

1-1-2007

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DOYMUŞ, KEMAL (2007) "The Effect of Ionic Electrolytes and pH on the Zeta Potential of Fine Coal Particles," *Turkish Journal of Chemistry*. Vol. 31: No. 6, Article 3. Available at: <https://journals.tubitak.gov.tr/chem/vol31/iss6/3>

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The Effect of Ionic Electrolytes and pH on the Zeta Potential of Fine Coal Particles

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Received 22.08.2006

Many environmental problems are attributed to coal combustion and utilization, a subject receiving increasing attention worldwide. Some of these problems could be minimized or even avoided if coal cleaning, properly applied, was considered an economical and effective technique for removing hazardous elements or reducing their concentrations before combustion. The coal samples used in this study were separated into particle sizes of 4, 12, and 40 mesh. Then these samples were subjected to sink-float treatment in a $ZnCl_2$ solution of 1.3 density. The sample used for zeta potential determination was prepared by grinding both sink and float coal samples down to -100 mesh. A coal-water suspension of given solid content (wt %) was prepared at its natural pH of 4.5 (except for the experiments for determining the effect of suspension pH) with the desired concentrations of cation and anion electrolytes. The results of the experiments to investigate the effect of suspension pH and concentration of electrolytes on the zeta potential of coal particles were analyzed using analysis of variance (ANOVA). According to the results of this analysis, K^+ , Ca^{2+} , and NO_3^- ions on the surface of coal particles had a minor effect on the observed zeta potentials. However, Al^{3+} , SO_4^{2-} , and CO_3^{2-} ions on the surface of coal particles had a significant effect on the observed zeta potentials. In addition, the zeta potential of the coal particles reached a maximum in 1×10^{-1} M solutions of both cationic and anionic electrolytes. Furthermore, in this study it was observed that the surface charge of the coal particles decreased at low pH and increased at high pH.

Key Words: Zeta potential, cationic electrolytes, anionic electrolytes.

Introduction

Many environmental problems are attributed to coal combustion and utilization, a subject receiving increasing attention worldwide. Some of these problems could be minimized or even avoided if coal cleaning, properly applied, was considered an economical and effective technique for removing hazardous elements or reducing their concentrations before combustion. Conventional coal cleaning is a mature technology, as

applied in the removal of ash-forming minerals and sulfur; however, only limited information concerning the removal of trace elements is available.^{1,2}

Low-rank coals generally have high moisture and mineral matter contents, and consequently have low heating value per unit weight, making them economically unattractive for utilization due to the high transportation cost per thermal unit of coal.³ In addition, lignites can be used as adsorbents for the removal of impurities from aqueous effluent or an effluent treatment medium.⁴ This makes them more attractive, because there is growing interest in the preparation of low cost adsorbents for these uses.^{5,6}

Modification of the surface properties of solid particles by adsorption of surface-active agents is widely used in industrial procedures.⁵ Various mineral separation and coal preparation processes, such as froth flotation, oil agglomeration, selective coagulation and fluxing, wastewater treatment, and the stabilization of colloidal dispersions in liquids, involve the adsorption or deposition of suitable small molecules or polymers capable of forming monomolecular surface films on solid surfaces.⁷

In addition, the behavior of coal particles in electrokinetic experiments may provide information on coal surface properties and the interactions among coal particles suspended in a liquid.⁸ Such information may be extremely valuable in explaining the removal of impurities from coal, which is based on differences in the surface properties of coal, and gangue particles and coal-water properties. Such a phenomenon depends on the fact that a potential difference is developed between them when 2 phases are in contact. There are several ways to generate this effect in aqueous systems. The water dipoles may be oriented at the interface, thus creating a potential difference. Ions or excess electrons in one or both phases give rise to a non-uniform distribution of electric charges at the interface between the phases.⁹ Furthermore, in the development of a surface charge that exists on the solid surface, whether by ion adsorption from the liquid phase on the particle or ionization of groups, the surface acquires a potential with respect to the solution.

