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# An Electrokinetic Study on the Oil Flotation of Oxidized Coal

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## ABSTRACT

The objective of this investigation was to study the electrokinetic behavior of oxidized coals and of hydrocarbon emulsion droplets of flotation reagents to indicate the feasibility of separating the oxidized coals from ash materials and pyrite by an oil flotation process. The effects of surfactants and hydrolyzed metal ions were also included. The electrokinetic behavior of the oxidized coals and the hydrocarbon emulsion droplets were studied by an electrophoresis technique. Generally the isoelectric point (IEP) of the coals decreased with increasing degree of oxidation.

A model of selective flotation of oxidized coal is postulated on the basis of the electrokinetic results. This model simply states that in the presence of a suitable amount of collector and frother, the optimal selective flotation of oxidized coal will occur at the IEP of the oxidized coal. To

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achieve this condition at the coal surface, it is necessary to adsorb heavy metal hydroxide ions prior to flotation and to absorb hydrocarbon oil droplets containing positively charged organic functional groups during flotation. Oxidized coal becomes more hydrophobic at its IEP because most of its surface is relatively non-polarizable. In contrast, pyrite and ash minerals have relatively polarizable surfaces and remain in suspension even when they are at an IEP.

## INTRODUCTION

Coal is relatively easy to float by froth flotation, when compared to other minerals, due to its native floatability. Practically, alcohol-type frothers, kerosene, and fuel oils are the commonly used reagents for coal flotation. However, if the coal is oxidized by weathering or by storage, a reduction of its hydrophobicity and floatability will result. This effect is attributed to surface oxidation, which takes place readily at normal atmospheric temperatures, and is characterized by the formation of acidic groups at the coal surface (1,2,5). In almost all cases, oxidation reduces floatability when aliphatic alcohol frothers are used; however, when nonpolar oils are used in emulsion flotation (oil flotation), a slight oxidation may increase coal floatability (1,3). This peculiar phenomenon still remains unexplainable.

The oxidation of coal begins at the surface of a coal particle. A slight oxidation of coal is considered to be surface oxidation. Therefore, if such an oxidized surface layer is removed, the floatability will be restored (4). However, coals such as outcrop coal have been exposed to weathering for many thousands of years; their bulk is oxidized. When a few percent of this outcrop is blended with the unoxidized coal, the floatability of the unoxidized coal is deteriorated almost completely. In order to float this type of oxidized coal by flotation, an understanding of the characteristics of oxidized coal is necessary.

Oxidized coal produces soluble products, such as iron sulfate and humic acids. The presence of these inorganic and organic ions in the aqueous phase is a possible factor that affects the coal floatability. The mechanism of oxidized coal flotation is not clearly understood. However, electrokinetic studies on such complex systems are able to indicate the adsorption of flotation reagents and thus predict the flotation behavior of the oxidized coal.

Campbell and Sun (6,7) reported that hydronium and hydroxyl ions are the potential-determining ions for anthracite and bituminous coals. Wen and Sun (5,11) also reported that hydronium and hydroxyl ions are the potential-determining ions for moderately oxidized coal and that in the presence of electrolytes, the minimum hydrophobicity of coal and oxidized coal would be near its isoelectric point.

## EXPERIMENTAL METHODS

The coals studied are listed in Table 1. The oxidized coal samples were prepared in a laboratory oven using pure oxygen (5). The coal samples used for the electrokinetic study were pulverized before oxidation. The oxidized high volatile A(HVA) bituminous vitrain studied was subjected to oxidation at 125°C for 48 hours unless some other condition is specified. Crystal pyrite from Rico, Colorado, and purified quartz were used. All chemicals were reagent grade. The pine oil used was from Hercules, Incorporated.

Moderately weathered bituminous coal from the Balmer seam, Canada, was used to prepare the flotation feed. The minus 35 mesh oxidized coal contained 15.32 percent ash and 0.46 percent sulfur. Ground and washed beach sand and crystal pyrite of minus 100 mesh in size were added to the oxidized coal. A synthetic flotation feed having approximately 24.02 percent ash and 1.65 percent total sulfur was prepared.

TABLE 1

Ultimate and Proximate Analysis of the Coal Samples

| Rank | Type | Seam | Location |
|---|---|---|---|
| High Volatile A Bituminous | Vitrain | Pittsburgh | Thomas, Pennsylvania |
| Bituminous | Oxidized | Balmer | Canada |

| | Ultimate Analysis, % Dry, Mineral Matter Free Basis | | | | |
|---|---|---|---|---|---|
| | S | H | C | N | O |
| High Volatile A Bituminous | 2.08 | 5.55 | 83.32 | 1.52 | 8.61 |
| Bituminous | 0.46 | 4.84 | 87.38 | 1.35 | 5.97 |

| | Proximate Analysis, % | | | |
|---|---|---|---|---|
| | Volatile Matter | Fixed Carbon | Ash | Moisture |
| High Volatile A Bituminous | 35.73 | 50.97 | 10.47 | 2.83 |
| Bituminous | 20.19 | 63.89 | 15.46 | 0.47 |

The electrokinetic measurements were made by a microelectrophoresis technique (5). The values of zeta-potential were calculated from mobility data.

Flotation experiments were performed in a two liter Wemco laboratory cell at about 1200 rpm and with 16 percent solids. The samples were washed by distilled water to assure no electrolytes at an effective level prior to flotation. The pH of the pulp was adjusted by HCl and NaOH solutions. Distilled water was used throughout the flotation tests (5).

## RESULTS AND DISCUSSIONS

### Electrokinetics of Oxidized Coal

Figure 1 shows that the isoelectric point (IEP) of HVA-bituminous vitrain decreased from pH 4.5 for an unoxidized sample to pH 3.4 for a sample oxidized for 24 hr at 125°C. No IEP could be determined for the coal vitrain oxidized for 120 hr or more due to the increase of the magnitude of the negative zeta-potential. These results indicate that increases in the degree of oxidation of coal increase the magnitude of the negative value of the zeta-potential and that the hydronium and hydroxyl ions are the potential-determining ions for moderately oxidized coal but not for extensively oxidized coal.

The zeta-potential variations due to oxidation were relatively small in magnitude at pHs above 7 when compared to variations at pHs below 7. This phenomenon may be due to the solubility of humic acids, for which hydronium and hydroxyl ions are not the potential-determining ions (5). Humic acids are the major constituent of organic oxidation products and are formed on coal surfaces with various molecular weights for different oxidation conditions. They are insoluble in acidic solutions but become soluble in alkaline solutions. Their solubility varies with their molecular weight. Usually the lower molecular weight humic acids dissolve at lower alkaline solution strengths. When vitrain is oxidized at 125°C for 380 hr, the surface is converted completely to humic acids.

### Electrokinetics of Pyrite: Effect of Oxidation and Post-Oxidation Treatment

When coal is oxidized by natural weathering, pyrite is also oxidized. The soluble products from oxidized pyrite are ferrous sulfate ($FeSO_4$) and sulfuric acid. Winmill (8) measured the rates of oxidation for coal-pyrite to be higher than those for

