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NEW CONCEPT FOR COAL WETTABILITY EVALUATION AND MODULATION

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**NEW CONCEPT FOR COAL WETTABILITY
EVALUATION AND MODULATION
DOE PROJECT NO. DE-FG22-92PC92546
Final Technical Report
(January 1, 1992–September 30, 1995)**

EXECUTIVE SUMMARY

This final report, submitted to DOE on the project entitled "New Concept for Coal Wettability Evaluation and Modulation," contains a summary of work completed during the contract period, January 1, 1992 to September 30, 1995. The project team consisted of researchers at the University of Utah as the prime contractor with DOE.

The study was concerned with a new concept for coal surface wettability evaluation and modulation.

The objectives of the work were to study the fundamental surface chemistry for the evaluation of the surface wettability and floatability of coal and minerals. A new separation strategy will contribute to the advanced selective separation of coal and pyrite.

The theories of wettability and floatability of coal and mineral are discussed. A new concept of kinetic wettability, kinetic floatability, and kinetic collectability has been explored. In addition, their evaluation and correlation have been established. Some practical applications to improve the advanced selective flotation of coal and pyrite have been suggested.

Capillary-rise tests were conducted for three coal samples, Colorado mineral pyrite, and coal pyrite. It was observed that the kinetics of capillary rise are a measure of the interaction of liquids with the fine coal and mineral particles, and the slope of the plotted curve for capillary rise height versus time can be correlated with the hydrophilicity or oleophilicity of the fine particle surfaces.

H_{H_2O}/H_X , the ratio between the speeds of capillary rise of pure water and liquid X, where liquid X equals salt solution, kerosene, benzene, amyl xanthate solution,

methanol, ethanol, butanol, or hexanol, is a good measure of hydrophilicity/X-philicity (or relative kinetic wettability) of the coal and mineral samples. It is a simple and straightforward method for the evaluation of the kinetic wettability of fine particle surfaces by different reagents.

Mini-cell flotation tests were carried out for the five samples. The kinetics of mini-cell flotation of the fine coal with different media and different collectors are a measure of flotation yields versus flotation time. The flotation rate constants can be correlated with the kinetic floatability of coal and collectability of the reagents.

K_X/K_{H_2O} , the ratio of the flotation rate constant between reagent X, where reagent X is salt solution, kerosene, benzene, amyl xanthate, methanol, butanol, or hexanol, and pure water, is a useful evaluation of the relative kinetic floatability of coal and the effectiveness of the reagents.

The results of experiments with salt solution as a modifier on flotation of Upper Freeport coal indicate that electrolyte improves the separation efficiency.

Flotation test results using methanol, ethanol, and butanol as modifiers for the Upper Freeport coal showed that the modifiers increase the separation efficiency by as much as 15, 17, and 18%, respectively, as compared to the standard flotation test.

The beneficial effects of butanol on the flotation of Upper Freeport coal were investigated in more detail through closed-circuit flotation. The efficiency index associated with this separation is 75. These results are very close to 90% BTU recovery with 90% pyrite sulfur rejection.

I. INTRODUCTION

Among the most promising physical cleaning techniques for coal and mineral are the advanced flotation and selective coalescence processes. These processes exploit the differences in wettability and floatability between coal and pyrite, coal and ash, and valuable mineral and gangue. The success of separation processes can be positively affected by selectively modifying the particle's surface properties to impart the desired wettability and floatability in fine particles.

The objective of the work is to study the fundamental surface chemistry of the wettability and floatability of coal and minerals. New concepts are used to research the kinetic wettability and kinetic floatability and to study the relationship and the difference between wettability and floatability. These investigations are intended to evaluate the kinetic wettability and kinetic floatability of the coal and minerals in order to modulate their surface properties, thereby establishing a new separation strategy that contributes to advanced coal-cleaning and mineral separation.

Wettability characteristics of the coal and mineral particle play a predominant role in froth flotation and oil agglomeration. Hornsby and Leja⁽¹⁻³⁾ developed wettability tests in methanol/water solutions of progressively decreasing surface tension to estimate coal and mineral floatability. To provide a measure of the hydrophobicity of the particle surface, Garhsva et al.⁽⁴⁾ introduced a technique for estimating the critical surface tension of wetting by measuring the time required for the immersion of a mass of fine particles placed on the surface of liquids. Assessment of wetting behavior was made by Fuerstenau et al.,⁽⁵⁾ who determined the critical wetting surface tension of fine coal and minerals in methanol/water solution.

Contact angles have long been used to estimate the wetting behavior or hydrophilicity of coal and mineral.⁽⁶⁻⁸⁾ Many advanced techniques of measuring contact angles have been developed.⁽⁹⁾ Because of the heterogeneity of coal and mineral surfaces, conventional contact-angle measurements may yield questionable

information for characterizing the hydrophobicity of coal and mineral particles. Conventional methods for contact-angle measurement only characterize the bulk surface, and are not applied to fine particles. Most previous studies only investigated the thermodynamic aspects of the wettability or the equilibrium states. However, flotation is a kinetic and nonequilibrium process.

For contact-angle measurements of powder, the capillary-rise method has long been used.^(10,11) There are only a few studies of the kinetics of the immersion process^(12,13) to connect the velocity of rising liquids with interfacial parameters such as contact angles. Capillary rise expresses the driving force for spontaneous wetting in terms of the physicochemical and geometrical properties of the various interfaces concerned. This can, in principal, be done by considering the free energy of an instantaneous state of the system in relation to that of neighboring states. Further progress, however, meets the difficulty that a purely thermodynamic approach cannot in general give quantitative kinetic information; this can only be derived in relation to a particular model of the system. In this instance, Hu's suggestion is that kinetic wettability be measured by the slope of the square of the capillary rise height, h^2 , vs. time, t . The kinetics of the wettability of the coal and mineral particles can be easily determined by the capillary-rise test.

The ratio between the kinetics of wettability of pure water (H_2O) and those of different media or reagents (X), H_{H_2O}/H_X , is a simple and easy measure of hydrophilicity/ X -philicity (or relative kinetic wettability) of reagents and fine particles. It is a new concept for the evaluation of the relative kinetic wettability of different fine particle surfaces by different reagents.

K_X/K_{H_2O} , the ratio between flotation rate constants of different reagents (X) and that of pure water (H_2O) is a straightforward evaluation of the relative kinetic floatability.

The present work has been concerned with an experimental study to interpret

and consider kinetics of wettability, kinetics of floatability, evaluation of relative kinetic wettability, and evaluation of relative kinetic floatability. It also shows the correlation between kinetic wettability and kinetic floatability. Flotation interface modification is effective and can increase separation efficiency. Based on kinetic wettability and kinetic floatability studies, five-cycle closed-circuit tests of Upper Freeport coal was performed, and good separation efficiency is achieved.

These studies will contribute to the advanced selective separation of coal and its associated minerals.

