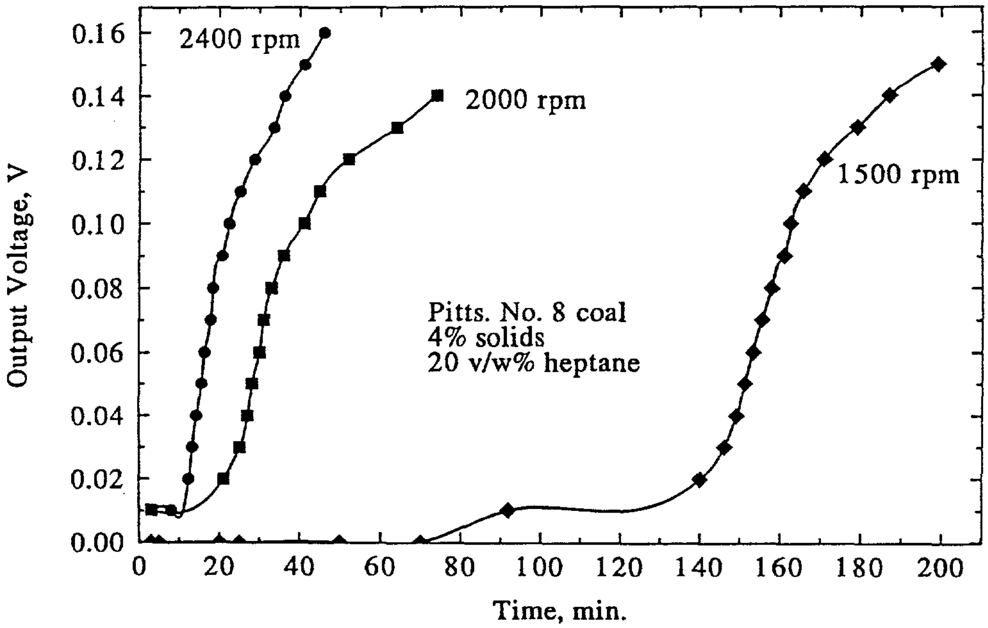
3. Results of agglomeration tests with coal suspended in water which had received different treatments.



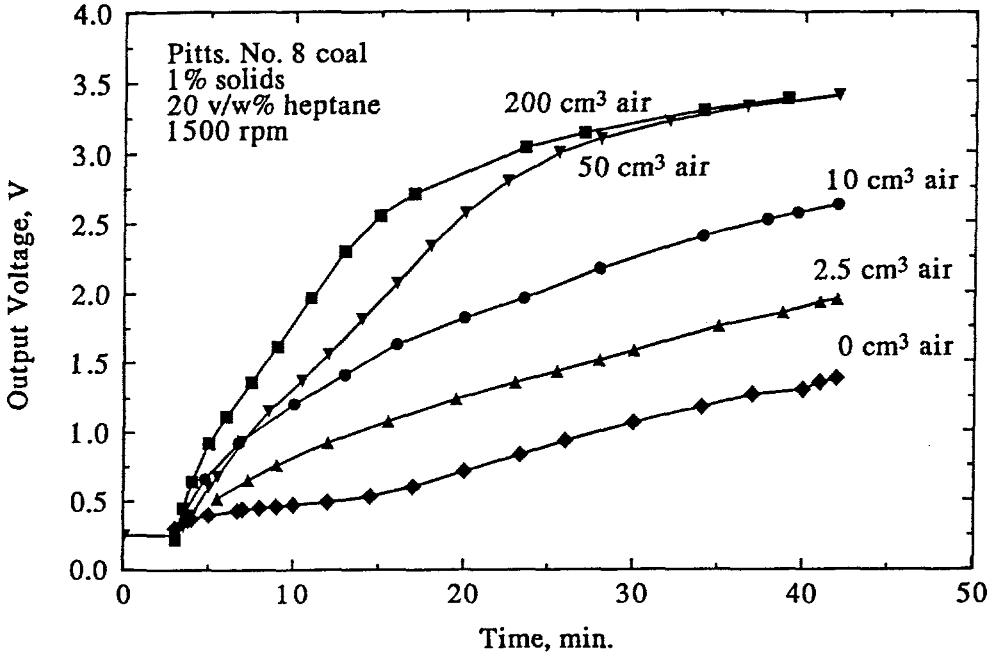
4. Results of treating coal with different agglomerants while suspended in water which had not been degassed.



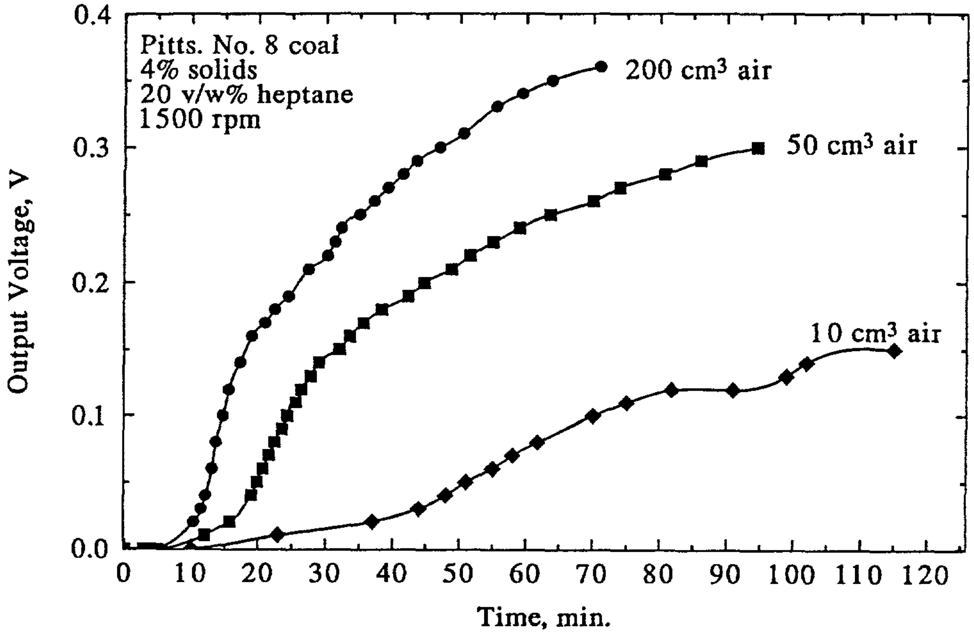
5. Results of agglomeration tests conducted with different solids concentrations. in nondegassed water.