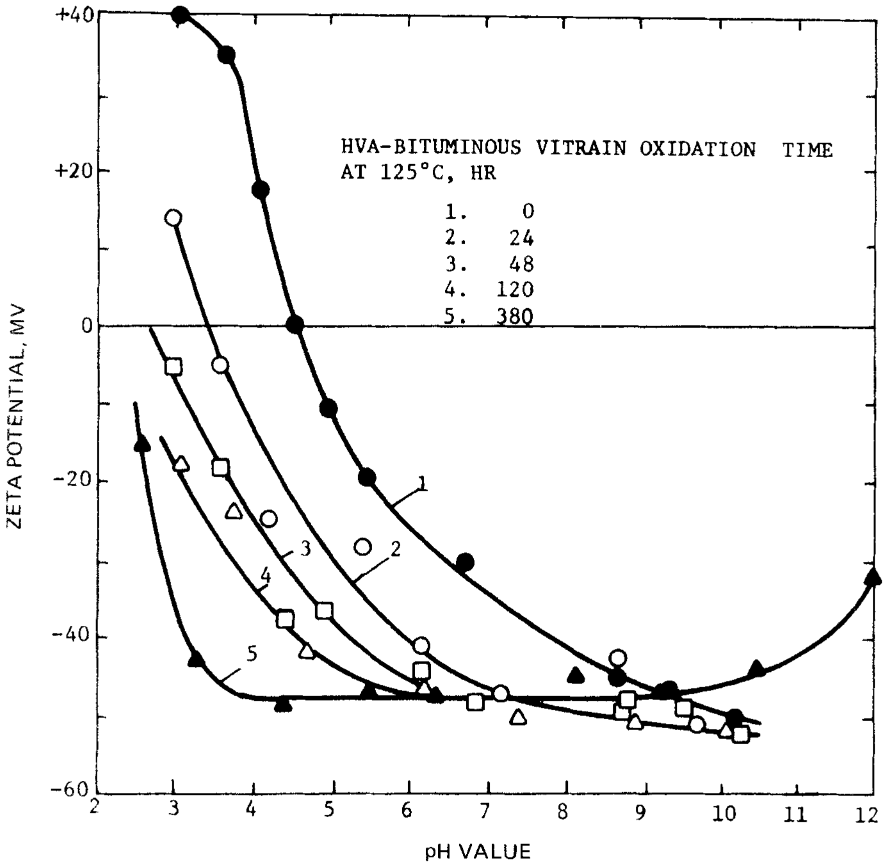

Figure 1. Effect of Oxidation Time on Electrokinetic Behavior of HVA-Bituminous Vitrain (PSOC 295).

coal of the same particle size. After one week of oxidation, the rate decreased to about 25 percent of the initial rate. Upon washing the pyrite with water, the rate increased to a point near the original rate. This result also showed that the oxidized products for pyrite can be washed away by water.

Figure 2 shows that the original crystal pyrite and the boiling-water-washed oxidized pyrite have IEPs of 4.2 and 3.9, respectively. They were found to have similar zeta-potentials

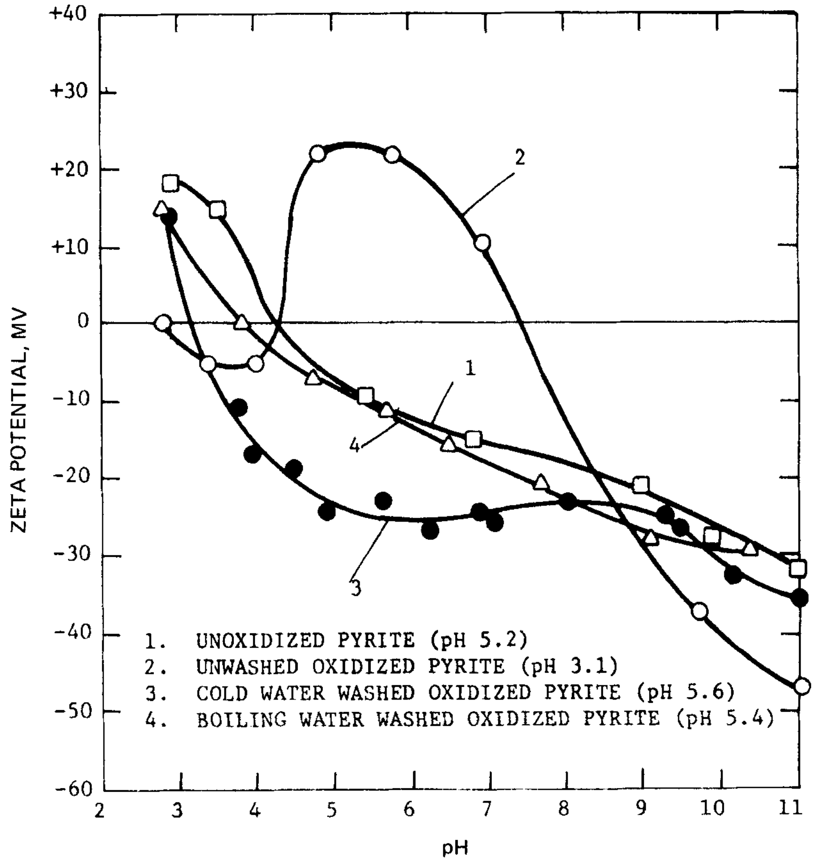

Figure 2. Effect of Oxidized Products of Pyrite on the Electrokinetic Behavior of Pyrite.

through the range of pH from 2.8 to 11.0. This indicated that oxidized products might be completely removed by boiling-water washing and that the remaining pyrite surface was restored to nearly the same state as the unoxidized pyrite.

Unwashed oxidized pyrite shows charge reversal points (CR) at the pHs of 2.8, 4.3, and 7.3. The negative charge might be due to $SO_4^{2-}$ adsorption between pH 2.8 and 4.3. The positive charge between pH 4.3 and 7.3 is believed to be due to the adsorption of positively charged ferrous hydroxy species. Above pH 7.3, the pyrite surface charge again reversed to negative. This may also be due to the adsorption of ferrous hydroxide. The zeta-potential of this pyrite almost follows the same zeta-potential curve as that for hydrolyzed ferrous ions, which indicated that the electrokinetic behavior of oxidized pyrite closely resembles the electrokinetic behavior of hydrolyzed ferrous ions. The more negatively charged surface of the cold-water-washed oxidized pyrite between pH 3.0 and 8.0 might be due to the presence of $SO_4^{2-}$ on the surface that was not removed by cold water washing.

## Electrokinetics of Hydrocarbon Oils

Six pure aliphatic hydrocarbon oils were studied. They are all liquids at room temperature except octadecane, which is solid below 28°C and thus was studied at 30°C. For each test, 0.05 gram of oil was added to 250 ml of water; the mixture was shaken by hand for two minutes and then diluted to 1000 ml. All measurements were made within one hour. The pure hydrocarbon oils were found to have similar zeta-potential characteristics regardless of their chain length, as shown in Figure 3. The IEP occurred for all hydrocarbons at pH 2.0. A zeta-potential of about -50 mv was found at pH 5.0 and about -95 mv at around pH 11.0. The origin of the negative charge of a hydrocarbon droplet was considered by Parreira an Schulman (9) to be due to preferential adsorption of $OH^-$ ions in comparison to $H_3O^+$ ions. At very low pH values, adsorption of $H_3O^+$ ions may give rise to a positive charge. They also considered the adsorption of halide. The maximum and minimum that occurred in all hydrocarbon curves provided evidence that the adsorption of $Cl^-$ions (10) had occurred. The maximum zeta-potential of about -40 mv occurred at pH 5.8. The minimum zeta-potential of -50 to -60 mv occurred at pH 4.8 for the pure hydrocarbon droplets. The increase in the magnitude of the zeta-potential between pH 4.8 and 5.8 may be

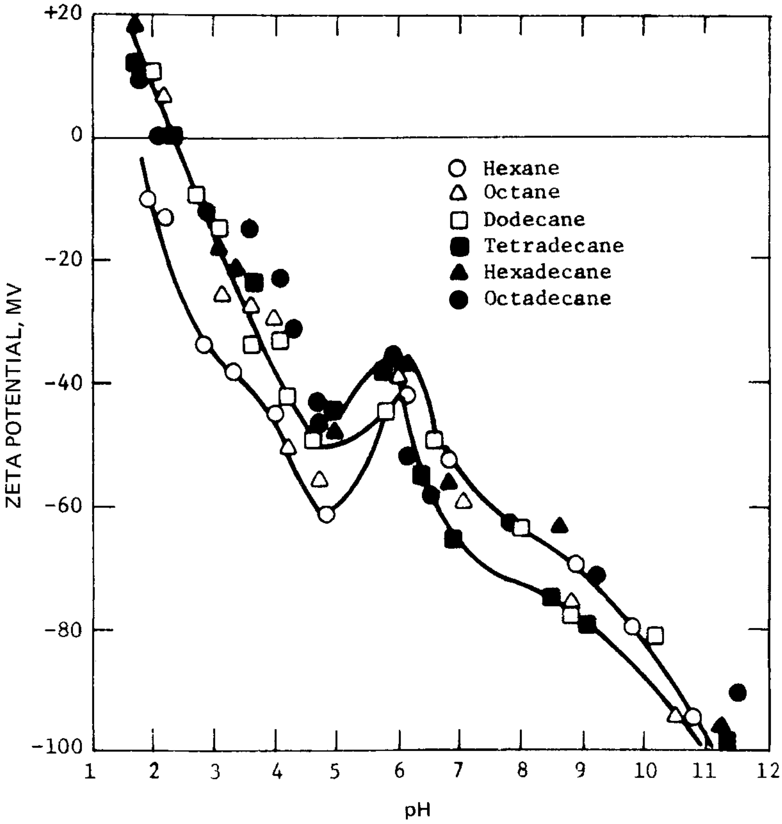

Figure 3. Electrokinetic Behavior of Pure Hydrocarbon Oil-in-Water Emulsion Droplets.