II. THEORETICAL ANALYSIS AND NEW CONCEPTS

2.1 Theoretical Analysis

Classical wetting thermodynamics applied to froth flotation have been analyzed in depth.⁽¹⁴⁻¹⁶⁾ Some generalized conclusions are presented here.

The free energy change resulting from the contact between a bubble and a particle in aqueous suspension is

$$\Delta G = \gamma_{lv} (\cos \theta - 1) < 0 \quad (1)$$

where γ_{lv} is surface tension of liquid and vapor interface and θ is contact angle.

Thomas Young⁽¹⁷⁾ proposed Young's Equation to treat the contact angle of a liquid as the result of the mechanical equilibrium of a drop resting on a plane solid surface under the action of three tensions:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (2)$$

where γ_{sv} and γ_{sl} are the interfacial tensions of the solid and vapor phases and of the solid and liquid phases, respectively, and γ_{lv} is the interfacial tension of the liquid and vapor phases.

For liquid to penetrate a porous plug, the free energy for penetration, ΔG_p , is given by

$$\Delta G_p = \gamma_{sl} - \gamma_{sv} \quad (3)$$

For liquid to spread over the surface of the solid, the free energy of spreading, ΔG_s , is given by

$$\Delta G_s = \gamma_{sl} + \gamma_{lv} - \gamma_{sv} \quad (4)$$

Substituting Young's Equation (2) into Equations (3) and (4), ΔG_p and ΔG_s change to:

$$\Delta G_p = -\gamma_{\ell N} \cos \theta \quad (5)$$

$$\Delta G_s = \gamma_{\ell N} (1 - \cos \theta) \quad (6)$$

Thus, penetration of a liquid should take place if the contact angle is less than 90 degrees, and spreading should occur only when the contact angle is zero. Therefore, for the immersion test, rapid immersion must be controlled by spreading wetting or by a condition close to zero contact angle.

When a liquid penetrates a single capillary of radius r , the square of the height of the capillary rise, h^2 , in the time t is given by the Washburn Equation^(18,19):

$$h^2 = \frac{\gamma t r \cos \theta}{2\eta} \quad (7)$$

where γ is the surface tension of the liquid, r is the radius of the capillary, θ is the advancing contact angle, and η is the viscosity of the liquid.

The rising force of liquid penetration is controlled by the pressure drop ΔP across the curved liquid interface. The liquid enters the capillary spontaneously only if the contact angle is less than 90 degrees. The pressure drop is given by

$$\Delta P = \frac{2\gamma \cos \theta}{r} \quad (8)$$

where r is the radius of the circular capillary. If the contact angle is more than 90 degrees, the capillary rise is zero, or no rise occurs in the capillary. A powder packed in a tube may be considered to consist of a bundle of capillaries of mean radius r . Applying the Washburn Equation to this system yields

$$h^2 = \frac{c r \gamma t \cos \theta}{2\eta} \quad (9)$$

where c is a constant (introduced to allow for the randomly oriented capillary). For a given packing of the powder, $c r$ will be constant. Consequently, there is a linear

relationship between h and t . The value of cr can be calculated, if a liquid is chosen for which $\theta = 0$ degrees (complete wetting or spreading). Bruil and Van Aartsen⁽²⁰⁾ used this method to determine the contact angles of aqueous surfactant solutions on powders.

Supposing there are only four phases in coal or mineral flotation, namely solid (coal or mineral), water, oil, and air bubbles, six interfaces may exist in the system: coal or mineral/water, coal or mineral/air bubble, coal or mineral/oil, water/air bubble, water/oil, and oil/air bubble interfaces. From Young's Equation (2), if we know the contact angle at the solid/water and the solid/oil interfaces, the surface tension of solid/air, and the interfacial tensions of the oil/water, oil/air bubble, and water/air interfaces, the interfacial tension or energy of the solid/water and solid/oil interfaces can be calculated. Accordingly, coal or associated mineral flotation behavior may be characterized. Also, some practical suggestions to improve coal/pyrite and valuable mineral/gangue separation may be established.

2.2 New Concepts

In order to understand the surface chemistry of coal and inorganic minerals more clearly, the new concepts of kinetic wettability, relative kinetic wettability, kinetic floatability, and relative kinetic floatability have been introduced.

2.2.1 Kinetics of wettability

Classic wettability and its evaluation by methods such as contact angle deal with systems which are in a static equilibrium condition. We propose that the kinetic wettability is a more meaningful evaluation since it is measured in a dynamic steady-state condition. Laboratory measurement of the rate of capillary rise is a straightforward, simple method to study the kinetics of wettability of fine particles. Kinetic wettability is an accurate and effective way to interpret the surface wettability of coal and inorganic minerals. The primary process of wetting, or displacement of air from

the surface of the individual particles by the wetting liquid, may in certain cases extend over considerable periods of time. The method of measurement for liquids in contact with powders has been based on the penetration of liquids into plugs of powder. Carrying out this study to the final end point needs many hours. Since a practical coal flotation process lasts only a few minutes, as most coal floats in 3 to 5 minutes, for practicality and simplicity the tests were confined to 240 seconds.

The kinetics of capillary rise are a measure of the rate of interaction of the liquid with the fine particles. The slope of the curve for the square of the capillary-rise height versus time can be correlated with the hydrophobicity and hydrophilicity, oleophobicity and oleophilicity, and X-phobicity and X-philicity (where X refers to reagents) of the coal and minerals.

Modulation of the physical and chemical properties of interfaces plays a role in most aspects of mineral separation processing. The role of surface properties in the mineral industry, especially wetting phenomena, is used to advantage. Kinetic wettability is shown to have an important correlation to floatability.

2.2.2 Kinetic wettability index

Hu's kinetic wettability index (H) is a measure of the speed of the capillary rise. The faster the capillary rise, the steeper the slope of the square of the height vs. time. The index of kinetic wettability is measured by the slope of the square of the capillary rise height, h^2 , vs. time, t . $h^2 = Ht$ is a linear function in a short time interval which fits the flotation process. In most cases the experiment is easy to perform and the data are reproducible, which shows that the effect of gravity can be neglected and suggests that the physical structure or porosity of the powder is constant throughout the wetting process. Hu's kinetic wettability index (H) is related to the Washburn equation (Eq. (7)) as

$$H = \frac{h \times h}{t} = \frac{c\gamma \cos \theta}{2\eta}$$

Of course, it is possible to calculate contact angle θ from H , but for the sake of simplicity the kinetic wettability index H is more straightforward and more practical in engineering applications. The method is based on the unopposed penetration of liquid through a bed of powder and provides a simple method to investigate the complex surface properties of coal and minerals.

2.2.3 Relative kinetic wettability

Ratios of kinetic wettability indices provide a measure of the relative speed of capillary rise. The ratio H_{H_2O}/H_X between the speeds of capillary rise of pure water and other liquids or reagents (X) (such as oil, kerosene, etc.) is a good measure of hydrophilicity/X-philicity (or relative wettability) of the coal or mineral samples. If

$H_{H_2O}/H_X = 1$, there is an equal balance between hydrophilicity and X-philicity.

