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FOSSIL ENERGY QUARTERLY REPORT

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Date Transmitted: April, 1990

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Pittsburgh, Pennsylvania**

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Prepared for: Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Project Monitor: J. Balzarini

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ABSTRACT

To achieve a better understanding of the effect of mild oxidation on the surface properties of coal and on the agglomeration response of the material, some finely ground bituminous coal from the No. 2 Gas Seam in Raleigh county, West Virginia, was oxidized by air at 150°C for up to 72 hr. As the treatment progressed, both the induction time (gas bubble attachment time) and the hydrophilicity index (based on infrared absorption spectra) of the material increased gradually. On the other hand, the heat of immersion of the material in water increased rapidly during the first 12 hr of treatment and then increased slowly for the next 36 hr. Surprisingly, the agglomeration response of the material did not appear to be affected significantly by the treatment. However, the data were somewhat scattered which may have masked an underlying trend. Also the agglomeration response based on turbidity changes may have been insensitive to the effect of the treatment because the coal particle size (-70/+100 mesh) was coarser than the -200 mesh particles used previously.

The role which hydrocarbon chain length plays in the oil agglomeration process was investigated for a series of paraffinic hydrocarbons which ranged from pentane to an oil with an average chain length of 30 carbon atoms. These hydrocarbons were used to agglomerate hydrophobic No. 2 Gas Seam coal from West Virginia. When starvation levels of the agglomerants were employed, the effectiveness of the hydrocarbons

increased significantly with carbon chain length. However, with large amounts of agglomerants, all of the hydrocarbons were equally effective so chain length appeared unimportant.

Further consideration was given to the use of pyrite depressants for improving the selectivity of the oil agglomeration process. Potential depressants were tested against mineral pyrite and coal-derived pyrite. The pyrites were sulfidized to improve their response to oil agglomeration. In some tests, pyrite alone was subjected to agglomeration with heptane, whereas in other tests the pyrite was mixed with Illinois No. 6 coal before being subjected to agglomeration with heptane. The effectiveness of sodium sulfide, ferric chloride, and thioglycolic acid as depressants for sulfidized mineral pyrite was confirmed using pyrite suspensions. While thioglycolic acid proved effective in both acidic and basic suspensions, smaller concentrations were required to depress sulfidized mineral pyrite in basic solutions than in acidic solutions. The agglomeration of sulfidized coal-derived pyrite was suppressed by thioglycolic acid and titanous chloride in much the same way as agglomeration of sulfidized mineral pyrite was suppressed. The selectivity of the oil agglomeration process for Illinois No. 6 coal over sulfidized mineral pyrite was improved significantly by a number of pyrite depressants. Thioglycolic acid, mercaptoethanesulfonic acid, and mercaptosuccinic acid proved very effective in this application, whereas thiolactic acid and titanous chloride proved somewhat less effective. Ferric chloride seemed to enhance pyrite recovery at the expense of coal recovery which was opposite to the effect observed previously when it was applied to the separation of mixtures of Upper Freeport coal and sulfidized pyrite.

BASIC PRINCIPLES AND MECHANISMS OF SELECTIVE OIL AGGLOMERATION

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OBJECTIVE

The overall objective is to determine the basic principles and mechanisms which underlie a number of selective oil agglomeration processes that have been proposed for beneficiating fine-size coal. An understanding of the basic principles and mechanisms will greatly facilitate technical development and application of such processes to various types of coal.

INTRODUCTION

The investigation of the basic principles and mechanisms of oil agglomeration advanced on several fronts. The effect of mild oxidation on the surface properties and agglomeration response of No. 2 Gas Seam coal from Raleigh county, West Virginia, was studied. Oxidation was accomplished by treating the finely ground material with air at 150°C for a number of hours. The effects of the treatment were determined by measuring the induction time, heat of immersion, infrared absorption spectra, and agglomeration response of the material. The untreated coal was also used to study the effect of employing different paraffinic liquids on the agglomeration characteristics of the material in order to determine the importance of carbon chain length.