interpreted as a rapid decline in the amount of chloride available to adsorb on the droplet surfaces. Below pH 4.8, the adsorption of $H_3O^+$ predominates over the adsorption of $Cl^-$, and the zeta-potential begins to rise again. Below the IEP at about pH 2.3 for the pure hydrocarbons, the carbon atoms of the molecules probably preferentially adsorb $H_3O^+$, thus rendering the whole surface positive.

Kerosene was also tested and showed a zeta-potential curve (Figure 4). The presence of excess $Cl^-$shows quite clearly the

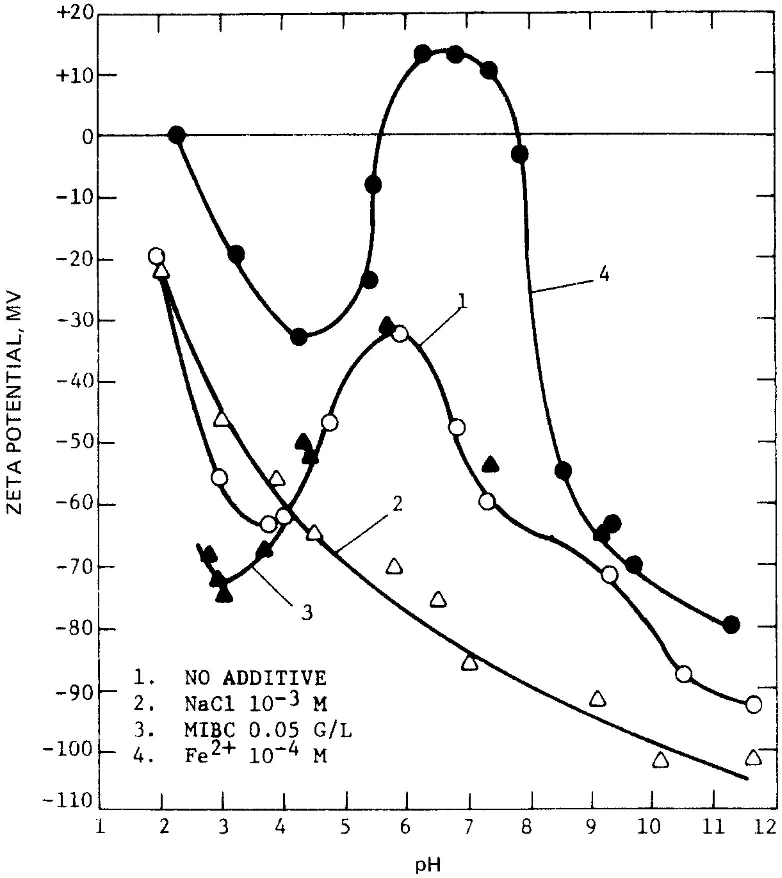

Figure 4. Effect of NaCl, MIBC and $Fe^{2+}$ on Electrokinetic Behavior of Kerosene-in-Water Emulsion Droplets.

effect of $Cl^-$ adsorption. The maximum normally found is suppressed, and the zeta-potential curve continues to drop as the pH increases. The NaCl concentration was $10^{-3}$ molar, which probably caused some double-layer compression. This double-layer compression probably accounts for the slightly less negative values of zeta-potential found between pH 2.5 and pH 4.0 for the NaCl tests. Similar behavior was found for pure hexadecane and is plotted in Figure 6.

## Electrokinetics of Hydrocarbon Oil: Effect of Inorganic Electrolytes

The most common soluble inorganic electrolytes produced by oxidizing coal were tested for their effect on the electrokinetic behavior of hexadecane emulsions, as shown in Figures 5 and 6. The charge reversal points of the hydrocarbon droplets in the presence of metal-ions were found to be similar to the charge reversal points of oxidized coal particles, as reported previously (11). According to James and Healy's definition (12), the first charge reversal, CR 1, was shown to correspond to the point-of-zero charge (PZC) of the mineral. The second charge reversal, CR 2, was shown to correspond to the surface precipitation of metal hydroxide on the colloid substrate, while CR 3 was shown to be the PZC of the metal hydroxide. It is clear that in the presence of metal ions, the surfaces of coal and hydrocarbon droplets are activated by the first hydroxy complex of the metal ions and then by the adsorption of the metal hydroxide as pH gradually increases. Figure 7 shows that CR 3 for the oxidized vitrain and for the hexadecane droplets occurs at the same pH when in the presence of $10^{-4}$ molar $Fe^{2+}$, though the charge reversal point CR 2 occurs at different pHs for the pair.

Metal ions like $Mg^{2+}$, $Ca^{2+}$, and $Na^{+}$ compress the electrical double layer but do not reverse the sign of zeta-potential between pH 2.0 and pH 11.0. However, $Mg^{2+}$ does show the charge reversal point CR 2 at pH 11.5. A compressed double layer may contribute to good emulsion flotation.

## Electrokinetics of Hydrocarbon Oil: Effect of Long-chain Flotation Reagents

The zeta-potential characteristics of hexadecane droplets were determined in solutions that contained heteropolar flotation reagents such as dodecylammonium chloride (DAC), sodium oleate, and sodium dodecylsulfate (SDS). At $10^{-4}$ molar, DAC shows a very

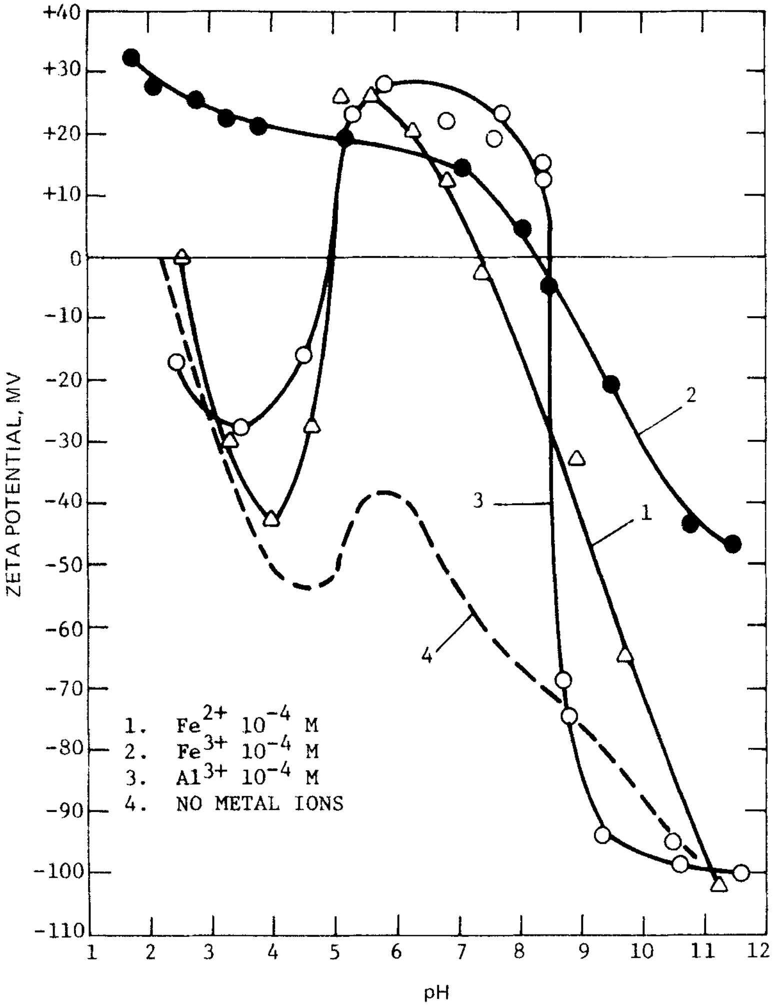

Figure 5. Effect of 1) $Fe^{2+}$, 2) $Fe^{3+}$ and $Al^{3+}$ at $10^{-4}$ Molar on Hexadecane Emulsion Droplets.

strong adsorption at the oil-water interface. The zeta-potential of the hexadecane is shifted strongly positive throughout the pH range, as shown in Figure 8. The rapid decrease in zeta-potential in the high pH range was due to the dissociation of the DAC ion (13). This eventually resulted in an IEP at pH 10.6.