The electrokinetic behavior of various coals, measured as a function of pH, has been studied as a function of background electrolyte type,¹⁰ surfactant and polymer addition,^{6,11} pre-treatment conditions, ion loading, and transport conditions. They range from completely positive for a coking coal over the pH range of 2-12 in some papers to completely negative for coals with ranks ranging from lignite to bituminous across the same pH range.¹²

The purpose of the present study was to measure the surface properties of particles for various mineral separation methods from coal and coal preparation processes, such as froth flotation, oil agglomeration, selective coagulation and fluxing, and wastewater treatment. The present work also aimed to determine the correlation between the response of a Turkish brown coal to ash, volatile matter, and sink-float coal particles, as well as the zeta potential of the coal.

Experimental

Material

Lignite from the Çanakkale-Çan coal basin in Turkey was chosen for this study. It was milled and sieved to $< 425 \mu\text{m}$ and then characterized by chemical and particle size analysis. The proximate and ultimate analyses were performed using Turkish and ASTM standards. In addition, the 2 principal oxygen-containing functional groups, carboxylic and phenolic, were determined. Total acidity (carboxylic plus phenolic) was determined by barium hydroxide using the reaction described by Miller et al.¹³ The carboxylic groups were determined by a reaction with calcium acetate, according to the method given by Blom et al.¹⁴ The phenolic

group concentration was then calculated by subtracting the carboxylic content from the total acidity. The results of the analyses together with the size analysis are given in Table 1.

Table 1. Proximate and ultimate analyses, and oxygen functional group contents of Çan lignite (wt %).

Proximate analysis	(as-received)
Moisture	8.2
Ash	17.8
Volatile matter	44.4
Fixed carbon	40.6
Pyritic sulfur	1.4
Ultimate analysis (daf)	
C	76.2
H	4.3
S (total)	2.4
N	1.9
O (by diff.)	15.2
Functional groups (daf)	
Carboxylic	1.3
Phenolic	1.5

Methods

Large chunks of as-mined coal samples were broken into small pieces using a hammer and were subsequently crushed in a Quaker mill in an open atmosphere. The crushed coal was separated into particle sizes of 4, 12, and, 40 mesh. Then these samples were subjected to sink-float treatment in $ZnCl_2$ solution of 1.3 density. The samples were washed with tap water and dried at room temperature. The sample used for zeta potential determination was prepared by grinding both the sink and float coal samples down to -100 mesh. In the experiments, 0.2 g of -100 mesh coal sample was conditioned for 5 min at room temperature in 100 g of solution in a 150-cm³ beaker. A coal-water suspension of a given solid content (wt %) was prepared at its natural pH of 4.5 (except for the experiments to determine the effect of suspension pH) with the desired concentrations of electrolyte of the cationic group (KCl, $CaCl_2$, $AlCl_3$) and the anionic group (Na_2SO_4 , $NaNO_3$, Na_2CO_3). The pH of the suspension was adjusted using aqueous solutions of HCl and NaOH; in preliminary tests, it was observed that the measured pH of the supernatant solution differed by only ~0.2-0.4 from that of the original suspension. After conditioning, approximately 25 mL of suspension was transferred into the sample cell of a Zeta-Meter 3+ instrument for zeta potential measurement.

The results of the analysis on ash, volatile matter, and zeta potential of the natural pH coal samples are shown in Table 2.

Table 2. The zeta potential, volatile matter, and ash content of coal samples (both sink and float) as a function of particle size.

Particle size (Mesh)		Weight (%)	Ash (%)	Volatile matter (%)	Zeta potential (mV)
4	Sink	26.7	22.0	31.5	-9.8
	Float	73.3	15.9	58.0	-18.1
12	Sink	37.9	20.2	31.4	-15.5
	Float	62.1	13.7	56.6	-17.8
40	Sink	37.8	22.8	30.9	-19.5
	Float	62.2	11.7	58.3	-26.2

Results and Discussion

The Effect of pH on the Surface Charge of Coal Particles

The results of the experiments that investigated the effect of suspension pH on the zeta potential of different particle sizes are shown in Figure 1. Zeta potential data of the sink and float coal samples were analyzed using ANOVA to determine whether there was a significant difference between pH values. This analysis indicated that there was a significant difference between pH values ($F = 68.2$; $P < 0.05$), and the zeta potentials of pH 3, 9, and 11 were different from those of other pH values.