Several reagents which had been shown previously to depress the agglomeration of sulfidized pyrite were studied in greater detail. Both mineral pyrite and coal-derived pyrite were employed in this study. The depressants included sodium sulfide, ferric chloride, thioglycolic acid,

and titanous chloride. The effects of depressant concentration, suspension pH, and application technique on the agglomeration response of sulfidized pyrite were investigated.

The effectiveness of a number of pyrite depressants was further evaluated by applying them in the separation of artificial mixtures of Illinois No. 6 coal and sulfidized mineral pyrite by oil agglomeration.

PROGRESS

Effect of Oxidation on Coal Surface Properties

To study the effect of mild oxidation on various coal surface properties as well as on the agglomeration response of the material, 100 g of No. 2 Gas Seam coal from Raleigh county, West Virginia, was prepared first by crushing, grinding, and screening. This material was selected because of its purity (4% ash, 0.2% pyritic sulfur, 0.6% organic sulfur) and good response to oil agglomeration. Grinding was accomplished with a high-speed impact mill. The -70/+100 mesh (-210/+149 μm) size fraction was used for the oxidizing treatment. This seemed to be the optimum size for both the induction time and infrared absorption measurements which were to be made. After collecting a sample of the untreated coal, the remaining material was spread in a very thin layer in two large aluminum pans which were placed in a convection oven set at 150°C. Samples of the coal were collected after 4, 8, 12, 24, 48, and 72 hr of treatment in the oven. A rotary sample splitter was used to insure collection of representative samples. After each sampling, the remaining material was mixed and respread. Also the material was mixed and respread after 2, 6, and 10 hr of treatment.

The samples of untreated and treated coal were characterized by several different methods which included measurement of the induction time, heat of immersion in water, and infrared absorption spectrum. In addition, the response of the coal to oil agglomeration was determined by monitoring the turbidity change of an agitated aqueous suspension treated with increasing amounts of heptane. This technique for characterizing agglomeration response was described previously (ref. 1,2).

The induction time was measured by two different techniques. The first technique involved determining the time required to attach a 2-mm diameter air bubble to one or more particles of coal submerged in water, whereas the second technique involved determining the time required to attach a 2-mm diameter heptane droplet to one or more submerged coal particles. For the untreated coal, the induction time determined by the first method was 0.8 ms, whereas the induction time determined by the second method was 0.65 ms. While the induction time determined by the first method increased significantly with increasing time of treatment, the induction time determined by the second method seemed to be unaffected by the treatment (see Figure 1). Therefore, the first method seemed to be a more sensitive indicator of surface oxidation than the second method.

The heat of immersion of the coal in water is shown as a function of treatment time in Figure 2. The heat of immersion increased greatly during the first 12 hr of treatment and then increased only slightly with further treatment.

Measurement of the infrared absorption spectrum was performed by Dr. McClelland's group. The results were used to determine the hydrophilicity index as defined below.

Figure 1. Effect of oxidation time on the induction time.

Figure 2. Effect of oxidation time on the heat of immersion of coal in water.

$$\text{Hydrophilicity Index} = \frac{(-\text{COOM}) + 2(-\text{OH})}{(\text{R-H}) + (\text{Ar-H})}$$

According to Ye et al. (ref. 3) this index provides a useful indication of the relative hydrophilicity of a coal surface.

For comparing the sensitivity of the different coal surface properties to oxidation, the relative value of each property was determined by dividing the value of the property for the oxidized coal by the corresponding value of the property for the untreated coal. The relative values of the different properties determined in this manner are shown as a function of treatment time in Figure 3. For this comparison, only the induction time determined with an air bubble is shown. It can be seen that all three properties increased as the length of treatment increased with the heat of immersion increasing the most and the hydrophilicity index increasing the least. However, most of the increase in the heat of immersion took place as a consequence of the first 12 hr of treatment, whereas the increase in the hydrophilicity index was more gradual and extended over the entire span of the treatment. At least qualitatively there appeared to be a better correlation between the induction time and the hydrophilicity index than between the heat of immersion and either of the other two properties.