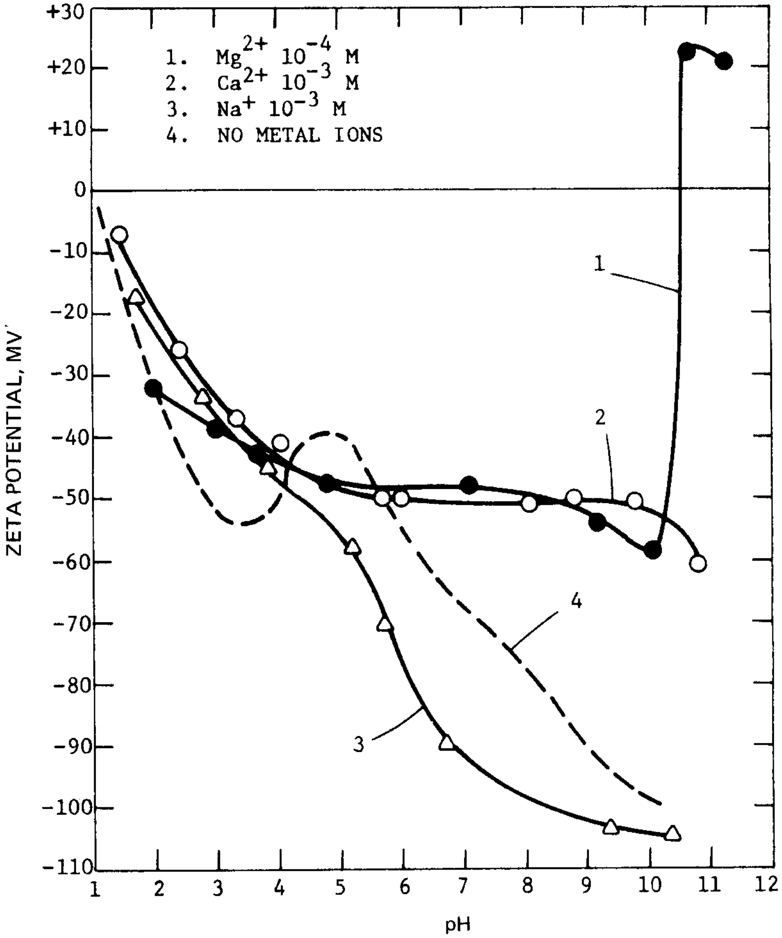

Figure 6. Effect of 1) $Mg^{2+}$, $10^{-4}$ M, 2) $Ca^{2+}$, $10^{-3}$ M and 3) $Na^{+}$, $10^{-3}$ M on the Electrokinetic Behavior of Hexadecane-in-Water Emulsion Droplets.

The electrokinetic characteristics of hexadecane droplets were little affected by the presence of oleate ions, indicating that the functional group of sodium oleate behaves similarly to the oil droplets. At low pH, the carboxyl group does not ionize and thus has little affect on the hexadecane, while at high pH, the ionization of the carboxyl group has little added affect on

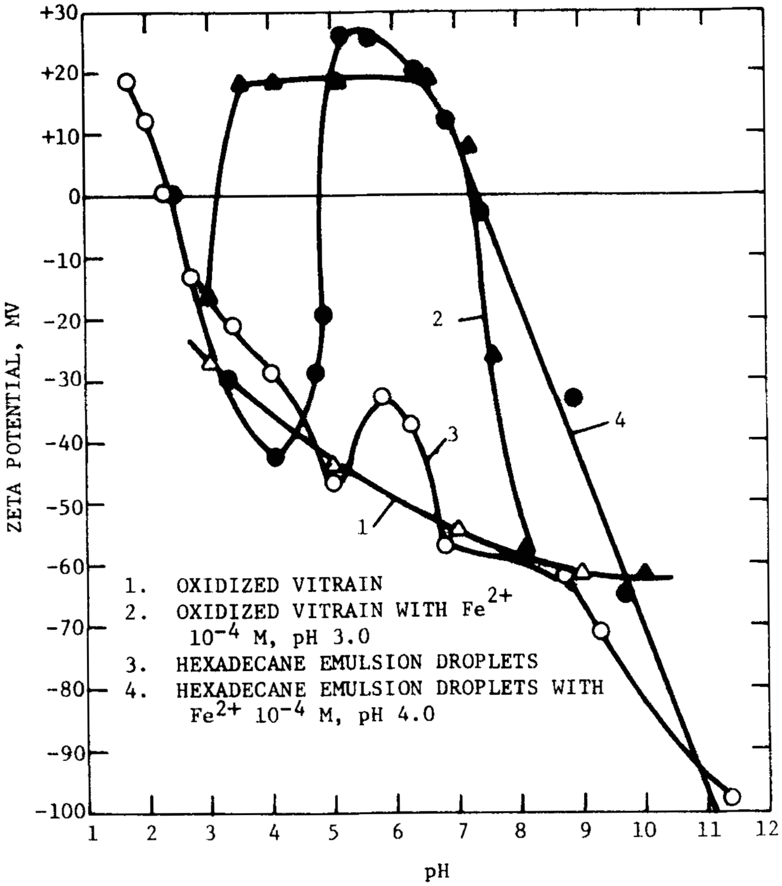

Figure 7. Effect of $Fe^{2+}$ ($10^{-4}$ Molar) on Oxidized HVA-Bituminous Vitrain (PSOC 295 at 125°C 48 Hours) and Hexadecane-in-Water Emulsion Droplets.

the already quite rapid drop in zeta-potential shown by the pure hexadecane.

Sodium dodecylsulfate would be expected to be strongly ionized even at quite low pH. Thus it would be expected to drive the hexadecane more negative in the low pH range. As expected, the zeta-potential for the system, as shown in Figure 8, was found to be more negative than the pure hexadecane in the low pH range.

