ELECTROKINETIC BEHAVIOR OF COAL

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ABSTRACT

Electrokinetic measurements show that coals generally exhibit a charge reversal at a certain pH because the surface charge on coal is controlled by the dissociation/ionization of oxygenated functional groups on the coal matrix and by the presence of siliceous contaminants. The lower the ash mineral content of a coal, the higher is the pH at which the charge is reversed (that is, its PZR). De-ashing a coal causes it to exhibit a higher PZR. Increased oxidation causes the pH for charge reversal to decrease due to the higher concentration of oxygen functional groups.

INTRODUCTION

When a solid such as coal is immersed in a liquid environment, a charge is developed on the surface by dissociation of functional groups ($COOH$, $C=O$, COH) from the surface or by adsorption of ions from solution. The surface charge on the coal together with the counter ions constitute the electrical double layer. For the study of charged systems, three interfacial potentials are of interest: i) the surface potential (or total double layer potential), ii) the Stern layer potential (the potential at the first layer of counter ions) and iii) the zeta potential. The electrokinetic or zeta potential is the potential at the shear plane, where slip must occur when the solid moves relative to the liquid. The behavior of the solid particle in a liquid under these conditions is governed by the charge density at the shear plane, not the charge density at the solid surface. The measurement of electrokinetic potentials is relatively easy and this often is the only direct electrical measurement that can be conducted. Although interpretation of the results is not straight-forward, often the useful assumption is made that the slipping plane and the Stern plane coincide. Since the zeta potential can be manipulated through adsorption of inorganic or organic ions at the Stern plane, the study of the electrokinetic behavior of solid is of practical importance in flotation, dispersion, flocculation, etc.

Important parameters for characterizing the surface of a solid in water is the condition when the surface charge and the surface potential is zero. Ions that constitute the surface charge are called potential-determining ions, and their activity in solution when the surface is uncharged is called the point of zero charge (PZC). Another condition of importance is when the Stern layer potential is zero. This can either be the PZC or can result if counter ions have such a strong affinity for the surface that more counter ions can adsorb than there are surface charges. The reversal of the zeta potential, which is often called the isoelectric point (IEP) of the solid, therefore can result either from the reversal of the surface potential or of the Stern po-tential. Because there is also an isoelectric point of a solution in equi-

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librium with a solid, the term point of zeta potential reversal (PZR) is less confusing and that term will be used here.

The electrokinetic behavior of coal is difficult to study because of the complex mineralogy and heterogeneity of coal and, more significantly, it has the tendency to undergo substantial alterations upon exposure to various environments (1). The literature does not contain many papers on the electrokinetic behavior of coal (1-13). Campbell and Sun (2,3) studied the electrokinetic behavior of anthracite and bituminous coal by streaming potential methods, and H^+ and OH^- ions were found to be the potential-determining ions. The PZC of anthracite (whole coal) was found to occur at about pH 4 and that of its vitrain at pH 5.0 to 5.2. The PZC of bituminous coal was found to occur at around pH 4.6. Substantial variations of zeta potential were observed with pH for the various marcerals. More recently, Wen and Sun (7,8) investigated the electrokinetic behavior of fine coals of different rank and oxidation degree by an electrophoretic technique. They suggested that H^+ and OH^- are the potential-determining ions for most of the coals. The PZR of anthracite, bituminous and lignite coal decreased in the reverse order of the rank and occurred at pH 5.0, about 4.5 and 2.3, respectively. The magnitude of the zeta potential increases as the rank of the coal decreases because the lower rank coal contains a greater fraction of oxygen functional groups which provide more negatively charged sites on the surface of the coal (7,8).

The objectives of our investigations were to delineate factors that control the zeta potential of coal, including coal rank, degree of oxidation and ash mineral content. An attempt to evaluate the PZC of coals is also presented.

MATERIALS AND METHODS

The coal samples used in this investigation included a Wyoming bituminous steam coal, a Colorado bituminous metallurgical coal, two samples of Pennsylvania anthracite, and a hand-picked sample of vitrain bands from a West Virginia bituminous seam supplied by the Coal Research Bureau, West Virginia University. Coal specimens were protected from atmospheric oxidation during transport and storage. Table 1 presents proximate and ultimate analyses of the samples. To study de-ashed coal, the siliceous ash-forming minerals were removed by leaching with an HF-HCl procedure, which removes over 90% of the contained mineral matter without attacking the coal substance according to Bishop and Ward (14). Table 2 summarizes the mineral matter content of the de-ashed samples studied. The other samples were oxidized by passing oxygen at $125^{\circ}C$ through the bed of coal particles for up to 260 hours.