$H_{H_2O}/H_X > 1$, there is more hydrophilicity or less X-philicity.

$H_{H_2O}/H_X < 1$, there is less hydrophilicity or more X-philicity.

$H_{H_2O}/H_X = 0$, there is very low hydrophilicity, or essentially X-philicity.

Relative kinetic wettability is a new concept to compare the wetting behavior of pure water with different reagents. The effectiveness of reagents on the floatability and/or collectivity of coal or mineral can be predicted by the evaluation. For example, if H_{H_2O}/H_X is greater than 1, it can be predicted that reagent (X) is not an effective collector in the system; if H_{H_2O}/H_X is less than 1, it can be predicted that the reagent (X) is an effective collector.

The ratio between the speeds of capillary rise of different minerals, H_{m1}/H_{m2} , provides a measure of the relative kinetic wettability of various solids. When

$H_{m1}/H_{m2} = 1$, there is equal wettability between mineral 1 and mineral 2;

$H_{m1}/H_{m2} < 1$, mineral 1 is less wettable than mineral 2;

$H_{m1}/H_{m2} > 1$, mineral 1 is more wettable than mineral 2; and

$H_{m1}/H_{m2} = 1$, mineral 1 and mineral 2 cannot be separated in the system.

It can be predicted that if H_{m1}/H_{m2} is less than or greater than 1, mineral 1 and mineral 2 can be separated by flotation or spherical agglomeration.

Different reagents can be evaluated by the relative effectiveness of wetting. The ratio of the speeds of capillary rise using several reagents, for example, reagent 1 and reagent 2, provides general cases:

$H_{x1}/H_{x2} = 1$ means reagent 1 and 2 wet the surface equally.

$H_{x1}/H_{x2} > 1$ means reagent 1 wets the surface more than reagent 2.

$H_{x1}/H_{x2} < 1$ means reagent 1 wets the surface less than reagent 2.

If $H_{x1}/H_{x2} > 1$ or $H_{x1}/H_{x2} \gg 1$, it means reagent 1 is more effective than reagent 2.

2.2.4 Kinetics of floatability

Determining kinetic behavior provides an important means to simulate and optimize flotation and spherical agglomerative processes. Flotation rates are determined by collecting flotation concentrates at different flotation times. Flotation yield-time profiles are then fitted to a flotation kinetic model. For some systems, kinetics obtained from short flotation times may not provide the whole picture of the flotation kinetic behavior over extended flotation times. Lai has suggested a proportionality law of the process⁽²¹⁻²³⁾ and has used it to analyze and interpret a multitude of kinetic phenomena. The mathematical form is given by the equation

$$\frac{dR}{dt} = K \frac{(R_i - R)}{t}$$

and the integration form:

$$\ln \left[\frac{1}{(R_i - R)} \right] = K \ln(t) + \ln(c)$$

where R_i is the ultimate recovery or yield, R is the recovery or yield at time t , t is the flotation time (minutes), K is the flotation rate constant, and c is the integration

constant. If the test sample is a single, pure mineral, the equation can be transformed as:

$$K = \frac{\ln \left[\frac{1}{(R_i - R)} \right]}{\ln[t]}$$

From this equation, the flotation rate constant (K) can be calculated. The flotation rate constant has been applied to determine the kinetic floatability and collectability of the coal and minerals.

2.2.5 Relative kinetic floatability

Relative kinetic floatability is a new concept to compare the kinetics or rate of flotation between different coals and minerals and between different reagent systems. The ratio between flotation rate constants of different coals and inorganic minerals, K_{m1}/K_{m2} , is an important evaluation of relative kinetic floatability. If K_{m1}/K_{m2} is greater than 1, sample 1 floats faster than the sample 2. If K_{m1}/K_{m2} is much greater than 1, sample 1 floats much faster than sample 2. It can then be predicted that sample 1 and sample 2 will be separated easily by the flotation system used to obtain the individual rate constants.

The ratio between the flotation rate constants for different solutions vs. that for pure water, K_X/K_{H_2O} , is a useful evaluation of the relative kinetic floatability for coal and mineral. For example, if the coal and mineral have better floatability in salt solution than in a pure water system, that is, K_X/K_{H_2O} is greater or much greater than 1, it can be considered that salt solution is a modifier for the coal or mineral flotation system.

Relative collectability can be used to determine the effect of the reagents in flotation. K_{x1}/K_{x2} greater than 1 indicates that reagent 1 is a better collector than reagent 2. If K_{x1}/K_{x2} is much greater than 1, it can be predicted that reagent 1 is a more powerful collector than reagent 2.

III. EXPERIMENTAL METHODS AND SAMPLE CHARACTERIZATION

3.1 Experimental Methods

There are many methods for measuring the wettability and floatability of minerals and coals, such as contact angle, capillary rise, immersion time, film flotation, Hallimond-tube flotation, vacuum flotation, mini-cell flotation, standard-cell flotation, etc. All methods have their merits and defects, according to the specific requirements of the research. The experimental methods of the capillary-rise test, mini-cell flotation test, and standard-cell flotation test are used in this study.

The experimental samples are chosen and their characterization is considered.

3.1.1 Capillary-rise tests

A known weight of dried powder was placed in a glass tube about 1.0 cm in diameter and 10 cm long, with a marked scale, and consolidated by tapping. The lower end of the column was supported on a filter bed to prevent the coal or mineral particles from sinking into the liquid. For each test, the powdered sample (100 × 200 mesh) was put in the glass tube and filled to the same height, keeping the packing density of the powder constant. The amount of powder was kept constant for each test of a given material (5 g of coal, 15 g of coal pyrite, or 19 g of mineral pyrite). In experiments involving a single powder with a number of liquids, in each case the same tube was used, with a standard weight of powder occupying a given length of the tube.

The packed tube containing the powder was placed vertically into a dish of the liquid, and the time at which the liquid commenced to wet the powder was recorded. The height was observed by means of a lamp at the position of the liquid level. All experiments were performed at room temperature. The equipment is illustrated in Figure 1.

It was found that the actual porosity of the packing used was immaterial in so

Figure 1. Experimental set-up for capillary rise test.

far as reproducibility of results was concerned, provided that the packing was not too loose. Considerable experimentation was done on the technique of packing the column, including tamping the powder and using compressed plugs. The technique described above, in which the powder was consolidated by manual tapping, was found to be the most satisfactory.

3.1.2 Mini-cell flotation tests

Mini-cell flotation tests were carried out in a flotation cell. Violent agitation in the cell due to the speed of the impeller creates a current in the cell. As the pulp is pushed by the blades of the impeller, it flows outward at the level of the blades, then moves upward along the wall of the cell and downward again toward the impeller at the edge of the vortex.