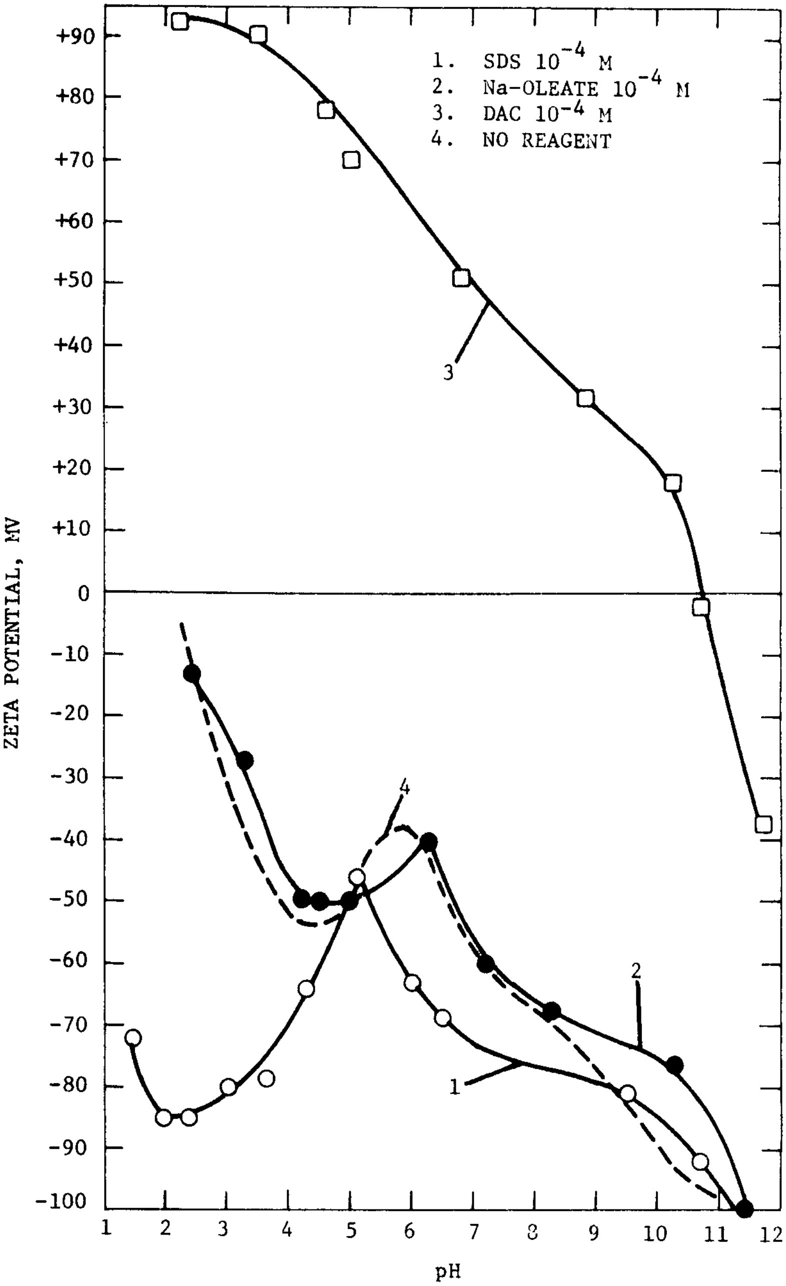

Figure 8. Effect of Flotation Collectors 1) Sodium Dodecylsulfate $10^{-4}$ M, 2) Sodium Oleate $10^{-4}$ M and 3) Dodecyl Amine $10^{-4}$ M on the Electrokinetic Behavior of Hexadecane-in-Water Emulsion Droplets.

The electrokinetic characteristics of emulsified hexadecane droplets in the presence of various concentrations of dodecylammonium chloride are shown in Figure 9. With the adsorption of amine ions, the IEP of hexadecane droplets increased from pH 2.2 to pH 10.7 as the amine concentration was increased from $10^{-7}$ to $10^{-4}$ molar.

## Electrokinetics of Industrial Oils

Fuel oils No. 2 and No. 6 (Bunker C) are the commercial oils which are used in industrial flotation of oxidized coal. A mixture of four parts of fuel oil No. 2 to one part of fuel oil No. 6 was reported to be the best combination for use as a collector for oxidized coal (14). A purification column of activated carbon and activated alumina was used to clean this mixture of commercial oils for testing. The purified oil was colorless and probably consisted mostly of No. 2 fuel oil, while the unpurified mixture was black in color.

Figure 10 shows that an emulsified mixture of four parts of No. 2 and one part of No. 6 fuel oils has a much higher positive zeta-potential (+58 mv at pH 2.0) than does No. 2 fuel oil. The IEP was found to be at pH 4.9. The purified mixture of No. 2 and No. 6 fuel oils in the same ratio as before purification shows a completely different electrokinetic curve when compared with the unpurified mixture. The zeta-potential curve of the purified mixture was very similar to the kerosene shown in Figure 4. It is believed that the major part of the purified oil was No. 2 fuel oil. The positive charge of the mixture of unpurified No. 2 and No. 6 oils is attributed to the impurities from the No. 6 fuel oil. These impurities are a group of polar compounds of undetermined polycyclic structures that contain amine and sulfur components, asphalt, and nickel and vanadium salts (15). Doubling the amount of No. 6 fuel oil in the mixture increased the IEP from pH 4.9 (No. 2 : No. 6 = 4:1) to pH 5.5 (No. 2 : No. 6 =

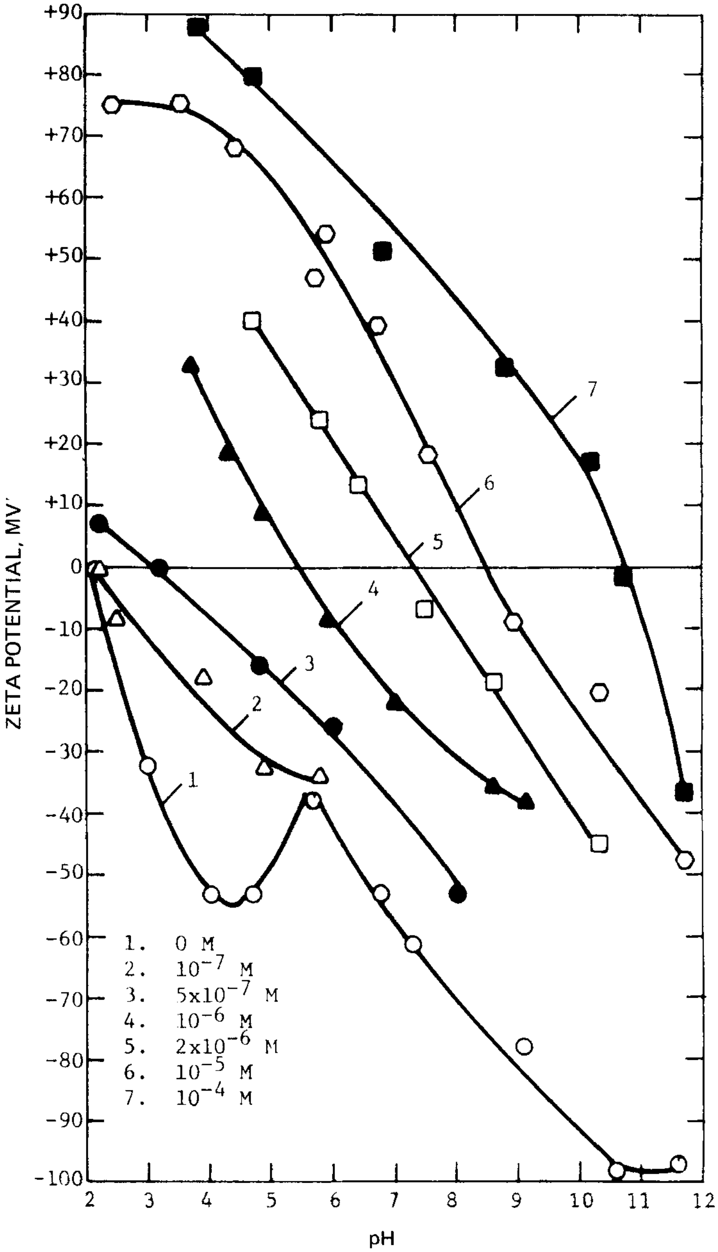

Figure 9. Effect of Dodecylammonium Chloride (DAC) at Varied Concentrations on the Electrokinetic Behavior of Hexadecane-in-Water Emulsion Droplets.