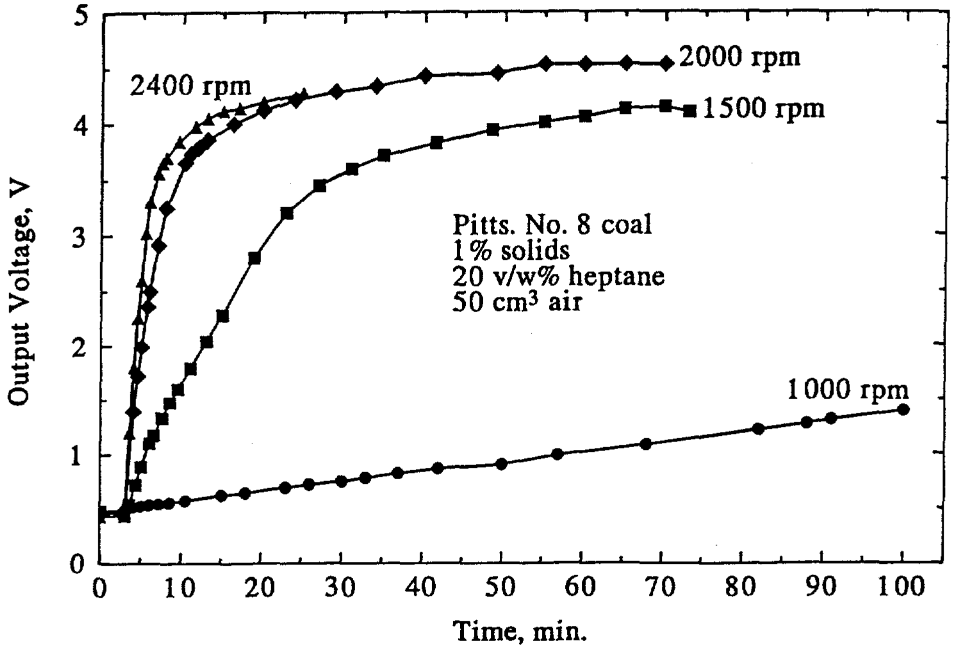
6. Effect of agitator speed on agglomeration of 4% solids suspensions in nondegassed water.



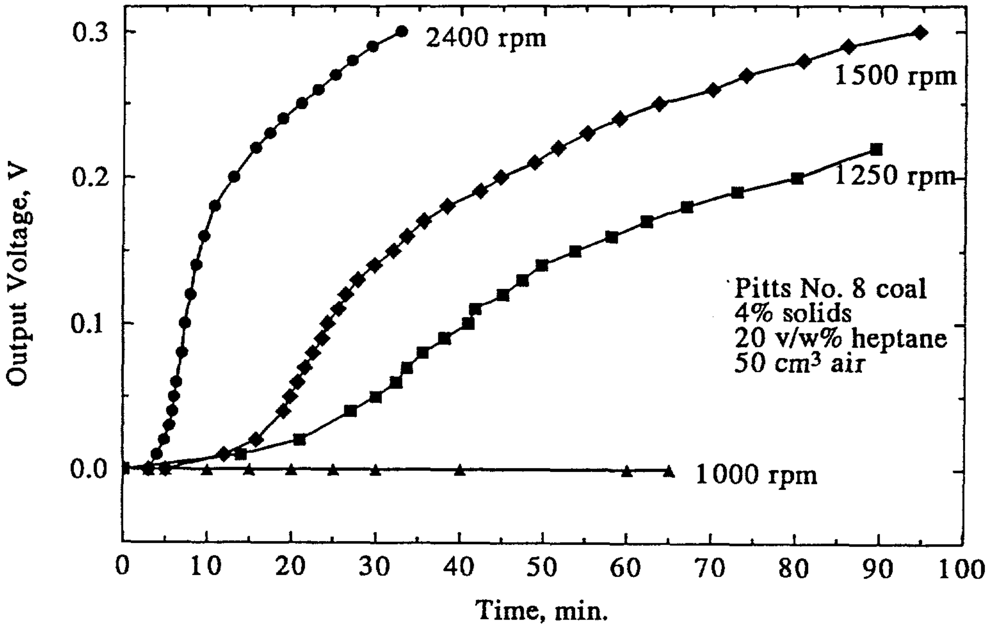
7. Results of agglomeration tests with 1% solids, nondegassed water, and the indicated amount of added air.



8. Results of agglomeration tests with 4% solids, nondegassed water, and the indicated amount of added air.



9. Effect of agitator speed on agglomeration of 1% solids suspensions in nondegassed water and with 50 cm^3 of added air.



10. Effect of agitator speed on agglomeration of 4% solids suspensions in nondegassed water and with 50 cm^3 of added air.