Although all three properties plotted in Figure 3 showed the coal surface to be affected by the oxidizing treatment, the results of the agglomeration tests presented in Figure 4 suggest that the treatment was not sufficiently rigorous to affect significantly the agglomeration behavior of the material as indicated by the change in turbidity of the suspension. The results seemed to agree with the induction time meas-

Figure 3. Effect of oxidation time on the relative values of certain surface properties.

Figure 4. Effect of oxidation on the agglomeration characteristics of No. 2 Gas Seam coal.

urements made with a heptane droplet. Perhaps both were equally insensitive to oxidation. On the other hand, the scatter in the turbidity values could have masked a trend attributable to the treatment. This scatter was somewhat greater than experienced in previous tests of agglomeration performance and may have been the result of using coarser particles. Previous agglomeration tests were usually conducted with -200 mesh particles of coal instead of -70/+100 mesh particles.

Effect of Hydrocarbon Chain Length

The effect of hydrocarbon chain length on the agglomeration characteristics of hydrophobic No. 2 Gas Seam coal from West Virginia was investigated by monitoring turbidity changes produced by adding increasing amounts of a given hydrocarbon liquid to an agitated suspension of the finely-ground coal in water. The coal was ground with a high-speed impact mill to pass a 140 mesh screen. The apparatus and technique were described previously (refs. 1,2). The hydrocarbon liquids were paraffinic in nature and ranged from pentane with a chain length of five carbon atoms to a purified paraffin oil having an average chain length of 30 carbon atoms. The latter was a mixture of relatively long-chain hydrocarbons obtained from Fisher Scientific. Except for the paraffin oil, each hydrocarbon liquid consisted essentially of a single component.

The results of treatment the coal suspensions with different hydrocarbon liquids are shown in Figure 5. It can be seen that there was a large variation in the turbidity of the suspensions when smaller amounts of the hydrocarbon liquids were employed but not when larger amounts were used. Thus, with starvation levels of the hydrocarbons, the turbidity decreased as the carbon chain length increased which indicates that the

Figure 5. Effect of hydrocarbon chain length on the agglomeration characteristics of No. 2 Gas Seam coal.

Figure 6. Effect of sodium sulfide on the agglomeration response of sulfidized mineral pyrite.

effectiveness of the agglomerant increased with chain length. However, with large amounts of agglomerants, all of the hydrocarbons were equally effective so chain length was unimportant.

Depression of Sulfidized Mineral Pyrite

A number of reagents were identified previously which depress the agglomeration of sulfidized mineral pyrite (refs. 4,5). These reagents were identified by observing their effect on the turbidity of pyrite suspensions subjected to agglomeration conditions with heptane. Sulfidized mineral pyrite was employed since it was readily agglomerated with heptane and it behaved consistently. High-grade mineral pyrite from Huanzala, Peru, was ground to pass a 90 μm -screen and was sulfidized by treating it with a freshly acidified solution of sodium sulfide. Although it was assumed that the sulfidizing treatment deposited a layer of elemental sulfur on the surface of the pyrite, the assumption remained to be proven.

It was shown previously that a dilute solution of sodium sulfide would suppress the agglomeration of sulfidized pyrite under both acidic and basic conditions (ref. 4). However, it required a sodium sulfide concentration of 10^{-2} M to completely suppress the agglomeration of the material at pH 5.7 but only a concentration of 10^{-4} M to obtain similar results at pH 9.8. In order to better understand the suppressing action of sodium sulfide, further experiments have been conducted with another batch (XIII) of sulfidized pyrite. The material was treated twice with the first version of the sulfidizing treatment (ref. 5) and then was washed with water, dried, and stored until used. To see if subsequent treatment of the sulfidized pyrite with sodium sulfide produced a lasting