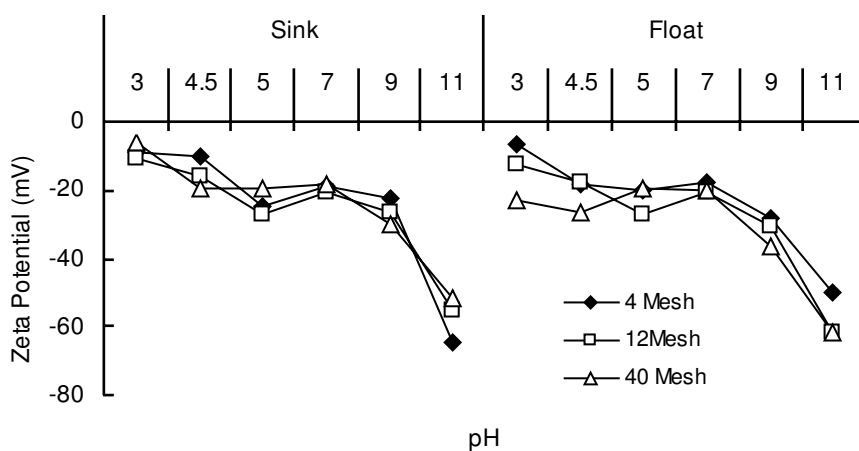


Figure 1. The effect of pH on the zeta potential of both sink and float coal samples of different particle sizes (natural pH = 4.5).

Considering these results, it can be seen that the surface charge of the particles decreased at low pH and increased at high pH. This may be attributed to the adsorption of H^+ and OH^- ions, which are potential-determining ions, by both the hydrophilic mineral matter and hydrophobic organic parts of coal.

In addition, the effect of pH on the zeta potential of the coal particles is explained by considering that the surfaces of these materials contain pH-dependent ionizable functional groups, both acidic and basic, that can undergo dissociation and protonation.^{3,14} A negative surface charge on coal arises upon dissociation of acidic surface functional groups, such as carboxylic, which exhibit a pKa value of 4.¹⁵ The positive surface charge arises upon protonation of basic nitrogen-containing functional groups, such as pyridine.¹⁶

The Effect of Cationic Ions on the Surface Charge of Coal Particles

The effects of the KCl, CaCl₂, and AlCl₃ electrolytes (same anion and different cation) on the zeta potential of coal samples at different particle sizes are shown in Figures 2-4, respectively, as a function of electrolyte concentration. Zeta potential data given in the figures were analyzed using ANOVA to determine whether there is a significant difference between the type of electrolyte and different concentrations of these electrolytes. These analyses indicated that there were significant differences between the electrolytes ($F = 12.4$, $P < 0.05$) and concentrations ($F = 17.9$, $P < 0.05$). According to these analyses, the zeta potentials of AlCl₃ as a function of electrolyte and 1.10^{-1} M as a function of concentrations were different from the zeta potentials of other electrolytes and concentrations.

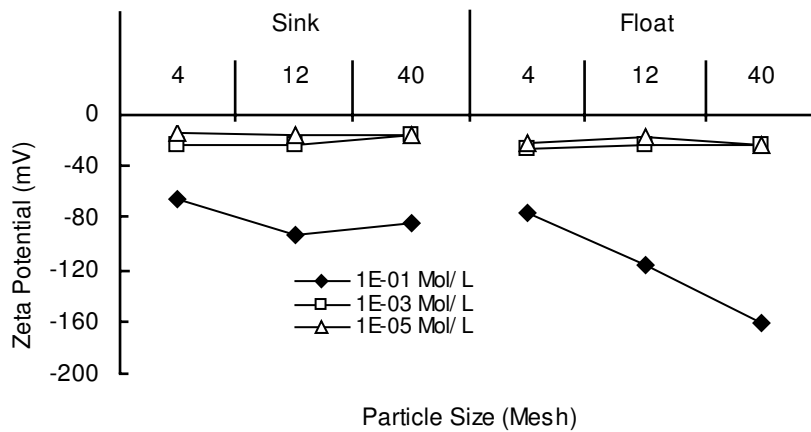


Figure 2. The effect of KCl concentration on the zeta potential of both sink and float coal samples as a function of particle size.

