Recovery of Fine-Particle Coal by Colloid Flotation

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Abstract

The purpose of the research was to investigate the technical feasibility of a novel flotation technique for the recovery of extremely small particles of coal from water. This approach, colloid flotation, utilizes microbubbles generated at low gas flow rates. A procedure was also developed for preparing stable and reproducible suspensions of colloidal coal as might be found in the effluents of preparation plants. Oxidation of the coal contributed to its ability to remain dispersed for long periods of time over a broad pH range. Several parameters controlling flotation were examined including collector type and concentration, pH, gas flow rate, and frother dose in batch, bench-scale studies. Recovery attempts with an anionic collector were not successful. The coal was removed very effectively, however, using a cationic surfactant collector. Rates of removal were greatest at low pH and depended on gas flow rate as well as the collector and frother doses. The results were related to the electrophoretic mobility of the coal.

The increased use of wet cleaning methods for coal preparation has resulted in the generation of enormous amounts of wash water laden with suspended particles. Modern methods of mechanized mining have also led to the large production of coal fines, most of which until recently were merely discarded. Presently, because of economic considerations, attempts are being made to recover as much of these coal fines as possible. Much additional fine coal is processed through cleaning plants as a result of technologies demanding smaller size coal and in an effort to greatly reduce coal sulfur content.

The problems associated with wash water fines, which range from 48 mesh downwards to colloidal sizes, include reductions in efficiency in wet cleaning

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methods, environmental pollution, and loss of the fines. The magnitude of these problems depends on the extent to which coal preparation plant wash waters are recycled or clarified. Most plants constructed today are designed for almost complete recirculation of wash waters with only intermittent or small continuous discharges. The recycled water is usually clarified by chemical flocculation and the thickened solids are wasted (*1*). Older preparation plants many of which are still in operation, were not designed for recycle, all wash waters being discharged to settling basins with the overflow entering a receiving stream (*2*).

Water pollution by coal preparation plants was recognized as early as 1874 by the British River Pollution Commission. The major problem noted was the discharge of suspended solids resulting in "silting." Although not a human health hazard, the sedimentation of such solids harms aquatic life and is an aesthetic nuisance. Farmers in West Virginia have complained of black deposits left on bottom land after spring floods, and one sand company in that state has recovered as much as 20,000 t of coal per year from its sand preparation operation (*3*). Recently in this country, as well as earlier in Britain, water quality standards have been set for discharge waters from coal preparation plants and associated operations. In the United States these standards limit total suspended solids to 0.07 g/L.

Because of inefficiencies in coal recovery in the smaller ranges much −48 mesh coal, of which a good percentage is utilizable, is wasted along with the high ash shales in the tailings. A survey of four West Virginia coal preparation plants which did not recycle wash water revealed fine coal discharges between 1 and 42 t/d (*3*). A more recent study on blackwaters in the eastern portion of the United States showed that, on the average, 60% of the suspended solids were carbonaceous which could be successfully removed by flotation and blended with coarse clean coal without significantly altering the quality of the final product (*4*).

Flotation appears to be the most promising method for the recovery of ultrafine coal (*5–7*). Accordingly, the objectives of this research were to investigate the feasibility of dispersed-air colloid flotation as an effective recovery method under laboratory conditions and to examine the major parameters that might control the process. These parameters included collector type and dosage, ethanol frother dosage, gas flow rate, and pH. It was also necessary to develop a procedure for the preparation of colloidally stable and reproducible suspensions of ultrafine particle coal to be used as a synthetic blackwater.

FOAM SEPARATION METHODS

Foam separations are a class of adsorptive bubble separation techniques for concentrating substances dispersed in a liquid phase through their

attachment onto rising gas bubbles. The separated substances are collected in a characteristic foam layer. Flotation methods are distinguished from foam fractionation in that they are directed at the removal of particulate matter while the latter deals with dissolved substances. Ore flotation, also referred to as macroflotation, is a basic operation applied to the beneficiation of metallic and nonmetallic minerals and of solid fuels such as coal. Colloid flotation, the process studied in this work, is similar to ore flotation but is directed at the removal of ultrafine particles. Compared to ore flotation, precipitate and colloid flotation utilize low rates of gas flow to prevent the redispersion of the float that is produced. Colloid flotation has been successfully employed for the removal of titanium dioxide (8) and the clays kaolin and montmorillonite (9) and illite ((10).

Flotability is governed by particle–bubble interactions and can be evaluated by contact angle and electrokinetic studies. The contact angle at a particle–bubble interface is considered to be a measure of the flotability of the substance; a large contact angle signifies inherent flotability. Most minerals cannot be floated without the addition of surface-active agents or collectors which render the particle surface hydrophobic and thus promote bubble adhesion. For most substances only fractional surface coverage is necessary to achieve successful bubble attachment. Electrokinetic studies help in evaluating flotability in that they can indicate particle hydrophobicity and the potential for bubble adhesion or collector adsorption. It has been suggested that maximum flotability occurs at the particle isoelectric point (11).

In addition to collectors, frothers and other modifying agents are used in flotation. Frothing agents lower water surface tension, resulting in the generation of smaller bubbles and inhibiting bubble coalescence. Frothers also aid in creating a surface float capable fo holding the mineral-laden bubbles. Other modifying agents include pH regulators, depressants which may inhibit collector adsorption, and activators which enhance collector adsorption (12).

COAL FLOTATION RESEARCH

Although most coal flotation research has been directed at standard beneficiation processes, much of the information can be applied as well to the flotation of colloidal coal. Critical to both techniques is the surface oxidation of the coal. It is generally accepted that coal oxidation, whether it be by exposure to the atmosphere or artificially, proceeds in three stages (13–15). Stage one is superficial oxidation characterized by the formation of coal–oxygen complexes with acidic properties. In stage two, organic components of coal form alkaline-soluble hydroxycarboxylic acids called humic acids. In stage three the humic acids degrade to simple water-soluble acids. Marinov

(16) and Czuchajowski (17), using IR spectroscopy, showed that inter-mediate oxidation, stage two, produces acidic carboxyl and phenolic groups on the surface of bituminous coal. Marinov reported that the carboxyl content of coal increased significantly within 100 h when subjected to oxidation in air at 60°C. After 600 h at the same conditions an increase in the content of phenolic groups was observed. Czuchajowski observed the for-mation of these functional groups on coal oxidized with hydrogen peroxide. His oxidation procedure involved the heating of 300-mg samples of pow-dered coal with 50 mL of 20% hydrogen peroxide solution to 60°C for 30 or 60 min. As a result of oxidation, the acidic functional groups are formed on the surface; these ionize, rendering the coal negatively charged.

Electrokinetic studies have been used in evaluating the effect of oxidation on the surface charge of coal and in estimating the zeta potential of coal in the presence of flotation agents. In general, both unoxidized and oxidized coal have isoelectric points in the acidic range. At pH values above the isoelectric point the coals are negatively charged. Wen (18) reported on an extensive series of electrokinetic studies with unoxidized and oxidized bituminous coal. With unoxidized samples, isoelectric points were reported between pH 4.5 and 5.0. Those of oxidized samples occurred below pH 4.0, shifting to lower pH with increasing oxidation. At pH values above the isoelectric point, the zeta potential of coal was shown to increase in magnitude with the degree of oxidation. Similar data were reported by Cambell and Sun (19) and Jessop and Stretton (20) who found isoelectric points of unoxidized bituminous coal to occur at pH 4.6 and 4.7, respec-tively. Baranov (21) observed isoelectric points at pH 1.4 and below with oxidized coals.