Electrophoretic mobilities of particles were measured with a microelectro-phoresis apparatus manufactured by Zeta-Meter Inc., using their Pyrex/Teflon electrophoresis cell. For most of the mobility measurements, about 0.02 gram of coal that had been ground to minus 400 mesh was suspended in 100 ml of solution for about 9 hours while agitating. Streaming potentials were evaluated using plugs containing 48 x 65-mesh coal particles in an apparatus identical to that described by Ball and Fuerstenau (15).

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Table 1 - Analyses of Coal Samples by Percent (dry basis)

	Penna. (I) Anthracite	Wyoming Bitum. (Steam)	Colorado Bitum. (metal.)	Penna. (II) Anthracite	HF-Treated Penna. (II) Anthracite	Vitrain
Carbon	88.24	72.91	71.68	79.83	93.03	81.93
Hydrogen	2.11	---	5.10	2.10	1.96	5.38
Nitrogen	0.65	---	1.60	0.94	0.74	1.24
Chlorine	0.00	---	0.02	0.02	0.52	0.02
Total Sulfur	0.75	0.68	0.60	0.86	0.78	1.03
Pyritic S	0.10	0.06	---	---	---	0.24
Organic S	0.61	0.62	---	---	---	0.78
Sulfate S	0.04	0.00	---	---	---	0.01
Oxygen	---	---	9.02	2.94	1.54	1.46
Moisture (as received)	2.93	---	2.94	2.08	1.42	---
Ash	1.67	5.53	11.50	13.31	1.43	3.33
Volatile Matter	4.02	41.35	39.49	---	---	37.91
8tu/lb	13,700	12,800	12,800	12,600	14,400	14,700

Acid-base titrations to estimate the surface charge density were carried out utilizing an automatic titrator with minus 37-μm Wyoming bituminous coal, using the Onoda-deBruyn "fast titration" method to estimate external charge density (16). A simple check of the pzc of the coal sample was carried out by the solids addition method, worked out by Fuerstenau (17).

RESULTS AND DISCUSSION

The PZR of high-ash anthracite II was found to occur at about pH 2.8. A series of leaching experiments was performed wherein various amounts of siliceous material were removed from the coal. Figure 1 gives the zeta potential, as measured by electrophoresis, of anthracite containing 13.3, 9.0, 2.0 and 1.4% ash content. As the amount of ash is reduced, the point of zeta potential reversal is increased to about pH 4.5, which is the same as found for anthracite I, a low-ash coal. The zeta potential of silica generally exhibits a reversal at pH 1-2 and that of graphite at about pH 4. Thus, coal behaves somewhat as a composite material. The Colorado bituminous coal containig 11.5% ash has a PZR less than pH 2, but after reducing the ash content to 0.3% the pH of the zeta potential reversal is increased to about 4.5 (Figure 2). Clearly, any studies involving raw coal must take into account the distribution of various components at the surface, that is silica, carbonaceous matrix, and oxygen functional groups.

The zeta potential of the low-ash Wyoming bituminous coal was determined by streaming potential measurements and the results are given in Figure 3. The PZR of this coal appears to occur at pH 4.5. Is this reversal in the zeta potential a surface charge reversal? The results of the titration of this same coal are presented in Figure 4, which shows that the isotherms cross at about pH 5. This cross point represents the PZC (16). Furthermore, experiments were carried out using the dry-solids addition method. If a dry solid is added to water, adsorption of the potential-determining ions will

Table 2 - The ash and silicon contents of various coals before and after HF-treatment

Coal		Percent Ash in Coal	Si content as percent of ash
Pennsylvania Anthracite II	Untreated	13.3	45.3
	HF-treated	1.4	0.7
Colorado Bituminous	Untreated	11.5	35.1
	HF-treated	0.3	6.6

cause their activity to shift towards the PZC (17). In the case of coal, if H^+ and OH^- are potential-determining, as more surface area is added to the system, adsorption of H^+ and OH^- occurs, shifting the solution pH towards the PZC. The results of such experiments, given in Figure 5, show that the PZC occurs at pH 4.8, indicating that the PZR given in Figure 3 is indeed also the PZC.