change in the surface properties of the material, several experiments were conducted in which the material was treated with a sodium sulfide solution for 5 min. at room temperature and then was washed with water and subjected to agglomeration conditions. The results presented in Figure 6 indicate that the treatment did affect the agglomeration response of the material, particularly at pH 11-12, and that the effect was not erased by washing. However, the changes shown in Figure 6 were not as pronounced as those shown previously (see ref. 4) for the case where the sodium sulfide solution was not removed before applying the agglomeration conditions. Therefore, the results suggest that the depressing action of sodium sulfide may involve two different mechanisms. Thus, one mechanism may require sodium sulfide to be present in the suspension and may involve reversible adsorption of sulfide ions on the pyrite surface, whereas another mechanism may not require sodium sulfide to be present after it has done its work. The latter may involve extraction of elemental sulfur from the surface of the sulfidized pyrite since basic sodium sulfide solutions are known to dissolve elemental sulfur to form soluble polysulfides.

It was also shown previously (see ref. 5) that ferric chloride depresses the agglomeration of sulfidized mineral pyrite and that ferric chloride has a lasting effect on the agglomeration response of the material. To see if these results could be duplicated with another batch of sulfidized pyrite, another set of experiments was conducted using batch XIII of sulfidized pyrite. This was the material used for the experiments described above which involved treatment with sodium sulfide solutions. The sulfidized pyrite was treated with a ferric chloride solution for 5 min. at room temperature, washed with water, and subjected to agglomera-

tion conditions. The experimental data presented in Figure 7 indicate that the baseline experiment produced results which were somewhat different from those shown for the baseline experiment in Figure 6. This difference appears to have been due to aging of the material, since the second set of experiments was conducted two weeks after the first set. In general, Figure 7 displays the same trends and effect of the ferric chloride treatment as those reported previously (ref. 5). Therefore, the depressing action of ferric chloride, particularly in higher concentrations, was confirmed as was the lasting nature of this action.

Since earlier preliminary results (see ref. 5) indicated that thio-glycolic acid (TGA) is one of the more effective depressants for sulfidized mineral pyrite, further experiments were conducted to study the combined effects of both TGA concentration and pH on the agglomeration response of sulfidized pyrite. Several different batches of sulfidized pyrite were combined to obtain batch XV used for these experiments. Some of the underlying batches had been prepared by the first version and some by the second version of the sulfidizing treatment. Generally, the sulfidizing treatment was applied twice to each batch. The response of the sulfidized pyrite to agglomeration with heptane in the presence of different concentrations of TGA is shown in Figures 8 to 10 for pH levels of 4.5, 7.5, and 10.4, respectively. The results indicate that TGA was an effective depressant for sulfidized pyrite at all three pH levels. Thus, with a TGA concentration of 10^{-3} M, the agglomeration of sulfidized pyrite was largely suppressed at all three pH levels. On the other hand, a TGA concentration of 2×10^{-4} M was a less effective depressant at pH 4.5 than at pH 7.5 or 10.4. Therefore it appeared that a smaller concentration of

Figure 7. Effect of ferric chloride on the agglomeration response of sulfidized mineral pyrite.

Figure 8. Effect of thioglycolic acid at pH 4.5 on the agglomeration response of sulfidized mineral pyrite.

Figure 9. Effect of thioglycolic acid at pH 7.5 on the agglomeration response of sulfidized mineral pyrite.

Figure 10. Effect of thioglycolic acid at pH 10.4 on the agglomeration response of sulfidized mineral pyrite.

TGA was required to depress sulfidized pyrite in a basic solution than in an acidic solution.

To see if TGA had a lasting effect on the agglomeration response of sulfidized pyrite, a set of experiments was carried out with TGA-treated material to compare the response in the presence of the treatment solution with that in the absence of the treatment solution. Sulfidized pyrite (batch XV) was treated with 3×10^{-3} M TGA at pH 4.5 for 5 min. at room temperature. In one experiment the pyrite was subjected to agglomeration with heptane in the treatment solution, whereas in another experiment the pyrite was removed from the treatment solution, washed with water, and then subjected to agglomeration conditions. The results presented in Figure 11 indicate that agglomeration of pyrite was largely suppressed when agglomeration was attempted in the presence of the TGA-treatment solution, whereas it was not suppressed effectively when the pyrite was removed from the treatment solution. Therefore, TGA did not appear to have a lasting effect on the agglomeration response which indicates that the effect was due likely to reversible adsorption of TGA on the pyrite surface.