The presence of flotation agents has been shown to affect the zeta potential of coal. Wen (18) performed electrokinetic studies with oxidized bituminous coal at different pH in the presence of dodecylammonium chloride (a cationic collector), sodium oleate (an anionic collector), hexadecane, a mixture of fuel oils Nos. 2 and 6, and hexyl alcohol. The oxidized coal used was negatively charged above pH 2. In the presence of the cationic collector the coal exhibited a less negative zeta potential at all pH. The observed trend was that the isoelectric point shifted to a higher pH with increasing collector concentration. At the largest collector dose the coal was positively charged below pH 11. The anionic collector effected a small shift to a more negative zeta potential at all pH values. With hexadecane, a hydrocarbon oil, the electrokinetic properties of coal assumed those of hexadecane alone which corresponded to more negative zeta potentials. The fuel oil mixture acted somewhat like the cationic collector in shifting the zeta potentials to less negative values; however, the coal never attained a positive charge. In the presence of hexyl alcohol the change in zeta potential was insignificant.

Baranov (*21*) also reported that nonionic agents such as aliphatic alcohols have little affect on the surface charge of oxidized coal.

It has been shown that unoxidized coal is more easily recovered in typical flotation operations which use neutral, oily collectors (*22, 23*). The reduction in the natural flotability of coal by oxidation, as expressed by a smaller contact angel, has also been reported (*24, 25*) although cationic collectors have been shown to effectively float oxidized coals (*23, 26*). On the other hand, it was found by Sun (*23*) and Gayle et al. (*22*) that superficial oxidation increased the flotability of some lignites and anthracites. This was attributed to the collecting and/or frothing properties of their water-soluble products of oxidation. Highest flotation recoveries for unoxidized bituminous coal using standard oily collectors or alcohol frothers generally occur between pH 5 and 9 (*27*). Sun (*23*), using borneol, a cyclic alcohol, achieved a maximum recovery at pH 7. With xanthate collectors, Janata (*28*) reported maximum flotation below pH 6. Optimum recovery of oxidized coal has been shown to occur in the acidic range. Sun (*23*) achieved maximum flotation of oxidized bituminous coal around pH 2.5 using laurylamine hydrochloride, a cationic collector. Attempts to float the same coal with a petroleum oil-pine oil mixture, while achieving much lower overall recoveries, also produced maximum removals at approximately the same pH. Baranov and Stankevich (*26*), who obtained superior flotation of oxidized coal below pH 3, suggested that cationic collectors were satisfactory only at a pH where coal could obtain a maximum negative charge without dissolving excessive humic acids which themselves adsorb flotation agents. There has been very little, if any, research reported in the literature which deals specifically with the flotation of oxidized, colloidal coal.

EXPERIMENTAL METHODS AND MATERIALS

Preparation of Coal Suspensions

Coal suspensions were prepared with a stoker coal from the Elkhorn seam in Kentucky donated by Battelle Memorial Institute in Columbus, Ohio. The Btu and volatile matter content indicated that the coal is a highly volatile, bituminous type. Its low ash and sulfur content signify that the coal is relatively pure with the bulk of the sulfur probably combined organically and not in the pyrite form.

In order to prepare a stable and reproducible colloidal suspension of the coal, a lengthy preparation procedure was developed. The stoker coal as received, between 0.5 to 1 in. in size, was gound to a coarse power by passing it through a Quaker City Mill (Model 4-E with 3½ in. grinding plates,

No. 4B). This rough-ground coal was then milled for 24 h in 1-qt porcelain jars on an Abbé pebble mill at 109 rpm. The grinding medium was flint pebbles filling the jars half full at a charge weight of 660 g. The coal charge was 50 g at a volume of approximately 120 mL. The milled coal was sieved by lightly brushing it through a 400-mesh standard U.S. Series sieve which had 37 μm openings. The -400 mesh product was stored in an air-tight container as were the rough-ground and milled coals.

The fine coal was oxidized in 500-mL Erlenmyer flasks in a Eberbach constant temperature shaker bath for 4 h at 80°C. In each flask were placed 2 g of coal, 200 mL of carbonate-free distilled water, and 10 mL of 30% hydrogen peroxide solution. The flasks were sealed with aluminum foil having a pin hole to allow evolved gas to escape. The shaker speed was set such that coal could not remain clinging to the necks of the flasks. Following oxidation, the contents of each flask were filtered under vacuum through a 0.3-μm, 47-mm diameter Millipore filter to remove the coal particles from the slurry. While under vacuum the coal solids were rinsed with 250 mL of distilled water to remove water-soluble oxidation products. While moist, the coal was resuspended by moderate shaking in a small amount of distilled water in either a 1000- or 600-mL Erlenmeyer flask, depending on the amount of suspension to be prepared. All suspensions were allowed to settle and age for at least 8 d in order to retain the most stable particles. After aging, the required volume was siphoned from the top and adjusted to the initial turbidity of approximately 0.6 absorbance units.

Solutions, Reagents, and Analyses

Carbonate-free, double-distilled water was used in the preparation of all solutions and coal suspensions. Distilled water was boiled to remove carbon dioxide before storing in a 5-gal carboy equipped with an Ascarite air vent. While stored, the water was frequently purged with nitrogen gas to prevent the reabsorption of carbon dioxide.

Hydrochloric acid and sodium hydroxide solutions at various concentrations prepared from the reagent-grade chemicals were used to adjust pH. Acid was stored in glass bottles and base in polyethylene bottles. Reagent grade hydrogen peroxide (30%) was used to oxidize the coal. Collectors for the flotation studies were hexadecyltrimethylammonium bromide (CTAB), a strongly ionized cationic quaternay ammonium salt, and sodium laurylsulfate (NaLS), a strongly ionized anionic surfactant. The frother was ethanol (EtOH). The collectors and frother were combined with distilled water in 100-mL volumetric flasks so that 2 mL of the mixture gave the desired collector–frother dosage when added to the 400-mL coal samples to be floated. The collector–frother solutions were never more than 5-d old when used.

Sample turbidities were estimated by absorbance measurements taken with a Coleman Model 14 spectrophotometer using 19-mm round Coleman cuvettes at a wavelength of 400 nm. The absorbance was linear with suspension concentration. A wavelength sensitivity scan using a Coleman Model 124 recording spectrophotometer showed that in the visible region, 800 to 370 nm, sensitivity increased linearly with decreasing wavelength. In the UV region the suspension was opaque.

Measurements of electrophoretic mobility were taken with a device manufactured by Zeta-Meter Inc., New York. With electrophoresis samples having a specific conductance above 1000 μmhos/cm, the low-carbon molybdenum anode was used to prevent oxygen generation at the electrode. At lower specific conductances the standard platinum-iridium anode was used. A Sargent-Welch model LS pH meter with a Sargent-Welch combination electrode was used to measure pH.

Flotation Apparatus

The experimental apparatus used in this investigation, as shown schematically in Fig. 1, was similar to that used in previous flotation studies (*10, 29*). The apparatus consisted of a compressed nitrogen gas supply, a gas humidifier, a glass-wool filter to remove water droplets, a Manostat rotameter (Model 36-541-05) with sapphire float, and a mercury U-tube manometer for monitoring upstream line pressure. The gas rate was controlled with a fine Nupro needle valve (Model B-4M) in combination with a Moore low flow-rate controller (Model 63 BU-L). The flotation cells were 600-mL Büchner funnels of 10-cm diameter with fine sintered glass frits. The different cells used in the studies had similar bubble flow patterns and sizes.

