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MICROGAS DISPERSION FOR FINE COAL CLEANING

Technical Progress Report for the Period September 1, 1980-February 28, 1981

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U. S. DEPARTMENT OF ENERGY

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INTRODUCTION

The purpose of this project is to develop a method of cleaning fine coal by flotation using very small microbubbles now known as Colloidal Gas Aphrons (CGA) and previously known as Microgas Dispersions (MGD). It was thought that MGD was not sufficiently descriptive of the nature of the small bubbles, and, hence, the change was made. The objectives of the past six months of investigation were as follows:

1. a fundamental study of the properties of CGA, which involved (i) a study of the stability of the bubbles generated with several frothers that are currently used in the mineral industry, (ii) a study of the charge on the bubbles, and (iii) a microscopic inspection of the bubbles during flotation,
2. a preliminary investigation of the flotation characteristics of coal, and
3. construction of an automatic batch flotation machine, similar to the one described by Miller (1980).

It was hoped that two graduate research assistants, one from the Chemical Engineering Department and one from the Mining and Minerals Engineering Department, as well as a half-time technician would assist the principal investigators in carrying out the project. However, we experienced a difficulty in recruiting a good chemical engineering graduate student, and, hence, have hired a full-time technician. This has proven to be much more satisfying considering that graduate students are not very productive in the first year due to course work. We also had problems with the purchase of equipment; the ordering of circulating pumps (1 HP Eastern Pump) took several months as it went through a bidding procedure, and when they did finally arrive, the parts were broken. As such, most of the data presented in the report was obtained with bubbles generated by using a less powerful pump.

RESULTS

Generation of CGA Bubbles

The CGA bubbles were generated by using the apparatus schematically represented in Figure 1. A frother solution placed in the reservoir (B) is pumped through the glass aspirator (A) by means of a centrifugal pump (D). Meanwhile, a pressurized gas (nitrogen in the present work) enters through the gas inlet tube (E). The gas leaks through the roughened ground glass joint of the aspirator to form bubbles which are dispersed through the liquid. The CGA thus formed is continuously recirculated until the volume of liquid reaches a constant level. It is then tapped from the stopcock C and transported for examination under microscope or use in a flotation cell. The stopcock F permits the frother solution to be drained after each experiment.

The pump used in the present work was a magnetic drive pump (Fisher Scientific Co., Model MD-80) with a 1/3 HP motor. Its casing and impeller were made of polypropylene for corrosion resistance.

Stability of CGA Bubbles

There was some initial difficulty in choosing which criteria to use in assessing the stability of CGA. Previously, the method employed was to tap a fixed volume of CGA from stopcock C (Figure 1) into a measuring cylinder and measure the time it took to develop a clear solution. This was found to be impractical because when the bubbles (gas-aphrons) reached the surface, they formed a classical froth, and this was quite durable, its life bearing no relation to the stability of CGA. Another method was, therefore, chosen. A fixed volume (100 ml) of CGA was put into a measuring cylinder and then, as the bubbles rose, a rising boundary separating the clear solution from the cloudy aphron suspension was observed. The time required for the boundary to reach finite volumes marked on the cylinder was measured, and this was plotted against volume.

Figure 2 shows one such plot, in which the stabilities of CGA's produced with various frothers are shown. Each CGA was generated by using 1 l solution of 1 ml/l frother concentration. It shows that Dowfroth 400 produced the most stable CGA and Dowfroth 200 the least. Among the Dowfroth homologues, the stability of CGA decreased in the order of decreasing molecular weight. MIBC

Figure 1 A schematic representation of the apparatus generating MGD bubbles

Figure 2. Stability of CCA's produced with various frothers.

has lower molecular weight than Dowfroth 200, but produced a more stable CGA. This may be contributed to the differences in their basic structural units.

Figure 2 was used in determining the half life, $\lambda/2$ of CGA. When all the bubbles and froth had eventually broken, the total volume of clear water was measured. The time taken for the bubbles to rise to half of that volume is defined as the half life, which can be read off the graph shown in Figure 2. Table 1 lists the half lives thus obtained. The half lives of the CGA's produced by using these frothers are much shorter than those obtained by using long chain surfactants. However, preliminary results obtained by one of the principal investigators showed that CGA's made with long chain ionic surfactants were not suitable for coal flotation, as ash-forming minerals floated with the coal.

TABLE I - The Half Lives of CGA's Produced by Using Various Frothers

<u>Frother</u>	<u>Total Volume of Clear Water (ml)</u>	<u>Half Life (second)</u>
DF 400	81.5	136
DF M-150	80.5	113
DF 250	70.5	106
MIBC	91	86
DF 200	91	69

Figure 3 demonstrates the stability of CGA's made with Dowfroth 400 at various concentrations. In each experiment 12 of frother solution was used. Stability is shown to steadily improve with increasing frother concentration. Similar measurements were made with MIBC with the results shown in Figure 4. Unlike with Dowfroth 400, stability did not seem to improve with increasing frother concentration beyond 4 ml/l.