Depression of Sulfidized Coal-Derived Pyrite

Since a number of reagents were found to depress the agglomeration of sulfidized mineral pyrite, several experiments were conducted to see if some of these reagents would depress the agglomeration of coal-derived pyrite equally well. The pyrite selected for these experiments had been recovered by a wet concentrating table at the Iowa State University coal preparation plant while cleaning coal from the Childers site in Mahaska county, Iowa. The pyrite had been ground in a hammer mill so that 75% was

Figure 11. Effect of removing the TGA treatment solution on the agglomeration response of sulfidized mineral pyrite.

Figure 12. Effect of thioglycolic acid on the agglomeration response of sulfidized coal-derived pyrite.

below 100 mesh. It had been stored in an unsealed jar for several years so that its surface was probably well-oxidized. The purity of the material was only 80%, and it contained 1.74% calcium and a number of trace elements. The pyrite was sulfidized by first mixing 50 g of the material with 20 ml of water and then treating this mixture with freshly-prepared sulfidizing solution for 30 min. at room temperature. The sulfidizing solution was prepared by mixing 200 ml of 1 M sodium sulfide with 45 ml of concentrated hydrochloric acid. The sulfidizing solution appeared to contain both dissolved hydrogen sulfide and colloidal particles of elemental sulfur. The solution had a pH of 0.8. After the treatment, the pyrite was recovered, washed with water, dried, and stored until needed.

A baseline experiment showed that the sulfidized pyrite was readily agglomerated by heptane when the pyrite was suspended in water which did not contain a depressant (see Figure 12). The pyrite suspension had a natural pH of 4.7. Other experiments showed that agglomeration of the pyrite was largely suppressed by TGA in concentrations ranging from 5×10^{-3} to 2×10^{-2} M in solutions having a pH of 4.5 to 9.5 (see Figures 12 and 13).

Another experiment showed that agglomeration of the sulfidized pyrite was also suppressed by first treating the material with 1.3×10^{-2} M titanous chloride for 5 min. at room temperature (see Figure 14). The treated material was recovered, washed with water, and resuspended before subjecting it to agglomeration with heptane. Since agglomeration was suppressed even after removing the treatment solution, the treatment appeared to have a lasting effect.

Since the preceding experiments with sulfidized coal-derived pyrite produced results which were similar in general to those obtained with

Figure 13. Effect of thioglycolic acid on the agglomeration response of sulfidized coal-derived pyrite.

Figure 14. Effect of titanous chloride on the agglomeration response of sulfidized coal-derived pyrite.

sulfidized mineral pyrite, it seems likely that more if not most of the reagents which depress one form of sulfidized pyrite will depress the other form as well.

Application of Pyrite Depressants to Coal/Pyrite Mixtures

A number of agglomeration experiments were conducted to test and compare the effectiveness of various pyrite depressants when applied to the separation of artificial mixtures of Illinois No. 6 coal and sulfidized mineral pyrite. The coal was ground with a high-speed impact mill to pass a 105- μ m screen. The coal had an ash content of 14% and total sulfur content of 3.8% on a dry basis. The coal was combined with different batches of -90 μ m, sulfidized mineral pyrite.