The rotameter was calibrated at a line pressure of 30 in. of mercury as was used for all of the studies. Flow rates were determined with a bubble meter, a volumetrically marked glass tube in which the gas rate is measured by timing the travel of a rising gas bubble along the tube.

Procedures

Electrophoretic measurements were taken as a function of pH to estimate the mobilities of unoxidized coal, oxidized coal, and oxidized coal in the presence of CTAB using the Zeta-Meter microelectrophoresis apparatus. Procedures were followed as outlined in the instrument manual. Suspensions of the unoxidized coal were prepared by dispersing −400 mesh coal in slightly alkaline distilled water using a Waring blender and aging it 24 h to allow the larger particles to settle. Samples used for measurements consisted of mixtures of 4 mL of the 1-d old suspension and 50 mL of distilled water. The oxidized coal samples used for mobility measurements were from a suspension prepared and aged as previously described. Oxidized coal and CTAB
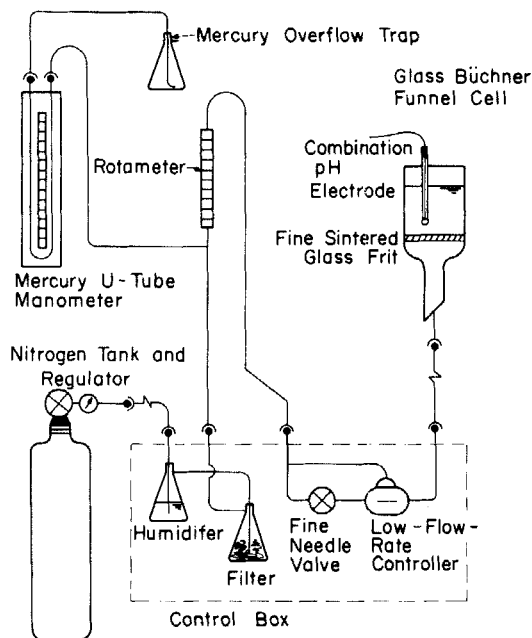
FIG. 1. Schematic of experimental apparatus.

samples consisted of a mixture of 50 mL of the oxidized coal suspension and 2 mL of a CTAB solution. The final CTAB concentration was 16.2 mg/L or 1.79 mg/mg coal which was a CTAB-to-coal ratio twice that of the maximum used in the flotation studies. Just prior to each measurement the samples were adjusted to the desired pH by the dropwise addition of acid or base. Between measurements the electrophoresis cell and electrodes were rinsed with distilled water and blown dry with air. The molybdenum anode was cleaned with hydrochloric acid whenever necessary to remove products of oxidation. Data were plotted as electrophoretic mobility (μm$\cdot$cm/V$\cdot$s) against pH.

The evaluation of colloidal coal flotability was performed with respect to collector type using NaLS and CTAB, alcohol frother and CTAB collector dosages, pH, and gas flow rate. Several flotation studies were run using 8 mg/L of NaLS, 0.76 mL of frother, and a 31 mL/min gas flow rate at various pH values. Cationic collector studies were performed using CTAB doses between 2 and 25 mg/L at variable pH, a constant frother dosage of 0.76 mL, and a gas flow rate of 31 mL/min. Studies to examine the effect of frother were run using ethanol doses between 0 and 1.71 mL/400 mL at pH 3.0 with a CTAB concentration of 5 mg/L and a gas flow rate of 31 mL/min. Gas

flow rate studies were performed at 16, 31, and 62 mL/min, also at pH 3.0 and the same doses of CTAB and frother.

All flotation experiments were conducted using 400-mL volumes of 8-d old coal suspension adjusted to an absorbance of 0.60. Several batches of identically prepared suspension were used. Just prior to flotation, 400 mL of coal suspension was placed in a clean Büchner funnel cell. With the needle valve fully open, gas flow was commenced. The line pressure was gradually brought up to 30 in. of mercury while the gas rate was carefully adjusted to the desired rotameter reading. The pH of the coal suspension was adjusted through the dropwise addition of acid or base. After stabilizing, the initial pH was recorded and 10-mL syringe was used to withdraw a time-zero sample of 7 mL for analysis. Shortly thereafter, 2 mL of collector–frother mixture were injected with a 2-mL syringe at the bottom center of the cell and the timer was started. At selected time periods up to 1 h, 7-mL samples were withdrawn from the bottom center of the flotation cell and the corresponding pH was recorded. Samples were place in cuvettes and stoppered. Upon completion of flotation, the turbidity of the samples was measured. Prior to each measurement the sample was gently shaken for 10 s and held in the spectrophotometer for 1 min to allow air bubbles to escape.

Between experiments, cuvettes and flotation cells were washed with soap and water, rinsed thoroughly with nitric acid, and finally rinsed with distilled water. Flotation data were plotted as percent removal against time using turbidity as an estimate of particle concentration.

EXPERIMENTAL RESULTS

Coal Suspension Preparation

An important result of this work that was critical to its completion was the development of a method for the preparation of a reproducible aqueous suspension of oxidized colloidal coal. The procedure consisted of both physical and chemical steps. The physical procedure aimed at producing the finest sized coal particles possible with simple commercial equipment. The chemical procedure was designed to produce a surface charge on the coal particles through oxidation so as to form the stable colloid.

The physcial preparation, as described previously, consisted of rough grinding the stoker coal, fine grinding in a pebble mill, and sizing with a 400-mesh sieve. Parameters affecting these steps were the extent of rough grinding, pebble and coal mill charge, and pebble milling time. These were optimized before proceeding to the chemical preparation step.

Before fine grinding the coal in the pebble mill, it was necessary to reduce

the coal to a size which the mill could handle efficiently. The finer the coal size used in the mill, the less milling time was needed to reduce the coal to a particular size. Passing the stoker coal three times through the rough grinder produced a much finer coal than a single pass, whereas more than three passes did not noticeably affect the final rough-ground size.

Pebble charge for the 1-qt mill jars followed the manufacturer's recommendation of filling the jars one-half full at a pebble weight of approximately 770 g. The coal charge had to be such that its volume never exceeded 25% of the jar volume or 236 mL. When coal was ground in the mill, the volume increased due to the increase in the number of particles and interparticle space. A charge of too large a volume reduces pebble contact and decreases the efficiency in milling, while a small charge, although increasing efficiency, limits the production of ground material. After measuring the weights of several coal charges and their volumes upon milling for 24 h, a charge of 50 g was selected. This weight of rough-ground coal had an initial volume of 120 mL and a final volume of 210 mL. The optimum milling time of 24 h was selected since 6 and 12 h of milling produced a much rougher coal while milling for 48 h did not produce a noticeably finer coal. Comparisons in the coal sizes were made by suspending equal amounts of the coals in distilled water and observing the time required for complete settling.

To place a limit on the upper size range of the milled coal, it was passed through a 400-mesh sieve. Obtaining the −400 mesh coal by using a sieve shaker proved futile since the coal was extremely light and agglomerated on top of the sieve. Consequently, the coal was manually passed through the sieve by brushing.