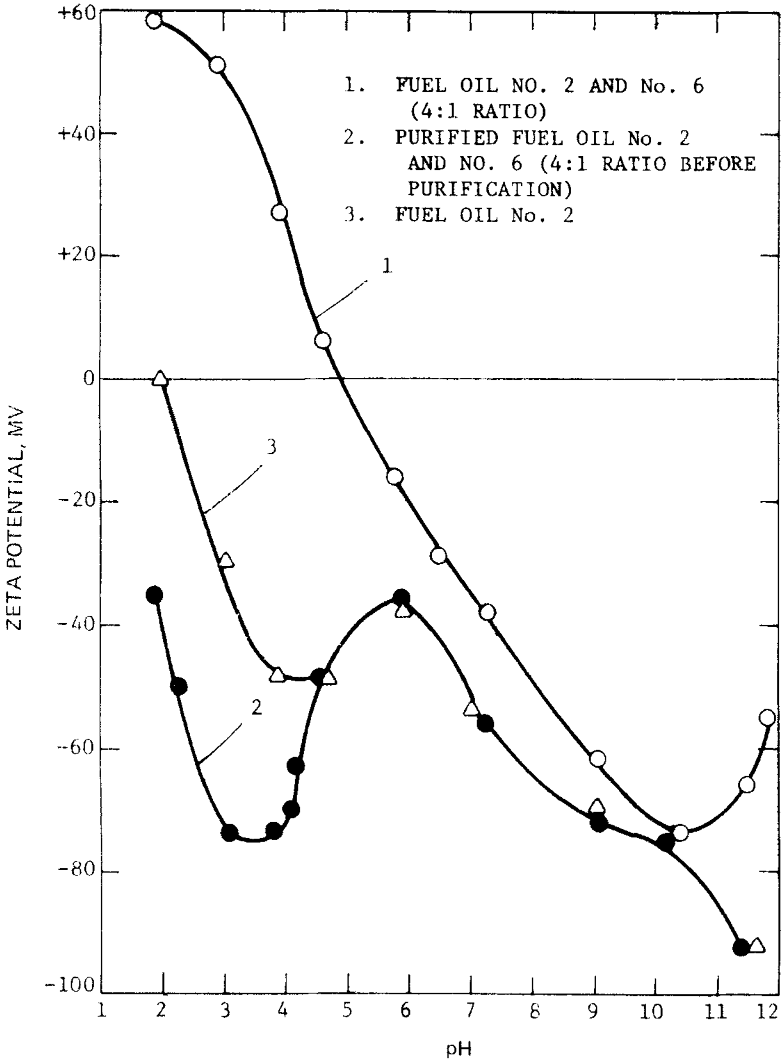

Figure 10. Electrokinetic Behavior of Oil-in-Water Emulsion Droplets. 1) Fuel Oil No. 2 and No. 6 (4:1 Ratio), 2) Purified Fuel Oil No. 2 and No. 6 (4:1 Ratio Before Purification), and 3) Fuel Oil No. 2.

2:1). Other test data indicated that the IEP remained unchanged at pH 4.9 when the ratio of No. 2 and No. 6 fuel oils was increased to 9:1.

The electrokinetic characteristics for the purified fuel oil mixtures are shown in Figure 11. The addition of DAC to the purified fuel oil mixture gave electrokinetics similar to those found for the mixture of unpurified fuel oils shown in Figure 10. If the oxidized coal flotation is a function of the zeta-potential of the hydrocarbon droplets, then the optimum flotation may be controlled by adjusting the concentration of surfactant and thus the zeta-potential of the emulsified oil droplets.

## Electrokinetic Studies of Several Proposed Methods to Restore the Floatability of Oxidized Coal

It has long been suggested that the floatability of oxidized coal could be improved by reversing the effects of oxidation. Two general methods have been proposed to achieve such a reversal. The most direct approach would be to physically remove the oxidized surface either by scrubbing and attrition, or by grinding. Other proposals would achieve the same effect by chemical means.

Gogitidze and Plaksin (16,17) reported that the floatability of oxidized coal has been restored either by dissolving the oxidized surface layer in a 1.0 percent caustic soda solution (flotation carried out in an alkaline medium) or by reduction of the oxidized surface by benzidine in benzoyl alcohol at 85°C. From the electrokinetic point of view, it is expected that the treatment of oxidized coal by benzidine would reduce the zeta-potential of the oxidized coal and thus would reduce the hydration of the oxidized coal surface, which in turn would increase the hydrophobicity of the oxidized coal surface.

Figure 12 shows that the NaOH treated oxidized vitrain was found to have a smaller magnitude of the negative zeta-potential

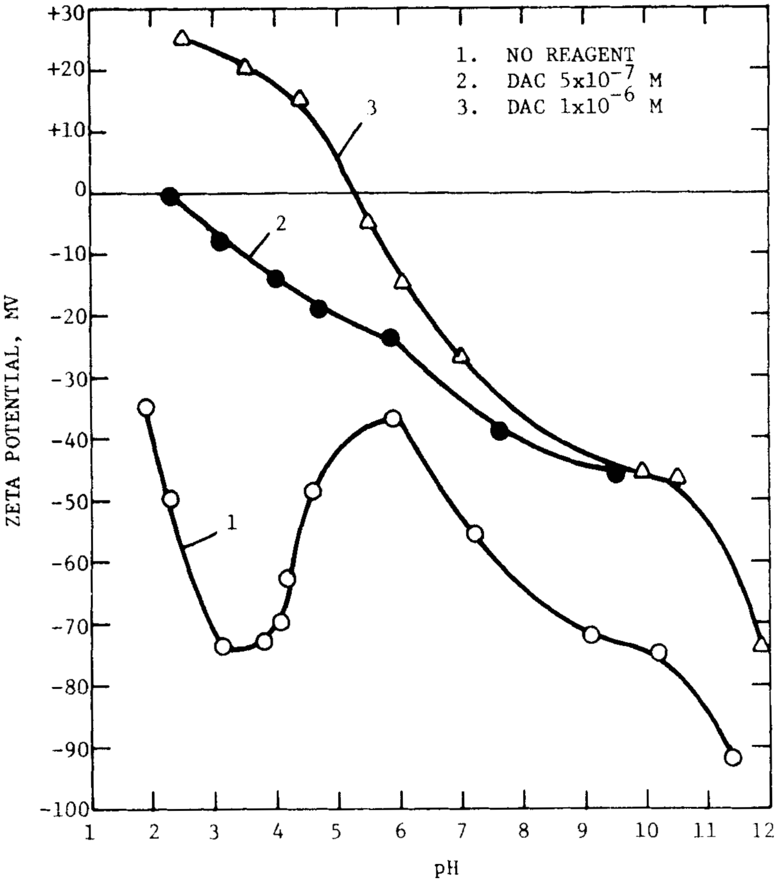

Figure 11. Effect of Dodecylammonium Chloride on the Electrokinetic Behavior of Purified Mixture of Fuel Oils No. 2 and No. 6 (4:1 Ratio) in Water Emulsion Droplets.

than the untreated vitrain. This effect was more pronounced in alkaline solutions. According to the correlation between contact angle and zeta-potential (11), smaller zeta-potentials mean better floatabilities.

Benzidine is a cationic-type organic substance with two aromatic rings. Its chemical formula is 4,4' $-NH_2C_6H_4C_6H_4NH_2$. When oxidized HVA-bituminous vitrain was treated with $10^{-4}$ or

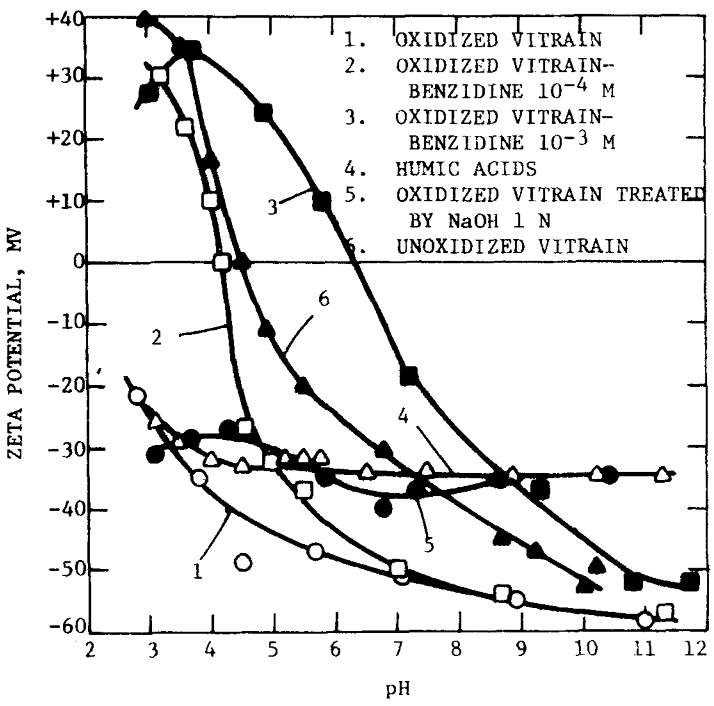

Figure 12. Effect of Chemical Treatment on the Zeta-Potential of Oxidized HVA-Bituminous Vitrain (PSOC 295).