In addition to this vertical circulation a horizontal motion is imparted to the pulp, concentric with the impeller shaft. Froth flotation of the samples (100 × 200 mesh) was carried out in 500-ml flotation cells. In experiments with the same sample weight and the same liquid level, the same agitation speed was used (900 rpm). The flotation procedure involved combining 35 grams dried samples with 400 ml distilled water, stirring for 3 minutes, conditioning with reagent for 2 minutes, and flotation for 96 minutes. The concentrate and tailing were collected, filtered, dried, and weighed to determine the flotation yield.

3.1.3 Standard-cell flotation tests

Standard flotation test procedures were developed using operating parameters within reasonable ranges so that the influences of grinding and surface-modifying reagents could be studied. The standard test was conducted at conditions generally adapted for laboratory experiments on coal and mineral. Preliminary tests confirmed that a number of flotation conditions should be kept constant for all samples. For example, the collector and frother dosages were selected to suit the flotation of each

sample. The flotation feed size was selected as 200 mesh. While a number of operation parameters were set at ranges considered suitable from past experience, others were determined empirically with the samples. These included the pulping time and the collector and frother conditioning times.

A Denver's Laboratory Model flotation machine was used for the flotation tests. It is shown in Figure 2. This flotation machine is especially designed for mechanical froth removal. Flotation stirring speed can be adjusted by mechanical control and air flow control. The flotation cell is made of plexiglas. The two-paddle design of the cell enables the removal of froth from two sides of the cell. A 2-liter cell was selected for batch flotation tests.

For the standard flotation cell test procedure, 500-gram samples of 2 mm size plus 700 ml distilled water were ground to 200 mesh and split into four equal parts by the riffler, each part weighing 125 ± 5 grams. The wet samples were then put into a 2-liter flotation cell and were stirred at 1100 rpm for 3 minutes, conditioned with reagent for 2 minutes, followed by aerating at an air flow rate of 4 l/min, and flotation for 5 minutes. The concentrate and tailing were collected, filtered, dried, and weighed to determine the flotation yield. The concentrate and tailing were each split by quartering method as analysis samples.

3.1.4 Closed-circuit flotation tests

In continuous plant operation, the middlings are usually fed back to the feed-conditioning tank or roughing cell and subsequently mixed with the new feed. In laboratory tests, the simulation of this flowsheet is called "closed-circuit" or "cyclic-circuit," as shown in Figure 3. The middlings of the first batch (Feed #1) are combined with the feed for the second batch (Feed #2), the middlings of the second batch with the feed for the third batch (Feed #3), and so on. The closed-circuit flotation test is based on standard cell flotation conditions. The five-cycle closed-circuit tests yielded five concentrates, one middling, and one tailing. These

Figure 2. Standard flotation apparatus.

concentrates, middling, and tailing are collected, filtered, dried, and weighed to determine flotation yield. Each sample was split by the quartering method for future analysis.

3.2 Sample Characterization

Three coal samples were analyzed for these investigations. The ultimate and proximate analysis of the samples are shown in Table 1. The assay of samples is listed in Table 2.

Table 1. Ultimate analysis and heat value of coal samples

Coal samples	C%	H%	N%	S%	O%	Heat value BTU/lb
Upper Freeport coal	75.6	4.7	1.45	2.38	3.85	13,370
Pittsburgh No. 8 coal	71.0	5.1	1.45	4.28	6.40	12,420
Illinois No. 6 coal	63.8	5.7	1.24	5.73	6.10	11,320

Table 2. Assay of pyrite

Samples	coal pyrite	mineral pyrite
FeS ₂ %	86.52	91.93

IV. RESULTS AND DISCUSSION

Capillary-rise tests, mini-cell flotation tests, and flotation cell tests were used in the present study. The results are summarized and discussed in this chapter.

4.1 Kinetics of Capillary Rise

4.1.1 Kinetic capillary-rise tests in distilled water

Capillary-rise tests were conducted for Upper Freeport coal, Pittsburgh No. 8 coal, Illinois No. 6 coal, Colorado mineral pyrite, and coal pyrite (hereafter referred to as the five samples) in distilled water.

The capillary-rise test results for the five samples in distilled water are shown in Figure 4. There is a good linear relationship between $h \times h$ and time.

It is clear from Figure 4 that the slopes increase as the wettability of the sample increases. It can be seen that the slope (H) of the Upper Freeport coal is zero, which means Upper Freeport coal is nonwetting in water.

Kinetic wettability indices for the five samples are listed in Table 3. The rank of kinetic wettability indices for the five samples in distilled water is:

Upper Freeport coal < Pittsburgh No. 8 coal < Illinois No. 6 coal $\leq$ coal pyrite < Colorado mineral pyrite

This shows that Upper Freeport coal has the least kinetic wettability, and Colorado mineral pyrite has the most kinetic wettability in distilled water.

Table 3. Kinetic wettability indices (H) in distilled water

samples	distilled water (H)
Upper Freeport coal	0.0000
Pittsburgh No. 8 coal	0.0123
Illinois No. 6 coal	0.1393
coal pyrite	0.1467
Colorado mineral pyrite	0.2797

Figure 4. The kinetic capillary rise test results of five samples in distilled water.

According to the new concept, the kinetic wettability with water should correlate reciprocally with the natural floatability. In this context, it can be predicted that Upper Freeport coal will be the most hydrophobic (or most floatable), and Colorado mineral pyrite will be the most hydrophilic (or least floatable) in distilled water.

The coals studied exhibit different hydrophobicity (or wettability), depending on their structure and surface properties. Most coals are nonpolar, and their surfaces have relatively weak molecular bonds that are difficult to hydrate. They also have low surface free energy. However, the wettability of different coal samples is different; for instance, the Upper Freeport coal is more hydrophobic than the Illinois No. 6 coal sample.

Pyrite is a polar mineral and has strong covalent or ionic surface bonding, and exhibits high free energies at its surface. Thus, this species is hydrophilic and has low natural floatability.

4.1.2 Kinetic capillary-rise tests in 3% and 6% NaCl solutions

Kinetic capillary-rise test results for the five samples in 3% and 6% NaCl solutions are shown in Figures 5 and 6.

Kinetic wettability indices for the five samples are presented in Table 4.

Table 4. Kinetic wettability indices in 3% and 6% NaCl solutions

samples	3% NaCl (H)	6% NaCl (H)
Upper Freeport coal	0.0000	0.0000
Pittsburgh No. 8 coal	0.0000	0.0000
Illinois No. 6 coal	0.0844	0.0595
coal pyrite	0.1463	0.1388
Colorado mineral pyrite	0.2762	0.2693

Figure 5. The kinetic capillary rise test results of five samples in 3% NaCl solution.

Figure 6. The kinetic capillary rise test results of five samples in 6% NaCl solution.

As can be seen from Figures 5 and 6, as salt concentration increases, the slope decreases for Illinois No. 6 coal, and the slope is zero for Upper Freeport coal and Pittsburgh No. 8 coal. There is little change in slope for the other samples in 3% and 6% solutions.