Preliminary attempts at suspending the fine coal included shaking the coal with distilled water by hand in a closed flask. It was observed, however, that the coal did not wet easily and a large portion tended to agglomerate and settle quite rapidly. Further attempts at suspending the coal with a blender and a sonifier did not improve its stability. In order to stablize the coal, oxidation with either oxygen gas or hydrogen peroxide was considered. In using oxygen, the -400 mesh coal was spread in a thin layer on a glass tray and heated in a sealed oven under a slightly pressurized oxygen atmosphere. A vacuum was drawn on the sealed oven to remove all air before filling with oxygen. Coal samples were oxidized at both 100 and 200°C for 24 and 48 h. Dilute suspensions of the oxidized coal were prepared in distilled water by hand shaking in a flask, mixing in a blender, and sonifying. In all cases the coal wetted easily but agglomerated and settled within 24 h.

Wet oxidation was attempted next using various mixtures of coal, 30% hydrogen peroxide solution, and distilled water in Erlenmeyer flasks heated in Eberbach constant temperature shaker bath. Flasks were covered with aluminum foil having a pin hole to allow evolved gas to escape. In trials using

0.2 g of coal, 3 mL of 30% hydrogen peroxide solution and 100 mL of distilled water heated at 70°C for 4 h, the resulting suspensions proved quite stable. The standard procedure used thereafter was similar but with slight modification. In 500-mL Erlenmeyer flasks, 2 g of coal with 10 mL of hydrogen peroxide and 200 mL of distilled water were oxidized for 4 h at 80°C. This was a lower H_2O_2/coal ratio than first used since it had been observed that smaller quantities of hydrogen peroxide produced equally stable suspensions. The temperature was increased 10°C to insure that the oxidation process was completed after 4 h and that all of the hydrogen peroxide had reacted.

The final suspension preparation steps included filtering and rinsing the oxidized coal to remove soluble oxidation products and resuspending the coal in distilled water. Upon resuspending the coal it was observed that a large fraction of the coal fines aggregated and settled after several days. In order to retain the most stable fraction, all suspensions were aged at least 8 d before being used. The aging proved beneficial in that more uniform and reproducible data were obtained. All suspensions oxidized and aged 8 d or longer exhibited pH values between 5.5 and 6.5 with only a few exceptions; these extremely acidic suspensions were discarded.

A particle size analysis was performed on the -400 mesh coal using an Andreasen pipette and ethanol as a wetting agent. Results showed that 97.5% of the coal was between 37 and 19 μm while the remainder was smaller than 19 μm. The surface areas of -400 mesh raw coal and oxidized coal aged 8 d in suspension were determined by single point BET using a Monosorb surface area analyzer manufactured by Quantachrome Corp. Areas for the raw and oxidized coal were approximately 6.7 and 7.9 m^2/g, respectively.

Electrophoretic mobility measurements as a function of pH of unoxidized coal, oxidized coal from a suspension aged 8 d, and oxidized coal in the presence of CTAB are summarized in Fig. 2. "Negative" mobility indicates negatively charged particles, while "positive" mobility indicates a positive charge. All coal samples exhibited changes in mobility with respect to pH but in different respects. Unoxidized coal had an isoelectric point at approximately pH 5. Between pH 4 and 5 the coal was positively charged with the maximum mobility measured of about 1.8 μm · cm/V · s at pH 4. Between pH 4 and 8 a large change in the mobility occurred, while between pH 8 and 11 the change was more gradual. The maximum negative mobility meaured was approximately 3.3 μm · cm/V · s at pH 10.8. The isoelectric point for oxidized coal occurred at about pH 1.2. A positive charge on oxidized coal was not recorded since measurements could not be taken below pH 1 due to limitations of the electrophoresis apparatus. Between pH 1.2 and 3 the mobility increased considerably, from 0 to approximately -3.0 μm · cm/V · s,
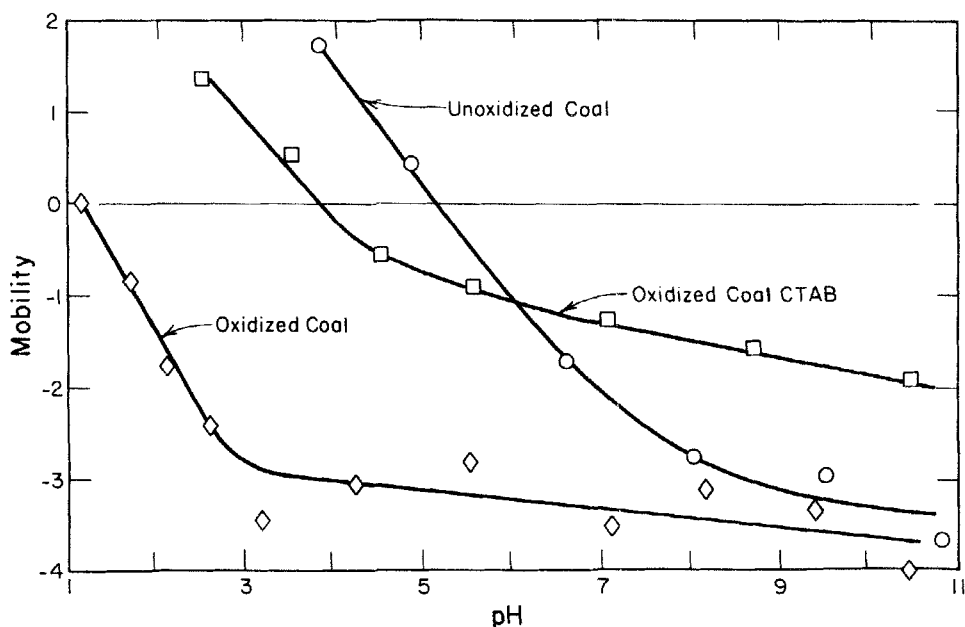
FIG. 2. Electrophoretic mobility of unoxidized coal, oxidized coal, and oxidized coal with CTAB as a function of pH.

while between pH 3 and 11 the mobility changed gradually down to -3.8 μm·cm/V·s. At all pH values the negative mobility for oxidized coal was of a greater magnitude than that for the unoxidized coal; however, above pH 8 the mobilities approached one another. The mobilities for oxidized coal in the presence of CTAB appeared to parallel those of the oxidized coal alone. Below the isoelectric point near pH 4 the coal was positively charged with the maximum positive mobility measured being approximately 1.4 μm·cm/V·s at pH 2.5. Above the isoelectric point the mobilities never attained the magnitude of oxidized coal alone. A maximum negative mobility of about 1.9 μm·cm/V·s was measured at pH 10.5.

Flotation Studies

Results of the colloid flotation of oxidized coal are summarized in Figs. 3 through 8. The data are presented as percent removal with respect to time. Different batches of identically prepared, 8-d-old suspensions with an average coal concentration 28.3 mg/L were used for all studies.

Flotation experiments run at different pH and CTAB concentrations of 2, 5, 10, and 25 mg/L are summarized in Figs. 3, 4, 5 and 6, respectively. The

initial pH of the coal suspensions is indicated on the plots. For all studies an ethanol frother dose of 0.76 mL/400 mL was used and the gas flow rate was set at 31 mL/min. Using 2 mg/L CTAB, studies were performed at pH 1.52, 2.50, 3.50, 4.45, 5.35, and 8.50. The results at pH 4.45, which are similar to those at pH 5.35, are not included in Fig. 3. Two types of removal patterns are apparent in the data. The first includes the data obtained at pH 1.52, 2.50, 5.35, and 8.50 in which the rates of removal, corresponding to the initial slopes of the curves, were high. However, the extent of removal varied depending on pH. At the low pH values of 1.52 and 2.50, maximum recoveries were obtained, recoveries being approximately 80 to 90% at 60 min. At pH 5.35 and 8.50, the removals were quite low for the entire flotation period. The maximum recoveries at pH 5.35 and 8.50 occurred after 60 min and were approximately 25 and 20%, respectively. The second removal pattern occurs with the data at pH 3.50 in which the rate of recovery was low and an irregular flotation curve resulted. At this pH recoveries were initially depressed but increased rapidly after 20 min. A maximum removal of approximately 90% was achieved at 60 min. Maximum foaming occurred at pH 1.52 and 2.50 while at pH 3.50 and froth developed quite slowly. Foaming was not observed at pH 5.35 and 8.50.