$10^{-3}$ molar benzidine, its electrokinetic behavior became nearly the same as the unoxidized coal, as shown in Figure 12. The IEPs for the treated oxidized coal were found at pH 4.3 and 6.2, respectively. The IEP can be adjusted, depending on the concentration of benzidine. The reported increase in floatability is believed to be because the decrease in the magnitude of the zeta-potential gives rise to an increase in surface hydrophobicity.

If oxidation affects only the surface layer of the oxidized coal particles, a slight grinding or attrition would remove the oxidation layer and expose a fresh surface, which could be less or not at all oxidized. The floatability of this ground oxidized coal should increase. For Balmer seam coal from Canada, it has been established by flotation testing that grinding does increase its floatability, thus indicating that oxidation does not extend throughout its bulk. Figure 13 shows that the +65 mesh Balmer seam coal after grinding shows an IEP at pH 3.2 and shows a reduction in zeta-potential as compared to the -400 mesh sample, which does not have a measurable IEP.

On the other hand, for an outcrop coal or an extensively oxidized coal, either grinding or attrition should not aid floatability much, as the oxidation extends throughout the bulk of the coal. The York Canyon mine outcrop coal is oxidized throughout its bulk. No IEP was found for either surface or core portions of this coal. Therefore grinding would not improve its floatability.

## Postulated Model for Selective Flotation of Oxidized Coal

The electrokinetic study of oxidized coal, pyrite, and hydrocarbon oil droplets indicated that the hydrophobicity of oxidized coal is at a maximum at its IEP and that the maximum adsorption of hydrocarbon droplets on oxidized coal is at the IEP of the hydrocarbon droplets. It has been established that the IEP of particles or oil droplets is controlled by pH, heteropolar reagents concentration, and metal ions adsorption.

These results also indicate that a partial native floatability of oxidized coal might exist. Partial native floatability means that the partially oxidized coal surface may consist of both hydrophobic sites and hydrophilic sites. Hydrophobic sites are similar to the surface of unoxidized coal, while hydrophilic sites consist of acidic insoluble oxidation products or of oxygen-containing functional groups. Hydrophilic sites form a hydration layer at zeta-potentials appreciably different from zero, thus covering the floatable sites. Therefore, the oxidized coal becomes less floatable. In the presence of metal

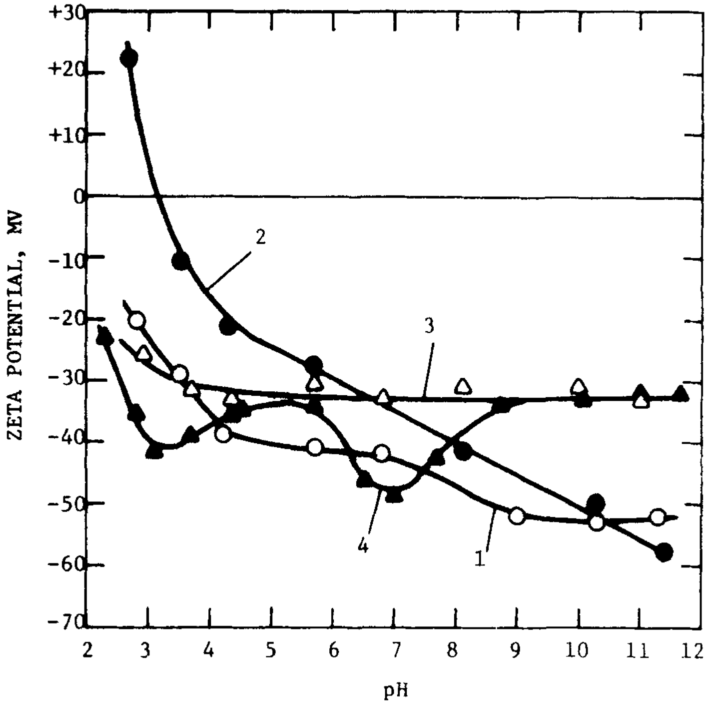

Figure 13. Effect of Grinding on the Zeta-Potential of Oxidized Coals.

1. Weathered Coal of Balmer Seam, Canada, -400 Mesh
2. Weathered Coal of Balmer Seam, Canada, +65 Mesh, Ground to -400 Mesh
3. Outcrop York Canyon Coal, N.M., -400 Mesh
4. Outcrop York Canyon Coal, N.M., +1/4 Inch

hydroxides, the coal surface is partially covered by metal hydroxide precipitate. When the surface reaches its IEP, the surface hydration layer is decreased. The oxidized coal becomes floatable again due to the exposure of its floatable sites.

On the other hand, the flotation frothers and oily collectors form emulsion droplets in the flotation pulp. The reagent droplets are negatively charged in water, and their magnitude of the negative zeta-potential increases as pH increases. The adsorption of these droplets on coal particles reaches an optimum when both droplet and particle are at or near their IEPs. Therefore, it is predicted that in the absence of metal hydroxide, the flotation of oxidized coal increases as the pH decreases and that in the presence of metal hydroxide, the optimum floatability of the oxidized coal is at the common IEP of the oxidized coal and the reagent droplet.

## Flotation of Oxidized Coal

The following flotation tests are an attempt to verify these electrokinetic findings and to establish a sound basis for improved recoveries of oxidized coal. However, a detailed evaluation of the flotation behavior of oxidized coal is beyond the scope of this study.

Pure hydrocarbon oil flotation results are shown in Figure 14A. At lower collector concentrations, a combustible recovery of 76.7 percent was found at pH 6.5, while a combustible recovery of 60.3 percent was found at pH 4.0. At the higher collector concentration, both pHs gave virtually total recovery of the combustibles. In the presence of a natural level of $Fe^{2+}$ (as $FeSO_4$), the recoveries of combustibles at pH 4.0 and 6.5 were found to be about the same as the recoveries at pH 4.0 without $Fe^{2+}$. However, the recovery at pH 9.0 with $Fe^{2+}$ was very low. The results indicated that pH is a control factor for hydrocarbon oil flotation.

The ash contents of the flotation products increased with the concentration of hexadecane oil, but no significant variation could be observed for the effect of pH or a natural level of $Fe^{2+}$ when the combustible recovery was above 60 percent.

The sulfur content of the flotation products increased as the hexadecane oil concentration increased. The average sulfur