Oxidation of the coal causes the zeta potential to shift to more acidic pH's. Figure 6 shows the electrokinetic behavior of anthracite I after it had been oxidized in oxygen at 125°C for various time periods. As for an explanation of this shift, the surface composition and orientations of surface functional groups in coals are generally not known, and must be inferred from analyses of the bulk coals. Acidity of surface sites in charcoals and carbon blacks has been attributed to carboxyl groups, phenolic groups and cyclic esters called lactones (18,19). As coals oxidize, large amounts of polymeric hydroxy-carboxylic acids called humic acids are formed which may further oxidize to phenolic aldehydes and water-soluble acids (20). It is the production of these acidic groups on the coal surface which is primarily responsible for the decrease in flotation recovery and the decrease in zeta potential of oxidized coals. It is likely that the majority of the observed change in electrophoretic properties upon oxidation is due to the formation of more and stronger acidic functional groups on the coal surface.

A vitrain sample was oxidized at 125°C and at this temperature, this particular sample was partially burned up. Gray ash could be seen in the oxidizing vessel during sampling. The electrophoretic mobility was found to change drastically with such severe oxidation. Subsequent experiments showed the mobility to be about the same as that of a sample of the ash itself. In order to oxidize the vitrain without combusting it, the temperature in the oxidizing oven was lowered to 80°C and another sample oxidized. Under these more mild conditions, the pronounced shift of the PZC to lower values with oxidation was observed and the results are shown in Figure 7.

It can be seen from the results that anthracite (Fig. 6) does not oxidize readily, even at 125°C, while the vitrain oxidizes quite easily at 80°C. This is principally due to the difference in rank of the two coals. The anthracite is 88.2% carbon versus 72.9% for the vitrain, and contains considerably fewer reactive functional groups that may be susceptible to oxidation.

SUMMARY

Because the charge on the surface of coal results from the dissociation/ionization of various oxygenated functional groups, H^+ and OH^- appear to be potential-determining. Electrokinetic experiments show that pH controls the charge reversal on coals, depending upon the ash content and the degree of oxidation. High-ash coals exhibit charge reversal at lower pH's. When the coal is de-ashed, its PZR increases. Similarly, oxidation reduces the pH at which the surface charge is reversed, due to the increase in the concentration of oxygen functional groups.

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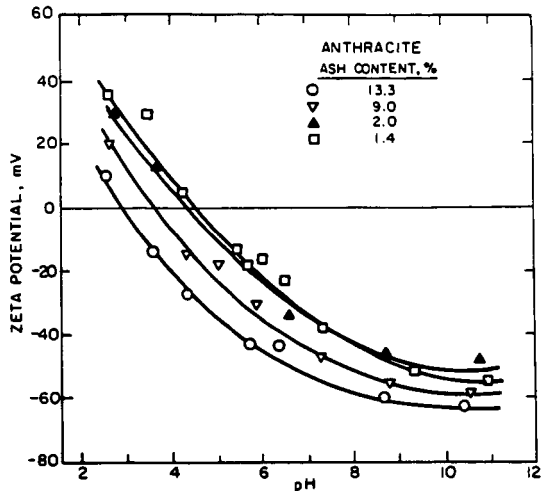20. Toda, Y., Fuel, 52, 36, 1973.

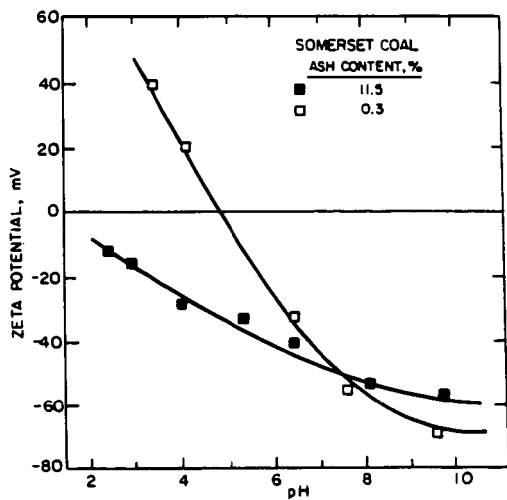Fig. 1 - The effect of removal of silica by leaching from coal on the zeta potential of anthracite.