Flotation experiments using 5 mg/L of CTAB were run at pH 1.60, 2.68, 3.55, 4.55, 5.25, and 9.59. Not plotted in Fig. 4 are results at pH 2.68 and 5.25 which lie between those of pH 1.60 and 3.55, and pH 4.55 and 9.95, respectively. At times between 0 and 20 min, maximum recoveries were
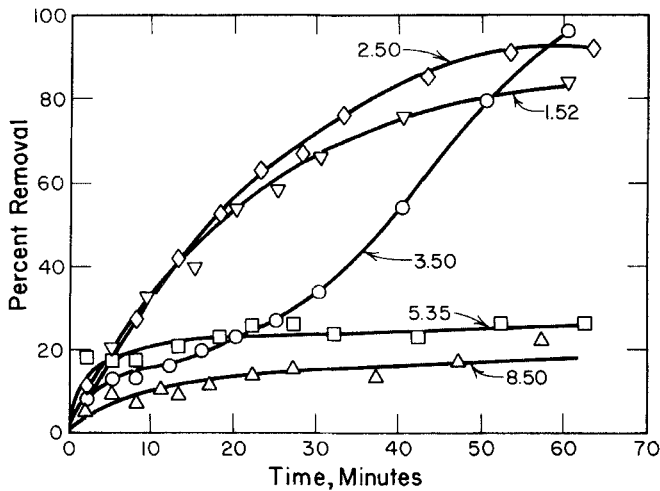

FIG. 3. Flotation of Colloidal coal with 2 mg/L of CTAB at different initial pH as a function of time. Frother dosage 0.76 mL and gas flow rate 31 mL/min.
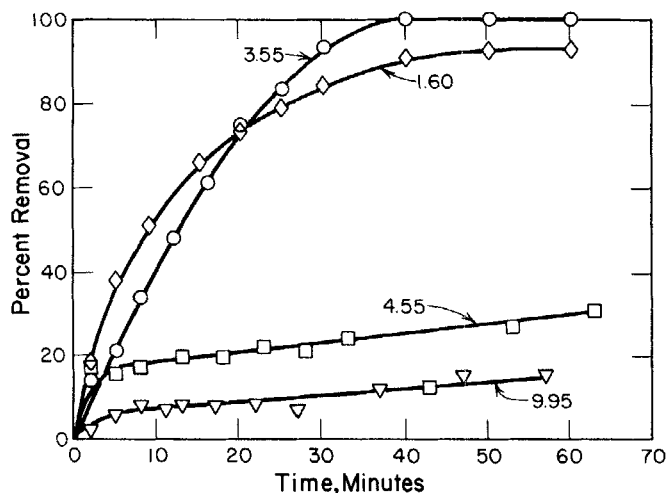
FIG. 4. Flotation of colloidal coal with 5 mg/L of CTAB at different initial pH as a function of time. Frother dosage 0.76 mL and gas flow rate 31 mL/min.

obtained at pH 1.60, while thereafter, removals were maximum at pH 3.55 with 100% removal occurring at 40 min. The pH 1.60 run reached a maximum of approximately 90% at 60 min. For pH 4.45 and 9.95, overall recoveries were quite low. At the end of the flotation periods maximum removals of about 30 and 15% were reached at pH 4.55 and 9.95, respectively. The highest level of foaming occurred at pH 1.60, followed by that at pH 3.55. There was no foam at pH 4.55 and 9.95.

Using 10 mg/L CTAB, flotation studies were performed at pH 1.32, 2.22, 3.30, 4.70, 5.30, and 9.20. The results in Fig. 5 do not include the data at pH 2.22 which fell between those of pH 1.32 and 3.30. As in the studies using 2 mg/L of CTAB, two distinct flotation patterns are observed; those with high rates of removal at pH 1.32 and 3.30 and those with low rates of removal removal at pH 4.70 and 5.30. Recoveries were greatest at pH 3.30, where 100% removal was reached at 30 min, and at pH 4.70 and 5.30 at approximately 45 and 60 min, respectively, for 100% removal. For the flotation run at pH 1.32, a maximum recovery of about 80% was reached in 60 min. At pH 5.30 an irregular flotation curve resulted as characterized by depressed initial recoveries with increased removals occurring after 20 min. The extent of foaming was maximum at pH 1.32, decreasing with increasing pH. At pH 5.30 the froth developed slowly. There was no foam at all at pH 9.20, which was also the pH of minimum recovery of coal.

Flotation experiments using 25 mg/L of CTAB were performed at pH 1.60, 2.50, 3.48, 5.20, 7.68, and 9.50. The results shown in Fig. 6 are
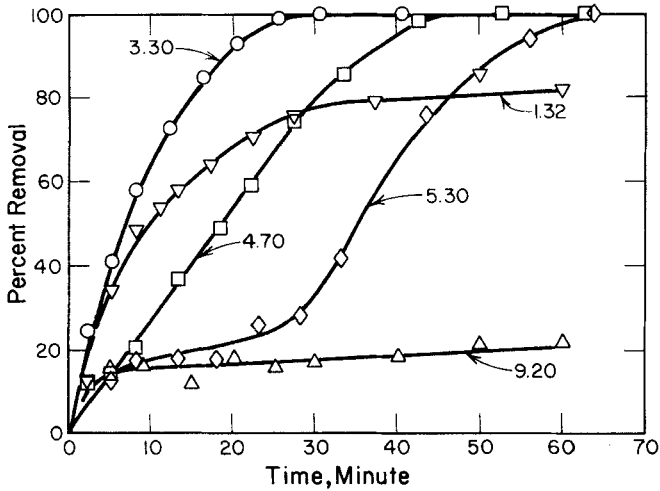
FIG. 5. Flotation of colloidal coal with 10 mg/L of CTAB at different initial pH as a function of time. Frother dosage 0.76 mL and gas flow rate 31 mL/min.
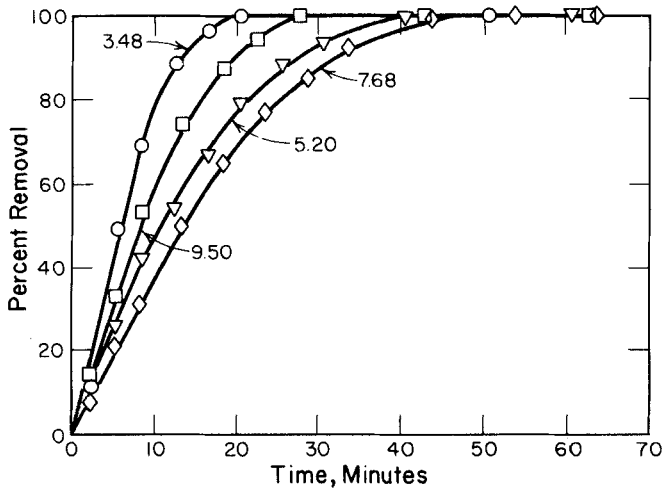

FIG. 6. Flotation of colloidal coal with 25 mg/L of CTAB at different initial pH as a function of time. Frother dosage 0.76 mL and gas flow rate 31 mL/min.

inclusive except for the data obtained at pH 1.60 and 2.50 which lie between those of pH 3.48 and 5.20. Removal rates depended upon pH. Both the rate and recovery were highest at pH 3.48 and decreased at pH both above and below that value. At all pH values 100% removal was achieved within the 60-min flotation period. Although excellent frothing was observed at each pH, it was maximum at the lowest pH and decreased slightly with increasing pH.