The data of Table 4 show that the kinetic wettability of some of the samples decreases with increasing salt concentration. That is attributable to the fact that the surface tension of inorganic electrolyte solutions increases with concentration of the electrolyte. The results obviously indicate that the surface excesses of the various salts are negative or, in other words, that the electrolyte as a whole is adsorbed from the interface. It may well be that one ion is repelled from the surface more strongly than the other, which can be explained by surface potentials. In general, the surface potential arises from charges both in the dipole orientation at the interface and in the ionic double layer. Since the inorganic electrolytes are adsorbed, the former contribution is probably small, and the surface potentials in these systems are usually thought to approximately reflect the change in the ionic double layer potential. For most instances the surface potential is positive. It would appear, therefore, that cations tend to be repelled more strongly than anions.

4.1.3 The relative kinetic wettabilities of water and 3% or 6% NaCl solutions

The relative kinetic wettabilities $H_{H_2O}/H_{3\%NaCl}$ and $H_{H_2O}/H_{6\%NaCl}$ are given in Table 5. These results indicate that the relative wettability is undefined for the Upper Freeport coal and Pittsburgh No. 8 coal, which could not be wetted by NaCl solutions. From the relative wettability of Illinois No. 6 coal, it can be seen that this coal is more hydrophilic and less NaCl solution-philic. The other samples have nearly balanced hydrophilicity and NaCl solution-philicity.

Table 5. Relative kinetic wettabilities for water and 3% or 6% NaCl solution

samples	$H_{H_2O}/H_{3\%NaCl}$	$H_{H_2O}/H_{6\%NaCl}$
Upper Freeport coal	-	-
Pittsburgh No. 8 coal	-	-
Illinois No. 6 coal	1.6500	2.3424
coal pyrite	1.0027	1.0569
Colorado mineral pyrite	1.0127	1.0386

The results in Table 5 show that the relative kinetic wettability of Illinois No. 6 coal changed from 3% to 6% NaCl solution, but the wettability of the two pyrites did not change significantly.

From theoretical analysis and the new concepts, it can be predicted that the coal samples will have better floatability than pyrite in salt solution.

4.1.4 Kinetic capillary-rise tests in kerosene, benzene and 30% amyl xanthate solution

Capillary-rise test results for the five samples in kerosene, benzene, and 30% amyl xanthate solution are presented in Figures 7 to 9, respectively.

Kinetic wettability indices for the five samples are listed in Table 6.

Table 6. Kinetic wettability indices (H) for kerosene, benzene and amyl xanthate

samples	kerosene (H)	benzene (H)	amyl xanthate (H)
Upper Freeport coal	0.1731	0.4851	0.0606
Pittsburgh No. 8 coal	0.1388	0.4125	0.1063
Illinois No. 6 coal	0.1257	0.3643	0.1065
coal pyrite	0.0799	0.3242	0.1327
Colorado mineral pyrite	0.0897	0.2502	0.1779

Figure 7. The kinetic capillary rise test results of five samples in kerosene.

Figure 8. The kinetic capillary rise test results of five samples in benzene.

Figure 9. The kinetic capillary rise test results of five samples in 30% amyl xanthate solution.

Figure 7 shows that the Upper Freeport coal, Pittsburgh No. 8 coal, and Illinois No. 6 coal are the most kerosene-philic. Coal pyrite and mineral pyrite behave less kerosene-philicly.

These results are important; they indicate that kerosene can be used as an effective reagent for selective flotation and oil agglomeration to separate coal from coal pyrite.

The kinetic wettabilities of the five samples in benzene are shown in Figure 8. It is interesting that the Upper Freeport coal and Pittsburgh No. 8 coal are the most benzene-philic, and Colorado mineral pyrite is the least benzene-philic. The other samples have medium benzene-philicity. The kinetic wettability indices (Table 6) indicate that benzene is the best of the wetting agents. Benzene's values of H are nearly twice as large as those for kerosene. The specific character indicates benzene has stronger collectivity for both coal and pyrite, and thus inferior selectivity to kerosene for the coal pyrite system.

Xanthate has long been studied for its mechanism on surfaces of sulfide minerals. Capillary-rise tests have been used to study the kinetic wettability of the five samples in 30% amyl xanthate solution. The results, shown in Figure 9, indicate that the mineral pyrite has the most xanthate-philicity, and Upper Freeport coal has the least xanthate-philicity. The measure of the kinetic wettability is interesting. It can be seen that the xanthate solution has a strong penetration capability for mineral pyrite. This property of xanthate depends on molecular structure. It can be predicted that not only the mineral pyrite but also the coal pyrite and coal will float in a xanthate/water system. This test result reveals that pyrite could not be effectively separated from coal in xanthate/water systems.

4.1.5 Relative kinetic wettabilities for water vs. kerosene, benzene, and amyl xanthate

Table 7 shows the relative kinetic wettabilities of the five samples for water vs. kerosene, water vs. benzene, and water vs. amyl xanthate.

It is interesting to compare the results of $H_{H_2O}/H_{\text{kerosene}}$, $H_{H_2O}/H_{\text{benzene}}$, and $H_{H_2O}/H_{\text{amyl xanthate}}$. The coal surfaces are kerosene-philic or relatively hydrophobic. The coal pyrite and mineral pyrite are more hydrophilic and less kerosene-philic.

According to the new concepts, kerosene may modify the coal surfaces, but it cannot modify pyrite surfaces. It can be seen that pyrites are more strongly wetted by water than by kerosene. Hydrated pyrites should repel kerosene. It can be predicted that coals will tend to float better than pyrite if kerosene is used as a collector of flotation.

Column 3 of Table 7 indicates that coals and coal pyrite are less hydrophilic and more benzene-philic.

Column 4 of Table 7 shows that Illinois No. 6 coal, coal pyrite, and mineral pyrite are more hydrophilic but less amyl xanthate-philic.

Table 7. Relative kinetic wettabilities between water and kerosene, benzene, or amyl xanthate

samples	$H_{H_2O}/H_{\text{kerosene}}$	$H_{H_2O}/H_{\text{benzene}}$	$H_{H_2O}/H_{\text{amyl xanthate}}$
Upper Freeport coal	0.0000	0.0000	0.0000
Pittsburgh No. 8 coal	0.0734	0.0252	0.1408
Illinois No. 6 coal	0.8918	0.3925	1.3615
coal pyrite	1.7926	0.4480	1.0676
Colorado mineral pyrite	1.6187	1.1213	2.0529

4.1.6 Kinetic capillary-rise tests for the five samples in methanol, ethanol, butanol and hexanol

Kinetic capillary-rise tests for the five samples were conducted in the alcohol homologues methanol, ethanol, butanol, and hexanol. Results are shown in Figures 10 to 13.

The kinetic wettabilities for the five samples in methanol shows that Upper Freeport coal and Pittsburgh No. 8 coal are the most methanol-philic, and that the coal pyrite is the least methanol-philic. From Figure 10, it can be seen that the rate of wettability is fast for the five samples. Because the viscosity of methanol is small, its penetration force is large for fine particles.