Streaming Current Measurements

Perhaps the most difficult experimental determination thus far was the determination of the nature of the charge on the aphron. It is of fundamental importance to know this before planning a separation, as it is desirable to

Figure 3. Stability of CGA as a function of frother (Dowfroth 400) concentration.

Figure 4. Stability of CGA as a function of frother (MIBC) concentration.

have aphrons charged the same as the ash constituents so that the ash can be repelled by the aphrons and not be brought up by them.

Having a Rank Brothers Particle Electrophoresis Apparatus, Mark II, we thought we could determine the charge on colloidal aphrons in exactly the same way as is done on colloidal particles, and considerable time was spent on this. We found, however, that the CGA bubbles rose too quickly to take meaningful mobility measurements. It was quite clear that using this electrophoresis instrument for determining the charge on the aphrons would necessitate considerable modification in design of the cell and would be a research project in itself. It was, therefore, decided that this was not the objective of this project and we would have to use some other method.

The method chosen was one developed by Dibbs, Sirois and Bredin (1974). In this method, bubbles are allowed to stream past electrodes and the streaming current is measured. Figure 5 shows the apparatus used in the present work. The glass apparatus was kindly loaned to us by the authors of the paper noted above. There was some initial difficulty in generating reproducible results, but it was discovered that if the Ag/AgCl electrodes were permitted to stabilize for 12 hours, reproducible results could be obtained.

Figure 6 illustrates the method of determining the streaming current of bubbles. The current was measured in 4.05×10^{-5} moles/l dodecylamine hydrochloride (DAC) solution as a function of the distance separating the two electrodes. The curve 1 represents the current measured when no bubbles were generated, and the curve 2 represents the current measured when bubbles were generated through the frit. The current generated without bubbles is most likely due to the battery effect of the Ag/AgCl electrode pair. The curve 3 is obtained by subtracting the current without bubbles from the current with bubbles, so that it can represent the current generated solely due to the charges carried by the bubbles. One may observe from Figure 6 that the bubbles generated in 4.05×10^{-5} moles/l of DAC solution are slightly positive when the electrode distance is larger than 15 cm. The negative value at shorter electrode distances is probably due to turbulence. It should be noted that the bubbles generated in the absence of surfactants were negatively charged.

Figure 5. Streaming Current Apparatus.

Figure 6. Variation of streaming current with electrode separation in dodecyl amine hydrochloride (4.05×10^{-5} moles/l) solution.

Figure 7 shows the streaming current of the conventional bubbles generated by the sparging mechanism at 5×10^{-5} moles/l of sodium dodecyl benzene sulfonate (SDBS) solution. It is clear that the bubbles armoured by the anionic surfactant are negatively charged.

The next set of experiments was conducted with the CGA bubbles generated in 1×10^{-3} moles/l SDBS solution at pH 6.25. The CGA was passed through the bubble column to measure streaming current. The results are given in Figure 8, showing that the CGA bubbles generated with anionic surfactant are negatively charged.

The streaming current measurements described in this report were preliminary in nature. More extensive studies will be made by using non-ionic surfactants, since the frothers that are used in coal industry are invariably non-ionic.

Microscopic Examination of Bubbles

Figure 9 depicts the arrangement employed for observing the CGA apfrons. The bubbles passing through the flow-through cell are magnified in the microscope and displayed on the TV monitor. Figure 10 shows the schematics of the flow-through cell. It is designed primarily to examine the bubbles in action during flotation, but it can also be used for other purposes such as measuring the size of bubbles, and examining the oil-films coating the bubble surfaces.

Following is the procedure used in examining the modes of bubble collision and particle capture during flotation. Solution A (Figure 10) is usually distilled water and Solution B is a dilute aqueous suspension of fine graphite particles. These two solutions can be drawn into the flow-through cell in arbitrary proportions by properly manipulating the stopcocks with the vacuum line T open. Once Solutions A and B are introduced into the cell, the vacuum value is switched to B, and stopcock C is opened. This draws a fresh CGA through the tube at the base of the cell. When the vacuum is turned off, the CGA bubbles flow into the cell through the hole at the bottom.

The apparatus is now functioning satisfactorily, and observations have already demonstrated an important distinction between conventional flotation and CGA flotation. In conventional flotation, the bubbles are large compared

Figure 7. Streaming current due to conventional bubbles generated in sodium dodecylbenzene sulfonate (5×10^{-5} moles/l) solution,

Figure 8. Streaming current due to CGA bubbles generated in sodium dodecylbenzene sulfonate solution (1×10^{-3} moles/l).

Figure 9. Depiction of arrangement of flow-through-cell in conjunction with microscope, camera, and television console.

Figure 10. Schematic of Flow-Through-Cell

to the particles and it is possible for particles to penetrate the air/water interface. In CGA flotation, however, the bubbles are very small (only a few microns when a more powerful pump is used) and, hence, are under greater pressure. This will make it difficult for particles to penetrate the films around the small micron-size bubbles. Also, the CGA bubble has, unlike the conventional bubble (or hole in a liquid), an inner and an outer surface with the air encapsulated in a soap shell. This is probably another reason why the particles would have difficulty in penetrating the bubble surface.