The results for experiments in which the ethanol frother dosage was varied are summarized in Fig. 7. The frother concentrations examined varied between 0 and 1.71 mL/400 mL of coal suspension, while the pH, CTAB dosage, and gas flow rate were held constant at 3.0, 5 mg/L, and 31 mL/min, respectively. This particular pH value was selected since maximum removals were obtained at about this pH in previous flotation experiments using the same CTAB concentration and gas flow rate and an ethanol dose of 0.76 mL. The observed pattern in the removal data is that increased frother dosage was accompanied by a greater rate of removal, high recoveries, and increased foaming. All runs using a frother dose of 0.44 mL and above approached 100% removal with increasing time. Using 1.71 mL, the maximum dosage examined, 100% removal was achieved at 25 min. Not shown are the data for frother doses of 0, 0.57, and 1.33 mL. The results obtained without the
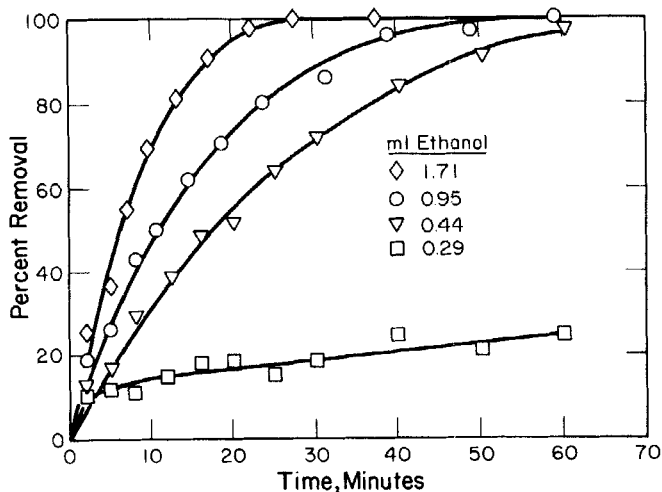

FIG. 7. Flotation of oxidized coal at different EtOH frother dose as a function of time at pH 3.0 CTAB dosage 5 mg/L and gas flow rate 31 mL/min.

addition of frother were almost identical to those using 0.29 mL; in both cases foam was not produced. The largest difference in removals for consecutive frother additions occurred between dosages of 0.44 and 0.29 mL.

Flotation experiments were performed at three different gas flow rates (16, 31, and 62 mL/min), with the results being summarized in Fig. 8. As with experiments at varying frother doses, the coal suspensions were maintained at an initial pH of 3.0. Also held constant were the CTAB concentration at 5 mg/L and the frother dose at 0.76 mL. Flotation rates and recoveries increased with increasing gas flow rate. 100% removals were obtained at 25 and 50 min for flow rates of 62 and 31 mL/min, respectively. At a gas flow of 16 mL/min, a maximum recovery of approximately 80% was reached at 60 min. Increased foaming accompanied the higher gas flow rates.

Several flotation experiments were performed to examine the effect of the anionic collector sodium laurylsulfate. Experiments were run at an acidic, neutral, and basic pH with a constant NaLS dose of 8 mg/L, and ethanol frother dose of 0.76 mL and a gas flow rate of 31 mL/min. In all cases, only negligible removals were obtained and no significant amount of foam was observed.
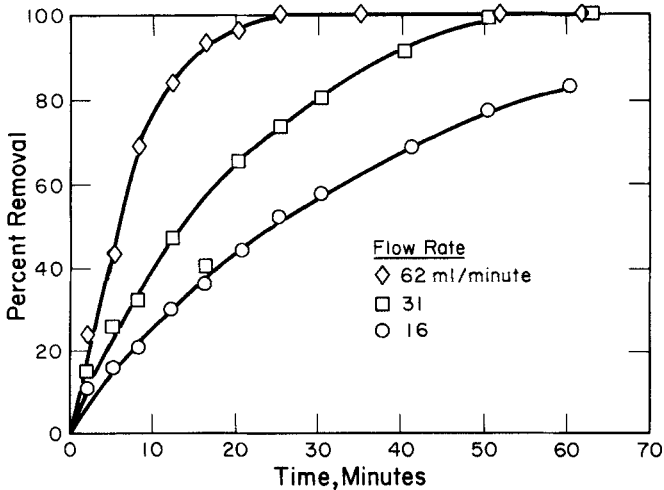

FIG. 8. Flotation of oxidized coal at different gas flow rates as a function of time at pH 3.0. CTAB dosage 5 mg/L and frother dose 0.76 mL.

DISCUSSION AND CONCLUSIONS

Suspension Properties

The procedure employed for the preparation of oxidized colloidal coal proved effective in producing not only stable but reproducible suspensions as well. Batches of the oxidized coal suspension remained dispersed for over 2 months while still retaining sufficient suspended solids for use in further experiments. The reproducibility of the suspensions was evidenced by the nearly identical results obtained from experiments using different batches of coal suspension. The initial pH of the suspensions just after their preparation were between 5.5 and 6.5. The few exceptions which were acidic, presumably due to the oxidation of pyrite, were discarded. The wet oxidation step was critical to the preparation of suspensions stable at pH 7.5 and below. Aging the suspensions aided in their reproducibility because of the removal by settling of the larger more unstable particles. The effect of oxidation was also observed in the ease at which the treated coal was wetted as compared to unoxidized coal.

Slight deviations in suspension characteristics were due to variations in the composition of the individual batches of coal and the subsequent products of oxidation. Coal is not a pure substance but rather a heterogeneous mixture of plant-derived organics and mineral or ash constituents. The organic structure of coal from a particular seam may be similar while the mineral content, which is also affected by mining and cleaning processes, may vary drastically. The bulk of the ash constituents associated with coal are clays, quartz, and gypsum. Secondary constituents include pyrite, carbonates, and chlorides (5). These impurities and others introduced during mining, if in sufficient quantities, are capable of altering the properties of aqueous systems and interfering with flotation. Pyrite and carbonates, in particular, may later suspension pH. The colloidal clay fraction of coal slurries, referred to as slimes, adversely affect coal flotation by adsorbing onto the coal surface, thus inhibiting collector adsorption (5). The low sulfur and ash contents of the coal used in these studies were influential in keeping deviations in suspension characteristics to a minimum.

The oxidation products of most coals consist of alkaline soluble humic acids which contain acidic carboxyl and hydroxyl groups (30). Baranov and Stankevich (26) suggested that the deterioration in the flotation of oxidized coal with cationic surfactants at pH above 3 might be due to the solvation of humic acids which react with flotation agents. Ryzhova (31) pointed out that the humic acids produced by the oxidation of coal by hydrogen peroxide suffer appreciable decomposition when the oxidizing temperature is above

70°C. In an effort to minimize these problems, the coal used in this research was oxidized at 80°C and rinsed with distilled water to remove water-soluble oxidation products.