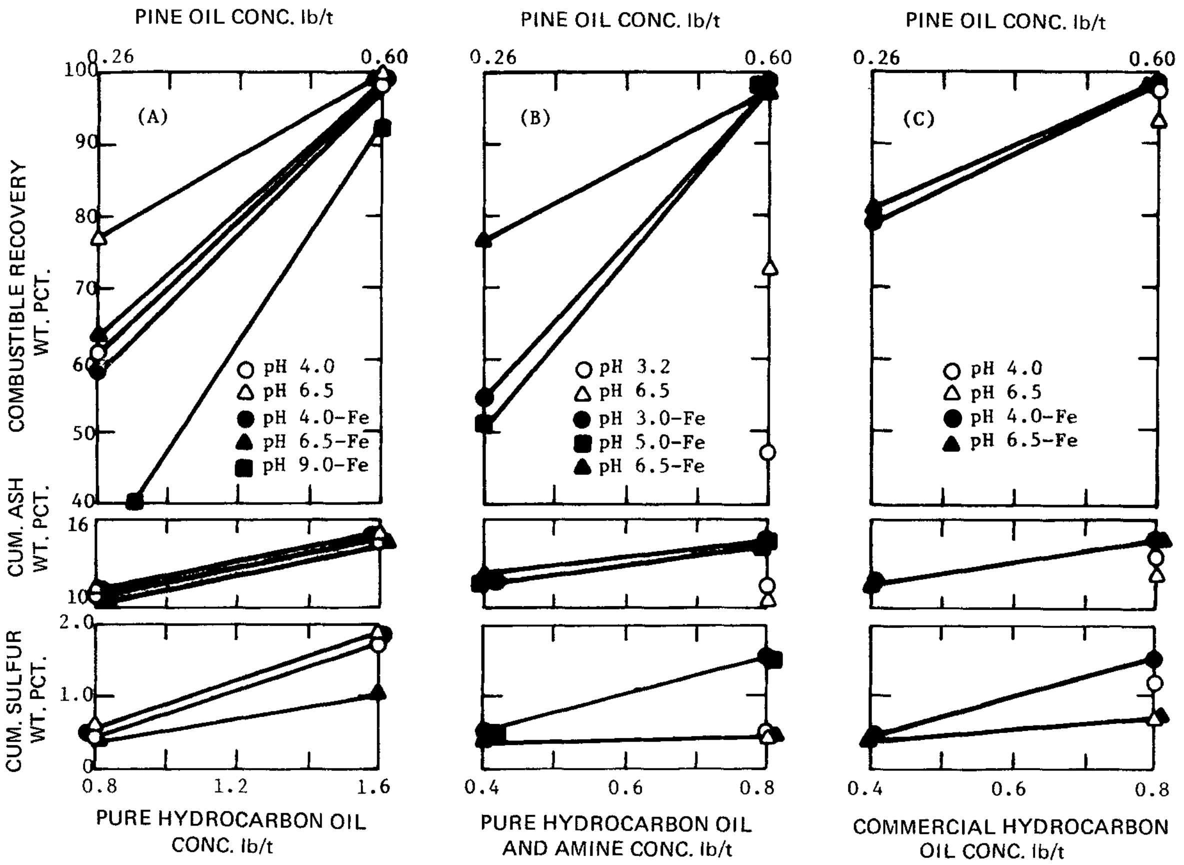

Figure 14. Oil Flotation of Oxidized Coal with the Effect of pH, $Fe^{2+}$ at $10^{-4}$ Molar and Hydrocarbon Oil on the Recovery of Cumulative Combustible, Ash and Sulfur.

content at the lower concentration was 0.5 percent, which increased to 1.8 percent at the higher concentration. However at pH 6.5 and with $Fe^{2+}$, the sulfur content was 0.93 and 1.05 percent, respectively. At this pH value, the pyrite could be depressed by the presence of $Fe^{2+}$, as discussed previously.

Comparison of the combustible recoveries with the electrokinetics of hydrocarbon droplets and oxidized coal with and without $Fe^{2+}$ shows that the optimum floatability of oxidized coal is near the respective IEPs of hydrocarbon droplets and oxidized coal. In the presence of $Fe^{2+}$, the IEPs of both droplets and oxidized coal occur around pH 6.5 to 7.0.

The flotation results for the hexadecane-DAC mixture are shown in Figure 14B. It was shown in Figure 9 that the electrokinetics of hexadecane could be varied in a controllable fashion by the addition of DAC. For these tests, a ratio of 162:1 was chosen for the hexadecane-DAC mixture. The effects of pH and of a natural level of $Fe^{2+}$ were also tested.

With no $Fe^{2+}$ in the system, the recovery of combustible material at 0.8 pound of reagent per ton of solid was 40.15 percent (pH 3.2) and 61.35 percent (pH 6.5), which was even lower than with no amine. The ash and sulfur contents in recoveries at pH 6.5 are respectively 10.49 and 0.43 percent, which appear to be low. However, these values were probably reduced by the low total recovery of the product.

The addition of $Fe^{2+}$ to the system improved the results considerably. The combustible recovery increased to the 97-99 percent range for all pHs tested, while the ash content remained almost the same as for pure hydrocarbon flotation without amine. The pyrite, again, seemed depressed by the presence of $Fe^{2+}$ at pH 6.5.

The flotation results for the commercial mixture are presented in Figure 14C. This mixture was a 4:1 blend of fuel oil No. 2 and fuel oil No. 6. This mixture was readily emulsifiable at room temperatures, even though fuel No. 6 is too viscous to be emulsified by itself at room temperature.

The results are somewhat similar in trend and are better than the other oily collector tests. Even without $Fe^{2+}$, the combustible recoveries at 0.8 pound of oil per ton of solid are around 93 to 98 percent. Ash content in the recoveries is also similar to that with the other oily collectors, and again, the pyrite seemed depressed by the presence of $Fe^{2+}$ at pH 6.5.

The pure hexadecane flotation without $Fe^{2+}$ shows that combustible recoveries of 75.7 percent at pH 6.5 and of 60.7 percent at pH 4.0 were obtained with 0.8 pounds of oil per ton of solid. The explanation for this pH effect seems to be correlated with the maximum and minimum zeta-potential found for oil droplets (see Figure 3). The zeta-potentials for oil droplets at 4.5 and pH 6.5 are approximately -50 mv and -35 mv, respectively. This difference in zeta-potential for the oil droplets could be responsible for the difference in oxidized coal flotation recovery.

Ash contents in recovered coal floated by pure hydrocarbon oils and in commercial oil flotation are generally low. The increase in ash content with the increase in percent of recovery is possibly due to mechanical entrapment or slime coating. Therefore, a cleaning flotation or pulp dilution may be necessary to reduce such entrapment.

The sulfur content in recovered coal is mainly due to recovered pyrite. Generally, the sulfur content increases with an increased percent of recovery. However, in the presence of $Fe^{2+}$ at pH 6.5, pyrite is depressed. This depressive effect has been observed in all the hydrocarbon oil flotations.

The mixture of pure hexadecane and amine did not show any better flotation recovery than the pure hexadecane alone at pH 6.5 in the absence of $Fe^{2+}$. This may be because the solubility of amine ions in water causes the oxidized coal particles and oil droplets to become similar in charge, which produces an electrokinetic repulsion and thereby reduces the adsorption of oil on coal. The flotation recovery is also reduced. It is therefore suggested that if the amine acid is mixed with the hydrocarbon oil, the addition of $FeSO_4$ and the control of pH to 6.5 are necessary to improve the flotation of oxidized coal. The flotation results verified that the optimum flotation of oxidized coal is at the IEPs of hydrocarbon oil droplets and oxidized coal particles. In the presence of $Fe^{2+}$, the IEPs of the droplets and coal particles are near pH 6.5 to 7.0. A hydrocarbon oil and pine oil combination was a good flotation reagent for the recovery of oxidized coal. The combustible recovery was over 90 percent and was obtained with a reagent consumption of 1.6 pounds per ton of coal. A commercial hydrocarbon mixture of fuel oil No. 2 and fuel oil No. 6 in a ratio of 4:1 was the best reagent found for oxidized coal flotation.

## CONCLUSIONS

1. A model of selective flotation of oxidized coal is postulated based on the results of an electrokinetic study of oxidized coal, hydrocarbon oil droplets, and flotation collectors. This model states that in the presence of a suitable amount of collector and frother, the optimal selective flotation of oxidized coal will occur at the isoelectric point (IEP) of oxidized coal particles. To achieve this condition at the coal surface, it is necessary to adsorb heavy metal hydroxide ions prior to flotation and to adsorb hydrocarbon oil droplets containing positively charged organic functional groups during flotation.

2. Oil flotation recovery increased by as much as 20 percent in the presence of $Fe^{2+}$ at $10^{-4}$ molar compared to the recovery without the ferrous ions. The optimal selective flotation

occurred around pH 6.5 to 7.0, which is the IEP of ferrous hydroxide. This could also be the reason that a slight oxidation may increase coal floatability.

3. Emulsified hydrocarbon oil droplets with different hydrocarbon chain lengths have similar negative zeta-potentials. The IEPs for all the tested pure hydrocarbons occurred at pH 2.0.

4. Hydronium and hydroxyl ions are the potential-determining ions for moderately oxidized coals and for emulsion droplets of hydrocarbon oils in aqueous systems. However, they were found not to be potential-determining ions for the extensively oxidized coal and for regenerated humic acids.

5. The studies on the physical and chemical methods to restore the floatability of oxidized coal indicated that oxidized coal shows an increased floatability at reduced zeta-potentials. Therefore, zeta-potential is an indicator of floatability and can also predict flotation behavior of oxidized coal.
6. Increasing oxidation times and temperatures decreased the measured IEPs and increased the magnitude of the zeta-potential for HVA-bituminous vitrain.

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