To study the separation of coal/pyrite mixtures, 4 g of coal and 4 g of pyrite were first placed in a 500 ml agglomeration vessel together with approximately 375 ml of deionized water. After mixing the materials briefly, an appropriate amount of a pyrite depressant in solution was added, and then the vessel was filled completely with water. The contents of the closed vessel were subsequently stirred for 5 min. at 5500 rpm using the agitator from a 14-speed kitchen blender. Next a single dose of heptane was introduced with a hypodermic syringe and stirring was continued for 5 min. The resulting agglomerates were recovered on a 150- μ m screen, washed into a bowl, and then recovered by filtration. The filter cake was dried in an oven, weighed and analyzed for total sulfur. Unagglomerated solids which passed through the screen were recovered by filtration, dried, and analyzed. A sulfur material balance was used to determine the distribution of pyrite between the agglomerated product and tailings.

In one set of experiments the depressants and conditions listed in Table 1 were applied to the separation of a coal and pyrite mixture. For this set of experiments batch XV of sulfidized mineral pyrite was employed. This batch was prepared by mixing batches X to XIV which previously had been sulfidized twice. The starting material was high-grade mineral pyrite from Peru. The results of the agglomeration tests are shown in

Table 1. Conditions used for obtaining the results presented in Figure 15

Ident. symbol	Depressant		Heptane, ml	Suspension pH
	type	<u>M</u>		
A	Milk whey	^a 2 x 10 ⁰	2	4.6
B ₁	Ferric chloride	2 x 10 ⁻³	1	3.0
B ₂	Ferric chloride	2 x 10 ⁻³	4	3.0
B ₃	Ferric chloride	2 x 10 ⁻³	8	3.0
C	Sodium hydrosulfide	1 x 10 ⁻³	1	5.5
D	Thioglycolic acid	3 x 10 ⁻³	1	4.5
E	Titanous chloride	3 x 10 ⁻³	2	2.0
F	Pyrogallol	5 x 10 ⁻⁵	2	4.8
G	Sodium sulfide	1 x 10 ⁻²	2	9.4
H	Oxone	3 x 10 ⁻³	2	6.0
I	Acetic acid	3 x 10 ⁻³	1	7.2
J	Ferrous sulfate	5 x 10 ⁻³	2	4.3
K	Sodium dithionite	3 x 10 ⁻³	2	7.0
L	Hydrogen peroxide	4 x 10 ⁻³	2	3.5
M	Quebracho	^b 5 x 10 ⁻³	2	4.8
N ₁	No depressant		2	4.7
N ₂	No depressant		1.0	4.1
N ₃	No depressant		1.0	4.7
N ₄	No depressant		0.5	4.7

^aConcentration = 2 ml prepared solution/liter suspension.

^bConcentration = g powder/liter suspension.

Figure 15. Effect of various depressants on the separation of Illinois No. 6 coal and sulfidized mineral pyrite.

Figure 16. Effect of various depressants on the separation of Illinois No. 6 coal and sulfidized mineral pyrite.

Figure 15. Points lying above the "no separation" line correspond to test conditions which favored the agglomeration recovery of coal over pyrite while points lying below this line correspond to conditions which favored the recovery of pyrite over coal. The reagents which favored the recovery of coal over pyrite included thioglycolic acid (D), titanous chloride (E), pyrogallol (F), sodium sulfide (G), hydrogen peroxide (L), and quebracho (M). Among these reagents thioglycolic acid and titanous chloride had the greatest effect. The reagents which favored the recovery of pyrite over coal included milk whey and ferric chloride. These results differed from those reported previously (see ref. 5) in which ferric chloride was found to favor the recovery of Upper Freeport coal over sulfidized mineral pyrite (batch XV). Since the same batch of sulfidized pyrite was used with both types of coal, the difference in agglomeration performance must have been due to the difference in surface properties of the two coals. Thus, it is well known that Upper Freeport coal is considerably more hydrophobic than Illinois No. 6 coal, and it is more readily agglomerated than Illinois No. 6 coal.