Electrokinetic Properties

The electrophoretic mobility data for oxidized and unoxidized coal, summarized in Fig. 2, are consistent with reports in the literature (*18, 19, 21*). Typical results show that both unoxidized and oxidized coal are negatively charged over a broad pH range. Isoelectric points for oxidized coal have been reported to occur below pH 4 (*18, 21*) and those for unoxidized coal between pH 4 and 6 (*19, 21*). The isoelectric point has also been found to shift to lower pH with increasing oxidation (*18*). In this work the isoelectric points for oxidized and unoxidized coal occurred at approximately pH 1 and 5, respectively. Above the isoelectric point the coals exhibited a negative charge which was due presumably to the ionization of acidic functional groups. Charge reversal at pH values below the isoelectric point is attributed to hydrogen ion adsorption.

CTAB was effective in reducing the negative mobility of the oxidized coal. The isoelectric point of the coal in the presence of the cationic surfactant shifted up to pH 4. The greatest CTAB adsorption would be expected at high pH where the oxidized coal attains maximum negative charge. The data obtained here are in agreement with that reported by Wen (*18*) who measured the zeta potential of oxidized coal in the presence of dodecylammonium chloride, a cationic collector. Wen not only observed that zeta potentials became less negative but also that the isoelectric point shifted to a higher pH with increasing collector concentration.

The stability of coal in the presence of hydrogen ion can be indicated by its pH_s for which a corresponding electrophoretic mobility can also be determined (*32*). The pH_s is the minimum pH at which the particles will remain stably dispersed. The oxidized coal in these studies exhibited a pH_s of 3.0 at a mobility of about $-3 \ \mu m \cdot cm/V \cdot s$. This value, therefore, is approximately the minimum mobility required for the coal particles to remain stably dispersed. A mobility of $-3 \ \mu m \cdot cm/V \cdot s$ corresponds to a pH of about 8 on the mobility curve for the unoxidized coal, which implies that above this pH a suspension should remain dispersed for an extended period of time. Further, oxidized coal in the presence of CTAB would be unstable at all pH examined since a maximum negative mobility of only $2 \ \mu m \cdot cm/V \cdot s$ occurred. The pH_s of unoxidized coal was determined in an independent experiment and was found to occur at pH 7.5, which is in excellent agreement with the predicted value (*32*).

Colloid Flotation

The flotation of oxidized colloidal coal was investigated over a wide pH range using CTAB and NaLS, which are cationic and anionic collectors, respectively. Additional studies involved varying either the ethanol frother dose or the gas flow rate while maintaining a fixed pH and CTAB concentration.

Colloidal coal flotation was successful when using CTAB but not with NaLS. CTAB, due to its positive charge, was adsorbed by the negatively charged coal producing a hydrophobic surface and thus permitting bubble attachment. Flotation using NaLS was not successful at acidic, neutral, or alkaline pH's since both the oxidized coal and collector were negatively charged, inhibiting collector adsorption. For adsorption of the anionic collector the oxidized coal would have had to attain a nearly neutral or positive charge which means lowering the suspension pH to 1 or below. The negatively charged colloids illite (10) and B. cereus (33) were successfully floated with NaLS by lowering the suspension pH to a point where the particle charge was reduced or reversed by hydrogen ion coagulation and adsorption. Otherwise, the flotation of oxidized coal with NaLS could be performed after enmeshing with aluminum hydroxide, which is positively charged, as has also been reported for illite (10) and B. cereus (33).

The flotation experiments in which the gas flow rate was varied resulted in proportionally increased rates of removal. This would be expected up to a point where too high a gas rate would disrupt the foam layer, redispersing the floated material. Because of the small bubble size formed in the colloid flotation process, a low flow rate can produce a sufficiently large foam layer as compared to techniques using higher gas rates (9). Studies with algae also produce a similar pattern of increasing recoveries corresponding to larger flow rates (29).

From the data for experiments in which frother dose was varied (Fig. 7), the 20-min removals were plotted against frother dose as is shown in Fig. 9. It is obvious that frother is critical to successful flotation. Below a dose of approximately 0.4 mL, frother addition had virtually no effect. Above this critical value removal by flotation increased significantly but less so upon further increases in frother dose. According to Gaudin (34), this response is typical. A similar recovery pattern for varying frother dose was reported in floating E. coli with 5 mg/L of CTAB and using 50 mg/L of aluminum sulfate as a flotation aid at a flow rate of 30 mL/min. The critical ethanol dose in that study was approximately 0.25 mL in 400 mL (29).

Effect of pH on Flotation

From the results of the flotation experiments using between 2 and 25 mg/L of CTAB (Figs. 3 through 6), the 20 and 40 min removals were plotted as
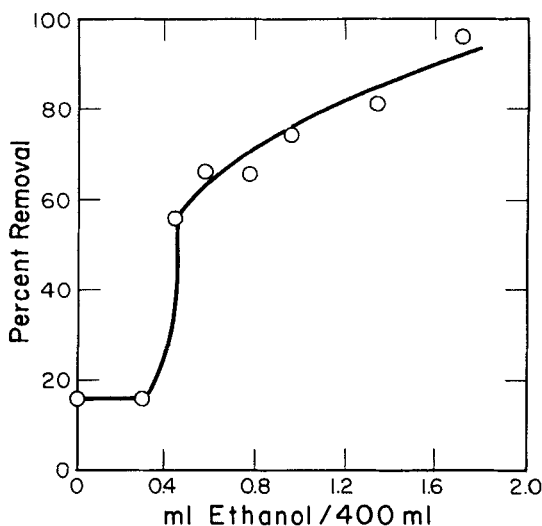
FIG. 9. Twenty minute flotation removals of oxidized coal at different EtOH frother dosages. CTAB dosage 5 mg/L and gas flow rate 31 mL/min.

shown in Figs. 10 and 11. In order to maximize the effects of pH, an intermediate frother dose of 0.76 mL and a gas flow rate of 31 mL/min were used. In general, superior recoveries were obtained with larger CTAB concentrations and the highest removal rates occurred in the acidic pH range. At 20 min, maximum recoveries using CTA dosages of 2, 5, 10, and 25 mg/L occurred over pH ranges of approximately 1.5 to 3, 1.5 to 3.5, 1.5 to 4, and 1.5 to 5, respectively. With 25 mg/L of CTAB, 100% removal occurred about pH 3.5 while recoveries were depressed only slightly above pH 5. With 10 mg/L and less, recoveries declined significantly at higher pH. At 40 min, overall recoveries improved, with the 25 mg/L studies achieving 100% removal at all pH. Using 2, 5, and 10 mg/L of CTAB, the pH range of maximum recovery broadened, being approximately from pH 1.5 to 3.3, to pH 4, and to pH 5, respectively. At high pH the recoveries were again much lower. The observed trend of the range of efficient removal shifting to higher pH with larger collector dose was also observed in the flotation with CTAB of negatively charged TiO_2 (8).