Concerning kinetic wettabilities in ethanol, the three coals are more wettable than the coal pyrite and the mineral pyrite. Figures 10 and 11 indicate that the rate of wettability is smaller for ethanol than for methanol. It is apparent that the kinetic wettability of particle surfaces is dependent on the carbon chain length of the alcohols.

The kinetic wettabilities of the five samples using butanol are presented in Figure 12. The slopes (H) also are small for the five samples. It seems that hydrocarbon chains impact kinetic wettability.

Figure 13 shows the kinetic wettability of the five samples in hexanol. It is observed that the wetting speeds for the five samples are very slow. All slopes are very small. That is, the five samples have low hexanol-philicity.

As can be seen from Figures 10 to 13, as the carbon chain length of the alcohol increases, the kinetic wettabilities in the alcohols decrease. Because alcohol molecular groups act on fine particle surfaces, it is possible to influence the kinetic wettability. It is found that the kinetic wettability is dependent on the viscosity of the alcohol. The shorter the carbon chain, the smaller the viscosity; thus, the greater the kinetic wettability.

Figure 10. The kinetic capillary rise test results of five samples in methanol.

Figure 11. The kinetic capillary rise test results of five samples in ethanol.

Figure 12. The kinetic capillary rise test results of five samples in butanol.

Figure 13. The kinetic capillary rise test results of five samples in hexanol.

Kinetic wettability indices for methanol, ethanol, butanol and hexanol are listed in Table 8. These test results indicate that the kinetic wettability decreases as the carbon chain length increases for the five samples.

The kinetic wettability of a liquid on solid surfaces is dependent on properties of the solid surface, the viscosity of the liquid, the surface tension of the liquid, and the interfacial tensions of the three phases for homologous alcohol series.

4.1.7 Relative kinetic wettabilities for water vs. methanol, ethanol, butanol, and hexanol

The ratio between kinetics of the capillary rise for different media is a measure of relative wettability. From Table 9, the relative kinetic wettabilities of the five

Table 8. Kinetic wettability indices for methanol, ethanol, butanol and hexanol

samples	methanol (H)	ethanol (H)	butanol (H)	hexanol (H)
Upper Freeport coal	0.3673	0.1779	0.1277	0.0679
Pittsburgh No. 8 coal	0.3654	0.1652	0.1203	0.0659
Illinois No. 6 coal	0.2698	0.1585	0.0837	0.0643
Colorado mineral pyrite	0.2189	0.0995	0.0705	0.0396
coal pyrite	0.2117	0.0896	0.0657	0.0445

Table 9. Relative kinetic wettabilities between water and methanol, ethanol, butanol, or hexanol for the five samples

samples	$H_{H_2O}/H_{\text{methanol}}$	$H_{H_2O}/H_{\text{ethanol}}$	$H_{H_2O}/H_{\text{butanol}}$	$H_{H_2O}/H_{\text{hexanol}}$
Upper Freeport coal	0.0000	0.0000	0.0000	0.0000
Pittsburgh No. 8 coal	0.0337	0.0745	1.02224	0.1866
Illinois No. 6 coal	0.5163	0.8789	1.1643	2.1664
coal pyrite	0.6930	1.6373	2.2329	3.2966
Colorado mineral pyrite	1.2778	2.8111	3.9674	7.0631

five samples in methanol, ethanol, butanol, and hexanol show that the kinetic wettability is dependent on the carbon chain of the alcohol.

The relative kinetic wettabilities of the water/methanol, water/ethanol, water/butanol, and water/hexanol systems for the five samples indicate that Upper Freeport coal has very low hydrophilicity, or better floatability than coal pyrite and mineral pyrite. It means that if methanol, ethanol, butanol, or hexanol is used as a collector, Upper Freeport coal will be selectively separated from coal pyrite.

4.2 Mini-Cell Flotation Test

4.2.1 Kinetic mini-cell flotation tests of the five samples without collector

Kinetic mini-cell flotation tests were carried out without collector on the five samples. The natural floatability measurement of the five samples is plotted in Figure 14. The ranks of the floatability of the five samples are as follows:

Upper Freeport coal > Pittsburgh No. 8 coal > Illinois No. 6 coal > coal pyrite > Colorado mineral pyrite.

Upper Freeport coal has the best natural floatability or greatest hydrophobicity, and Colorado mineral pyrite has the least natural floatability or greatest hydrophilicity.

The results of investigation of kinetic floatability are compatible with those for kinetic wettability from capillary-rise tests. The natural floatability of coals and minerals is an important basic characteristic for selective flotation, floatability evaluation, mineral surface modification, and design of the flotation reagent. The results show that there is good agreement between the experimental observations and the new concepts of kinetic wettability and kinetic floatability. Some materials with low wettability has high hydrophobicity and better floatability in a water system.

Figure 14. The kinetic mini-cell flotation test results of five samples without collector.

4.2.2 Kinetic mini-cell flotation tests with different concentrations of salt solution

The kinetics of the floatability of the five samples with 3% and 6% NaCl solutions were studied. The results are plotted in Figures 15 and 16. The flotation tests demonstrated that the floatability of coal was greatly enhanced by the presence of the electrolyte NaCl. The results indicate that the kinetic floatability of the coal increases as the NaCl concentration increases.

The kinetic flotation rate constants of the five samples with distilled water and with 3% and 6% NaCl solutions are listed in Table 10. The test results indicate that the kinetic flotation rate constants of coals are increased, or the coal surface hydrophobicity is improved, by the addition of NaCl. The flotation rates of the pyrites were not significantly influenced by NaCl.

4.2.3 Relative kinetic floatability between 3% or 6% NaCl solutions and water

$K_{3\%NaCl}/K_{H_2O}$ and $K_{6\%NaCl}/K_{H_2O}$ for the five samples are listed in Table 11. It can be seen that the flotation rate constants of the coal samples increase rapidly as the NaCl solution concentration increases. The test results for NaCl solution show that the surface free energy of the inorganic electrolyte decreases with increasing concentration of the electrolyte.

Table 10. The flotation rate constants of mini-cell flotation with 3% and 6% NaCl solutions for the five samples

samples	K_{H_2O}	$K_{3\% NaCl}$	$K_{6\% NaCl}$
Upper Freeport coal	0.1435	0.4498	0.6869
Pittsburgh No. 8 coal	0.0722	0.3359	0.3744
Illinois No. 6 coal	0.0585	0.2425	0.3039
coal pyrite	0.0413	0.0424	0.0740
Colorado mineral pyrite	0.0366	0.0398	0.0547

Figure 15. The kinetic mini-cell flotation test results of five samples with 3% NaCl solution.

Figure 16. The kinetic mini-cell flotation test results of five samples with 6% NaCl solution.