For another set of agglomeration tests, Illinois No. 6 coal was mixed with a different batch (101) of sulfidized mineral pyrite. This batch was prepared by applying the sulfidizing procedure twice. The screening procedure which was used for recovering the agglomerated product was modified slightly in that the material which passed through the 150- μ m screen was recycled through the screen so that the agglomerates had two opportunities to be recovered. The application of different pyrite depressants in a series of agglomeration tests with the coal/pyrite mixture achieved the results presented in Figure 16. The experimental conditions and depressants are identified in Table 2. This diagram

Table 2. Conditions used for obtaining the results presented in Figure 16^a

Ident. symbol	Depressant		Heptane, ml	Suspension pH
	type	<u>M</u>		
A	Mercaptoethanesulfonic acid	3×10^{-3}	2	4.5
B	Mercaptosuccinic acid	3×10^{-3}	2	4.5
C	Thioglycolic acid	3×10^{-3}	2	4.5
D	Thiolactic acid	3×10^{-3}	2	4.5
E	Titanous chloride	3×10^{-3}	2	4.5
F	Mercaptopropionic acid	3×10^{-3}	2	4.5
G	None	3×10^{-3}	2	4.5

^aAgglomeration suspension: 4 g Illinois No. 6 coal
 4 g sulfidized pyrite (101)
 500 ml water

employs special coordinates which expand the field between the lines representing a perfect separation and no separation of coal and pyrite. Thus, any points lying on the vertical axis would represent a perfect separation while any points lying on the horizontal axis would represent no separation. It can be seen that the best separation of coal and pyrite was achieved when mercaptoethanesulfonic acid (A) was used as a pyrite depressant. The separation achieved when either mercaptosuccinic acid (B) or thioglycolic acid (C) was used as a pyrite depressant was nearly as good. Thioglycolic acid seemed to enhance coal yield which was an extra benefit. Although not as effective as the preceding depressants, the following reagents improved the separation of coal and pyrite to some extent in decreasing order of their effectiveness: thiolactic acid (D), titanous chloride (E), and mercaptopropionic acid (F).

CONCLUSIONS

Oxidation of No. 2 Gas Seam coal from Raleigh county, West Virginia, by air at 150°C over a period of 72 hr resulted in gradually increasing values of both the induction time and hydrophilicity index. In contrast, the heat of immersion of the coal in water increased rapidly during the first 12 hr of oxidation and then increased gradually for the next 36 hr. Surprisingly, the response of the material to agglomeration with heptane did not appear to be affected significantly by the treatment. The apparent lack of response may have been due to the use of somewhat larger particles than normal and/or other experimental factors.

The agglomeration characteristics of No. 2 Gas Seam coal were affected by the carbon chain length of the paraffinic liquids used as agglomerants. When starvation levels of the agglomerants were employed, the effectiveness of the paraffinic liquids increased with increasing chain length. However, with large amounts of agglomerants, all of the paraffinic liquids were equally effective.

Sodium sulfide, ferric chloride, and thioglycolic acid were confirmed as effective agglomeration depressants for sulfidized mineral pyrite. The depressing action of sodium sulfide seems to involve two different mechanisms, one of which is reversible and one which is not. The depressing action of ferric chloride appears irreversible, whereas the depressing action of thioglycolic acid appears to involve reversible adsorption on the pyrite surface. While thioglycolic acid is an effective depressant in both acidic and basic solutions, smaller concentrations are required to depress sulfidized pyrite in basic solutions than acidic solutions.

Thioglycolic acid and titanous chloride depress the agglomeration of sulfidized coal-derived pyrite in much the same way as they depress the

agglomeration of sulfidized mineral pyrite. Hence, other depressants are likely to affect the two forms of pyrite similarly.

Several pyrite depressants proved effective when applied in the separation of artificial mixtures of Illinois No. 6 coal and sulfidized mineral pyrite by selective agglomeration with heptane. The most effective depressants were thioglycolic acid, mercaptoethanesulfonic acid, and mercaptosuccinic acid. Other effective depressants included thiolactic acid and titanous chloride. While ferric chloride had appeared previously to be a good pyrite depressant when treating mixtures of Upper Freeport coal and pyrite, it seemed to enhance pyrite recovery when applied to mixtures of Illinois No. 6 coal and pyrite.

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