Fig. 2 - Effect of ash content on electrokinetic behavior of HF-treated and untreated Colorado bituminous (Somerset) coal as a function of pH.
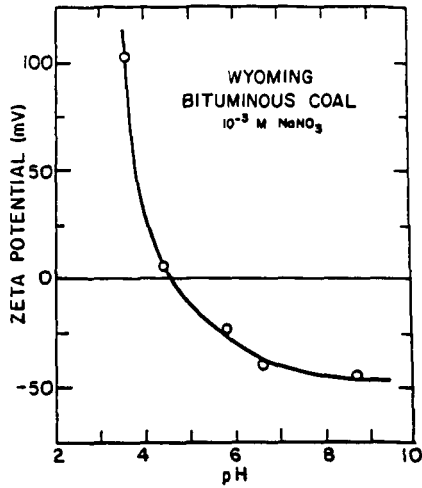
Fig. 3- The zeta potential of Wyoming bituminous coal
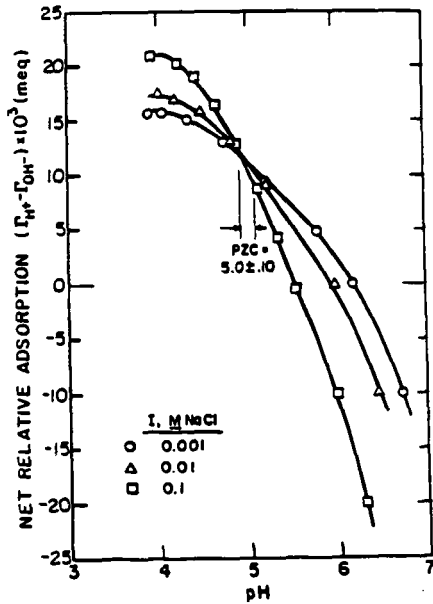as measured by streaming potential methods.

Fig. 4- Determination of the point of zero charge of
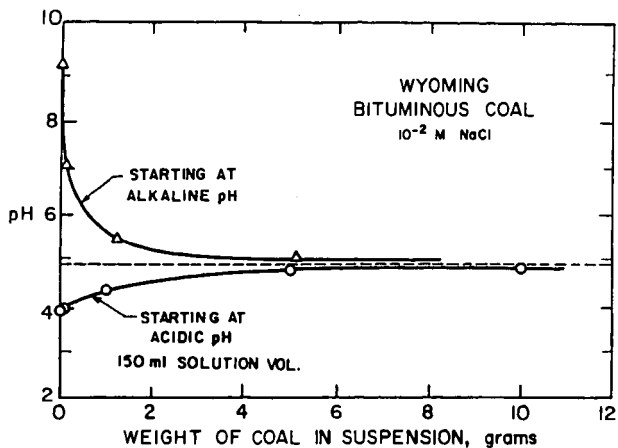Wyoming bituminous coal by potentiometric titation.

Fig. 5 - Determination of the point of zero charge of Wyoming
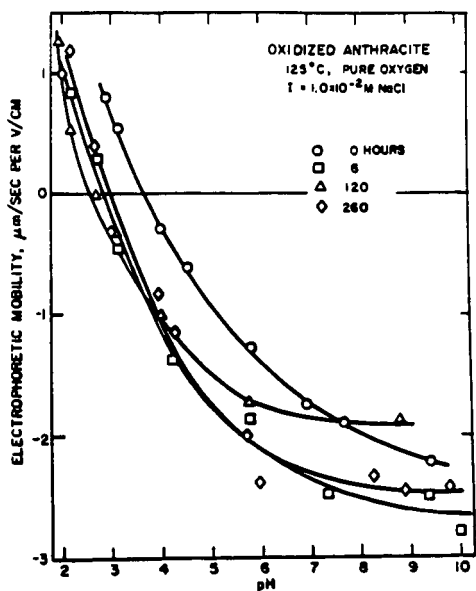bituminous coal by the dry-powder addition method.

Fig. 6 - Electrophoretic mobility versus pH
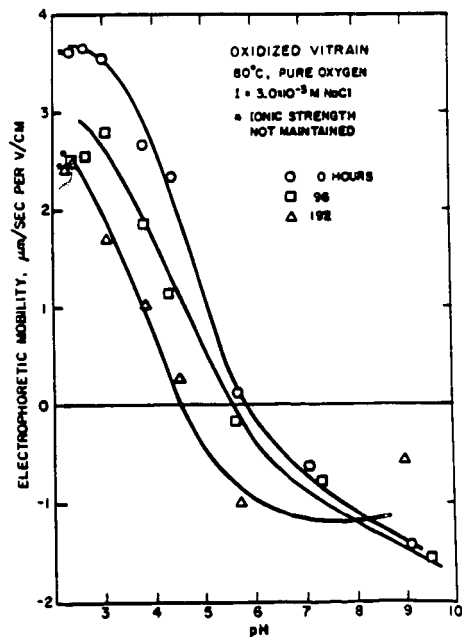for dry ground oxidized anthracite.

Fig. 7 - Electrophoretic mobility versus pH
of vitrain oxidized at 80°C.

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