Table 11. Relative kinetic floatability between
3% or 6% NaCl solution and water

samples	$K_{3\%NaCl}/K_{H_2O}$	$K_{6\%NaCl}/K_{H_2O}$
Upper Freeport coal	3.1345	4.7868
Pittsburgh No. 8 coal	4.6523	5.1866
Illinois No. 6 coal	4.1453	5.1949
coal pyrite	1.0266	1.7918
Colorado mineral pyrite	1.0874	1.3744

The results show the interesting fact that there is good agreement between kinetic floatability (mini-cell flotation tests) and kinetic wettability (capillary-rise tests) in the systems of 3% and 6% NaCl solutions.

The ratio of the kinetic rate constants for mini-cell flotation tests involving different media is a good measure of relative kinetic floatability. The test results indicate that the kinetic floatability of the coal and pyrite is dependent on the concentration of the electrolyte.

4.2.4 Kinetic mini-cell flotation tests with kerosene, benzene, and amyl xanthate as collector

Kinetic mini-cell flotation tests were carried out for the five samples with kerosene, benzene, and amyl xanthate as collector. The dosage of kerosene and benzene was 56 mg/L and that of amyl xanthate was 22.4 mg/L. The results of kinetic collectability are plotted in Figures 17 to 19.

The kinetic collectability showed that the yields of coal samples increase rapidly in the initial flotation time period. The test results indicate that the kerosene is strongly absorbed and exhibits better collectability on coal surfaces than on inorganic mineral surfaces.

Results of kinetic floatability tests (Table 12) indicate that a relatively higher rate of flotation is exhibited for Upper Freeport coal than for coal pyrite. The

Figure 17. The kinetic mini-cell flotation test results of five samples with kerosene as collector (kerosene: 56 mg/L).

Figure 18. The kinetic mini-cell flotation test results of five samples with benzene as collector (benzene: 56 mg/L).

Figure 19. The kinetic mini-cell flotation test results of five samples with amyl xanthate as collector (amyl-xanthate: 22.4 mg/L).

Table 12. The flotation rate constants of mini-cell flotation with kerosene, benzene, or amyl xanthate as collectors

Samples	K_{kerosene}	K_{benzene}	$K_{\text{amyl xanthate}}$
Upper Freeport coal	0.7639	0.2477	0.6323
Pittsburgh No. 8 coal	0.5995	0.1977	0.4225
Illinois No. 6 coal	0.5693	0.1639	0.3274
coal pyrite	0.1419	0.0508	0.1267
Colorado mineral pyrite	0.1308	0.0757	0.5051

kerosene can spontaneously absorb on the coal surface and decrease the interfacial energies of coal/kerosene, so that the floatability of coal is improved. The surfaces of coal pyrite and mineral pyrite are less kerosene-philic (more hydrophilic). Water has strong attractive forces for coal pyrite and mineral pyrite. Therefore, kerosene will be repelled by water on the pyrite surfaces in the kerosene/water system.

From Figure 18, it is evident that benzene is a moderately strong collector for coal flotation, but is a very weak pyrite collector. The adsorption of benzene seems to depend on the molecular structure of the aromatic ring. Benzene exhibited a weak polarity on the pyrite surfaces.

Figure 19 shows some interesting phenomena. The amyl xanthate behaved as a very strong collector of Upper Freeport coal and mineral pyrite, but exhibited much weaker adsorption on the surface of the coal pyrite. It was found elsewhere in our experiments that amyl xanthate is a flotation collector in the separation of coal pyrite from Upper Freeport coal.⁽²⁴⁾

4.2.5 Relative kinetic collectability by kerosene, benzene, or amyl xanthate and water

The relative kinetic collectabilities of three different collectors, kerosene, benzene and amyl xanthate, are given in Table 13. As can be seen from the table, the flotation rate constant of kerosene for coal is much larger than that of water.

Table 13. Relative collectability of the five samples by kerosene, benzene, or amyl xanthate vs. water

samples	$K_{\text{kerosene}}/K_{\text{H}_2\text{O}}$	$K_{\text{benzene}}/K_{\text{H}_2\text{O}}$	$K_{\text{xanthate}}/K_{\text{H}_2\text{O}}$
Upper Freeport coal	5.3233	1.7261	4.4063
Pittsburgh No. 8 coal	8.3033	2.7382	5.8518
Illinois No. 6 coal	9.7316	2.8017	5.5966
coal pyrite	3.4358	1.2300	3.0677
Colorado mineral pyrite	3.5738	2.0683	13.801

The kerosene was strongly adsorbed by the coal. It exhibited relatively weak adsorption by coal pyrite and mineral pyrite. Consequently, a good way to selectively separate pyrite from coal is to use kerosene as the collector.

The relative flotation rate constants in column 3 of Table 13 show that benzene is not effective. This might be due to the effect of the structure and properties of benzene. Its adsorption is very weak on the surfaces of the coals and minerals.

It is interesting to observe from column 4 of Table 13 that xanthate is a powerful collector of mineral pyrite.

4.2.6 Mini-cell flotation tests with methanol, butanol, or hexanol as collectors

Methanol, butanol, and hexanol were used as collectors at a dosage of 56 mg/L. The results are illustrated in Figures 20, 21, and 22, respectively, and the flotation rate constants are shown in Table 14.

The experiments indicate that the collecting abilities of the reagents increase with their carbon chain lengths. When the carbon chain length increases to 6, the reagent's collecting ability sharply increases for coal samples, but hardly changes for coal pyrite and mineral pyrite. The results suggest that hexanol would be an effective collector in separating coal from coal pyrite.

Figure 20. The kinetic mini-cell flotation test results of five samples with methanol as collector (methanol: 56 mg/L).

Figure 21. The kinetic mini-cell flotation test results of five samples with butanol as collector (butanol: 56 mg/L).

Figure 22. The kinetic mini-cell flotation test results of five samples with hexanol as collector (hexanol: 56 mg/L).

Table 14. The flotation rate constants of mini-cell flotation with methanol, butanol, and hexanol as collectors

samples	K_{methanol}	K_{butanol}	K_{hexanol}
Upper Freeport coal	0.2057	0.3976	0.7454
Pittsburgh No. 8 coal	0.1738	0.3286	0.6993
Illinois No. 6 coal	0.1495	0.2837	0.5473
coal pyrite	0.0540	0.1463	0.1827
Colorado mineral pyrite	0.0470	0.0912	0.1554

4.2.7 Relative kinetic collectability for homologous alcohol and water

The relative kinetic collectability of the five samples in methanol, butanol, or hexanol, and water are summarized in Table 15. It can be seen that the rank of kinetic collectability of homologous alcohols for Upper Freeport coal, Pittsburgh No. 8 coal, and Illinois No. 6 coal are as follows:

$$K_{\text{hexanol}}/K_{\text{H}_2\text{O}} > K_{\text{butanol}}/K_{\text{H}_2\text{O}} > K_{\text{methanol}}/K_{\text{H}_2\text{O}}$$

It is also apparent that longer carbon-chain alcohols are stronger collectors of coals. From Table 15, it can be seen that the relative flotation rate constants for coal pyrite and mineral pyrite increases slowly as the alcohol chain length increases. It is very useful in the selective separation of coal from coal pyrite with longer chain alcohols as collectors.