It has been observed, using graphite powder as a model hydrophobic solid before proceeding to look at coal itself, that the particle either hangs onto the bubble by attachment at just one point or is held between a cluster of bubbles. This observation immediately gives us two important criteria for fine particle flotation. Firstly, the flotation must be done under quiescent conditions. Otherwise, the one-point attachment between particle and bubble will be destroyed very easily. Secondly, the formation of a stable froth is essential to prevent the particles from falling back into the pulp once lifted to the surface by bubbles. Another important observation was that the small bubbles appear to induce floc-formation by a bridging mechanism. The bubble-particle aggregates were very stable, lasting hours unbroken. This property will be exploited extensively in actual flotation tests.

Flotation Characteristics of Coal as a Function of Particle Size

The difficulty of floating very fine and very coarse coal particles is well recognized, but the critical sizes below and above which the flotation becomes difficult are not known. It was, therefore, decided to determine the flotation characteristics of clean coal as a function of particle size.

The coal sample used in the present work is from the Jawbone seam. The run-of-mine sample was taken from the Hurricane Creek Mine of Clinchfield Coal Company, Dante, Virginia, and has been kept under a nitrogen atmosphere to minimize oxidation. The run-of-mine coal sample assayed 24.4% ash and 0.59 % sulfur. The sample was crushed and screened to obtain a -1/4 inch + 10 mesh fraction, which was subsequently cleaned of its ash by heavy medium separation at a specific gravity of 1.30. Magnetite was used as the dense

medium, and care was taken to remove the magnetite particles from the clean coal sample by repeated washings with water. The clean coal sample was crushed and pulverized with an agate mortar and pestle and then screened to obtain various size fractions. To obtain samples of -200 mesh fractions, the coal was further pulverized with a microanalytical mill (Tekmar A-10). Each size fraction, thus obtained, was stored in a sample vial and stored in a vacuum desiccator over silica gel.

The flotation tests were conducted by using the apparatus shown in Figs. 11 and 12. The glass flotation cell has the design features similar to the Flotaire cell, recently commercialized by the Deister Concentrator Company. It is designed to use 350 ml of water in each experiment. In the present work, a 3 grams of clean coal sample was used in each test.

The general procedure was as follows. The three-way stopcock was opened to the empty flotation cell for a minute and then switched to the dummy cell. Approximately 20 ml of double-distilled water was introduced into the flotation cell. After adding a three gram of coal sample, the coal suspension was agitated by means of a glass rod until all the coal particles were wet. More water was carefully added to fill the remaining volume (350 ml) of the cell. The gas flowrate was then adjusted to 20 ml/minute by means of Gilmont flow control valve before switching the three-way stopcock to the flotation cell to begin the flotation. After 20 seconds of flotation time, the float and sink products were filtered, dried and weighed to determine the floatability.

Figure 13 shows the results of the flotation tests conducted with and without using a frother (MIBC). When no frother was used the maximum floatability was only about 80%. The use of a frother improved the floatability to nearly 100%, but the effective flotation range in terms of particle size did not change significantly. It may be said that the coal flotation began to deteriorate above 48 mesh (295 microns) and below 200 mesh (74 microns). This finding appears to conform to general coal preparation practice.

Using the same apparatus and the same coal sample, experiments are in progress to determine the following:

1. to establish the floatability of fine coal particles in the microns range,
2. to establish the effect of kerosene on the flotation characteristics,

APPARATUS

<u>1</u> GAS SUPPLY	<u>5</u> 3-WAY STOPCOCK
<u>2</u> REGULATOR	<u>6</u> DUMMY CELL
<u>3</u> TYGON TUBING	<u>7</u> FLOTATION CELL
<u>4</u> FLOWMETER	<u>8</u> MAGNETIC STIRRER

Figure 11. Schematic representation of the microflotation apparatus.

Figure 12. Microflotation apparatus.

Figure 13. Results of the microflotation tests conducted with a clean bituminous coal as a function of particle size.

3. to establish the effect of oxidation on the flotation characteristics, and

4. to determine if the use of CGA bubbles improves the floatability of the fine coal particles.

Construction of an Automatic Batch Flotation Machine

Figure 14 shows the Denver Laboratory Flotation Machine, Model D-12, modified to improve reproducibility. The basic design is similar to the one that is being used at the DOE Coal Preparation Laboratory, but has a few improvements. The major features of the flotation unit are as follows:

1. Two mechanical scrapers are installed on opposite sides of a flotation cell, similar to large scale continuous flotation cells.
2. The mechanical scrapers are of variable speeds
3. Air is supplied from the compressed air line, which can be adjusted to any desired air flow rate independent of impeller speed.
4. The froth level can be kept constant by means of an electronic liquid level controller (Cole-Parmer 7187).
5. Two flotation cells, 4 l and 2 l capacity, are interchangeable, so that a two-stage flotation experiment can be performed.
6. The cells are made of plexi-glass, so that events in the flotation cell can be observed.
7. The flotation machine can also be used for manual operation, if so desired.

This flotation machine will be used for testing run-of-mine coal samples with and without using CGA bubbles. It will be particularly useful for kinetic studies.

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Figure 14, Automatic laboratory flotation machine.