The data for the 20-min removals show not only pH ranges of efficient recoveries for several CTAB dosages but also a pH of maximum removal which increased with increasing collector concentration. This suggests that optimum flotation occurred at the isoelectric point of the coal in the presence of CTAB. The mobility data of Fig. 2 show that the isoelectric points of oxidized coal alone and in the presence of CTAB occurred at about pH 1 and 4, respectively. It was pointed out that the CTAB/coal dosage was twice that
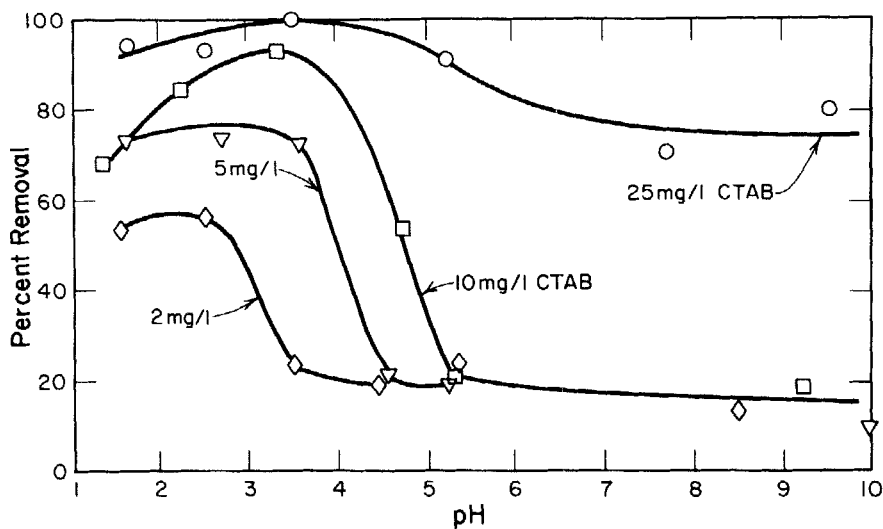
FIG. 10. Twenty minute flotation removals of oxidized coat at different CTAB dosages as a function of pH.
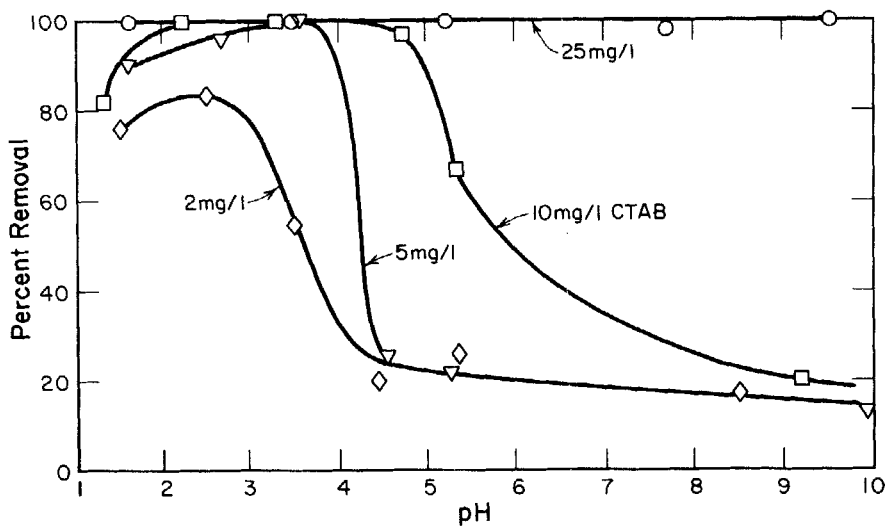
FIG. 11. Forty minute flotation removals of oxidized coal at different CTAB dosages as a function of pH.

of the highest used for flotation. At lower CTAB levels, equivalent to those used in the flotation experiments, isoelectric points would be expected to occur between the extremes of pH 1 and 4. Maximum flotation, in fact, occurred between these two pH values, specifically at pH 2.2, 2.7, 3.2, and 3.4 after 20 min for CTAB doses of 2, 5, 10, and 25 mg/L, respectively.

At pH values below the zone of efficient removal, the coal attained a positive charge sufficient to inhibit collector adsorption. At pH above this zone, the acidic functional groups on the surface of the coal ionized so as to make the coal more hydrophilic, overwhelming the hydrophobic effect of the adsorbed collector, and inhibiting bubble adhesion. A high enough concentration of collector, however, will render the coal hydrophobic as was shown by excellent removals obtained using 25 mg/L of CTAB.

Contributing to low removals at high pH was the lack of foaming. With CTAB doses of 10 mg/L and less, the foam was unstable between pH 4 and 6 and in some cases not forming at all at higher pH. Frother action not only appeared to be related to pH but also to collector concentration since at 25 mg/L CTAB foam formation was excellent even at high pH. Rubin and Haberkost (8) also found that the foam layer was unstable at alkaline pH when floating TiO_2 at CTAB concentrations of 5 and 10 mg/L and an ethanol frother dose of 1 mL/400 mL. Similar flotation studies with oxidized coal, showing superior removals in the acidic range, were reported by Baranov and Stankevich (26), Iskra and Laskowski (35), and Sun (23). In the flotation using CTAB of B. cereus, a negatively charged bacterium, Rubin and Lackey (33) also reported that removals were greatest in the low pH range.

Most of the coal flotation data obtained in this study appeared to be typical for flotation processes in that removal rate was high initially and the extent of recovery approached a constant value with time. The exceptions to this occurred at pH 3.50 using 2 mg/L of CTAB (Fig. 3) and at pH 5.50 using 10 mg/L of CTAB (Fig. 5). In those studies the flotation rates were small initially, removals being greatly depressed during the first 20 min and increasing rapidly thereafter. What occurred is not completely understood.

Summary of Conclusions

Based on the experimental results, the following conclusions are indicated:

1. Stable and reproducible suspensions of colloidal coal can be produced through a process in which the coal is ground to an ultrafine size, wet oxidized with hydrogen peroxide at elevated temperatures, rinsed to remove products of oxidation, and suspended in distilled water. Critical to preparing suspensions stable at neutral pH was oxidation. Oxidation of coal, as

reported elsewhere, forms acidic functional groups on its surface which ionize, producing a surface charge which enhances colloidal stability. As coal suspensions age they become increasingly more stable, improving uniformity and reproducibility of experimental results.

2. The zeta potential of colloidal coal, as approximated by its electro-phoretic mobility, is dependent upon pH as well as adsorbing species such as CTAB. Oxidized coal exhibits a greater negative mobility and an isoelectric point at a lower pH than unoxidized coal due to the larger number of acidic functional groups on its surface. Cationic adsorbing species, such as CTAB, are capable of reducing the negative charge of oxidized coal and shifting its isoelectric point to a higher pH.

3. The colloid flotation of coal can be successfuly achieved with CTAB, a cationic surfactant collector. Due to their opposing charges, CTAB is adsorbed by the fine coal particles. Flotation is not feasible with NaLS, an anionic collector, since it is not effectively adsorbed onto the negatively charged coal.

4. The rate of colloid flotation of the coal is dependent upon the ethanol frother dose and the gas flow rate. Frother is critical to flotation at intermediate CTAB concentrations. A minimum frother dose is required; efficient recoveries are not possible below this dose, in part because of the lack of foam formation.

5. Using CTAB, with ethanol frother, oxidized coal is most readily floated at low pH. At high collector doses, however, successful flotation can occur over the entire pH range. It appears that the highest rate of removal and recovery occur at the isoelectric point of the coal in the presence of CTAB. Otherwise, efficient recovery occurs within a specific pH range which can probably be correlated to a critical mobility. Depressed flotation at pH values below this zone is attributed to decreased CTAB adsorption which is due to particle charge reversal caused by hydrogen ion adsorption. At pH above this zone, reduced recoveries are attributed to the ionization of the acidic functional groups which render the coal more hydrophilic, over-whelming the effect of the adsorbed collector. It is concluded that colloid flotation with cationic collectors is an effective process for the removal of fine-particle coal from water.

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