Table 15. Relative kinetic collectability between methanol, butanol, or hexanol and water

samples	$K_{\text{methanol}}/K_{\text{H}_2\text{O}}$	$K_{\text{butanol}}/K_{\text{H}_2\text{O}}$	$K_{\text{hexanol}}/K_{\text{H}_2\text{O}}$
Upper Freeport coal	1.4334	2.7707	5.1944
Pittsburgh No. 8 coal	1.5272	2.8875	6.1450
Illinois No. 6 coal	2.5556	4.8496	9.3556
coal pyrite	1.3075	3.5424	4.4237
Colorado mineral pyrite	1.2842	2.4918	4.2459

4.3 Modification of Flotation Interfaces

In flotation, the separation of one material from another occurs by selectively altering and controlling the hydrophobicity of the various interfaces present. One way to enhance flotation is to selectively increase the hydrophobicity of the coal while leaving the mineral surface unchanged. The results of investigation with various types of surface modifiers and their effects on fine coal flotation are summarized in the following.

4.3.1 Flotation tests with salt as modifier

Flotation cell tests were conducted using 200-mesh wet-ground Upper Freeport coal and Illinois No. 6 coal, adding 3% and 6% NaCl solutions to the flotation pulp. Results are shown in Tables 16 and 17.

Table 16. Effect of NaCl solution on the flotation of Upper Freeport coal

Modifier	Flotation product analysis			Rejection		separation efficiency
	yield %	ash %	pyr. S %	ash %	pyr. S %	
none	23.8	4.01	0.27	92.1	96.0	22.0
3% NaCl	89.7	7.28	0.66	46.2	63.5	58.2
6% NaCl	96.6	9.22	0.90	26.6	46.3	46.1

Table 17. Effect of NaCl solution on the flotation of Illinois No. 6 coal

Modifier	Flotation product analysis			Rejection		separation efficiency
	yield %	ash %	pyr. S %	ash %	pyr. S %	
none	7.0	9.98	0.62	95.7	97.8	5.3
3% NaCl	33.6	10.25	0.93	78.7	87.7	23.8
6% NaCl	51.0	9.62	0.83	69.7	83.7	38.7

From Tables 16 and 17, it can be seen that the separation efficiencies of Upper Freeport coal and Illinois No. 6 coal increase with NaCl concentration.

4.3.2 Flotation tests using methanol, ethanol, or butanol with Upper Freeport coal

Results of flotation separation tests adding methanol, ethanol, and butanol to the pulp of 200-mesh wet-ground Upper Freeport coal indicate that methanol, ethanol, and butanol improve the separation efficiency as compared with standard flotation.

In addition, as shown in Table 18, methanol, ethanol, and butanol are effective modifiers to improve the interfacial chemical properties of the coal. Mechanistically speaking, methanol, ethanol, and butanol decrease interfacial free energy, so the coal floatability increases.

4.3.3 Closed-circuit flotation

The beneficial effects of butanol on the flotation of Upper Freeport coal were investigated in more detail through closed-circuit flotation. The results of five-cycle closed-circuit flotation of 200-mesh, wet-ground Upper Freeport coal with 4 lb/T butanol (no other reagents added) are given in Table 19. These results show that

Table 18. Effects of methanol, ethanol, and butanol on the flotation response of Upper Freeport coal

Mod. Name	Reagent dosage			Product analysis			Rejection		separation efficiency
	dodecane lb/T	MIBC lb/T	Mod. lb/T	yield %	ash %	pyr. S %	ash %	pyr. S %	
standard	0.48	0.27	0.0	68.2	5.30	0.51	71.1	78.5	52.3
methanol	0.48	0.27	2.0	82.7	6.50	0.27	58.2	78.1	66.4
ethanol	0.48	0.27	6.0	84.8	6.52	0.41	54.5	78.5	69.2
butanol	0.30	0.00	4.0	81.5	5.58	0.34	62.3	82.9	70.4

Table 19. Flotation results of Upper Freeport coal
for five cycles with 4.0 lb/T butanol

Product	Flotation product analysis					Rejection		separation efficiency
	Yield %	Ash %	Pyr. S %	CMR %	HVR %	Ash %	Pyr. S %	
Con. 1	54.6	3.40	0.20	60.2	61.6	84.1	93.0	53.2
Con. 2	79.8	4.44	0.25	87.1	88.6	71.5	87.2	74.3
Con. 3	83.9	4.87	0.28	89.9	91.5	63.6	84.9	74.8
Con. 4	82.6	5.10	0.28	89.5	91.1	65.9	85.2	74.7
Con. 5	82.0	4.95	0.26	88.9	91.5	67.1	86.3	76.5
Middling	34.8	16.9	1.48					

CMR = combustible material recovery

HVR = heat value recovery

after three cycles equilibrium was reached, resulting in a combustible material recovery (CMR) close to 90% (88.9%), a heat value recovery (HVR) of 91.5%, and a pyrite sulfur rejection of about 86.3%. The separation efficiency was about 76.5. These results are very close to 90% BTU recovery with 90% pyrite sulfur rejection.

CONCLUSIONS

1. The slope of the straight line obtained by plotting the capillary rise height vs. time is a measure of the kinetics of wettability. The ratio between the kinetics of wettability of a reagent and water for a coal or mineral sample permits evaluation of relative kinetic wettability.
2. The kinetics of wettability show a good correlation with the kinetics of floatability. Test results indicate a simple capillary-rise test can be correlated with laboratory flotation test.
3. The ratio between the speeds of capillary rise for pure water (H_2O) and another liquid (X), H_{H_2O}/H_X , is a good measure of the hydrophilicity/X-philicity (or relative wettability) of the coal and pyrite particle surfaces. Evaluation of the relative kinetic wettability of pure water and kerosene, benzene, methanol, ethanol, butanol, or hexanol demonstrates that Upper Freeport and Pittsburgh No. 8 coals are less hydrophilic or more reagent-philic than coal pyrite and mineral pyrite.
4. The ratio between flotation rate constants of different media or reagents (X) and pure water (H_2O), K_X/K_{H_2O} , is an important evaluation of relative floatability for coal and pyrite samples. The relative kinetic floatabilities of 3% and 6% NaCl solution, kerosene, amyl xanthate, or hexanol, and pure water indicate that salt solution can improve the floatability of the coals, and that kerosene, amyl xanthate, and hexanol are better collectors for coal than for pyrite.
5. The new concepts and experimental methods are straightforward and practical for qualitative comparison of coal and pyrite wettability and floatability.
6. Based on kinetic wettability and kinetic floatability studies, five-cycle closed-circuit tests of Upper Freeport coal were done, and a good separation efficiency was achieved.

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