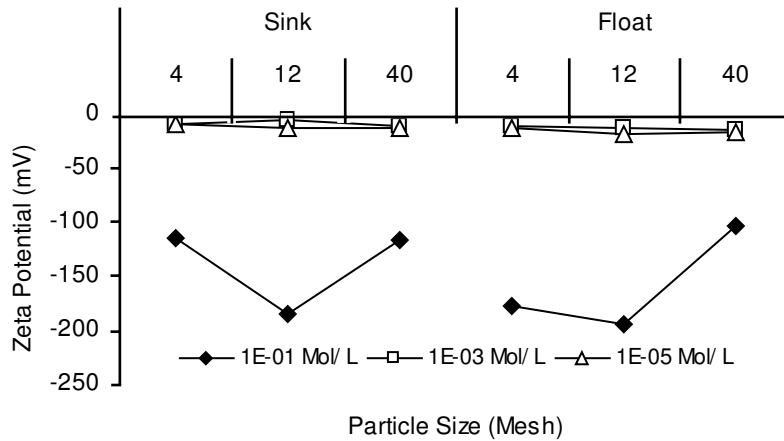


Figure 3. The effect of CaCl₂ concentration on the zeta potential of both sink and float coal samples as a function of particle size.

In the case of Çan coal, the electrolyte concentration may have changed due to the high mineral content and dissociation of ionogenic groups on the coal surface. It is obvious that the charge distribution of the solid surface should be considered, because pure coal particles (completely liberated) and particles with minerals (partially liberated) may behave in significantly different ways during electrokinetic measurement.

In short, liberation of the coal particles, in addition to the functionality of the coal surface and electrolyte concentration, may be important in determining the electrokinetic properties of the coal particles.

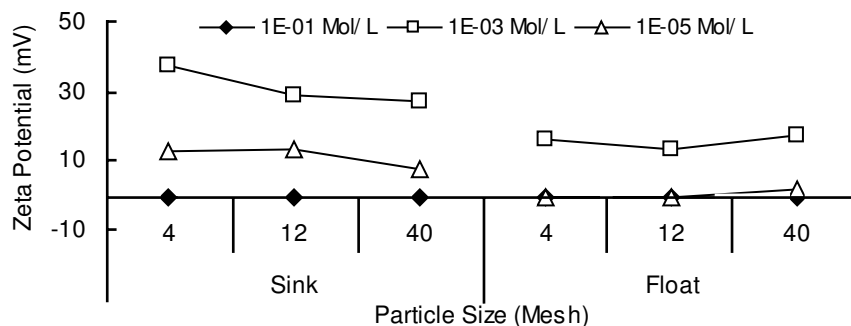


Figure 4. The effect of AlCl_3 concentration on the zeta potential of both sink and float coal samples as a function of particle size.

In addition, electrolytes such as AlCl_3 and FeCl_3 may be responsible for the increased charge of the coal particles, and hence for the increased repulsive interaction between particle and ion charge due to compression of the electrical double layers surrounding the individual particles.^{17,18}

The zeta potential of coal was determined as a function of ions in KCl , CaCl_2 , and AlCl_3 solutions of 3 different concentrations (1×10^{-1} , 1×10^{-3} , and 1×10^{-5} mol/dm³). Moreover, for all the cationic ions, increasing electrolyte concentration may have been responsible for the increase in the zeta potentials of the sink-float coal particles. In addition, concentrations of cationic ions increase by dissociation of ionogenic groups or decrease by re-adsorption of some ions in solution on the solid particle surface.⁹ As a result of this, the electrical double layer around the particle becomes thinner or thicker, and thus the electrophoretic mobility of the solid particle changes. In the case of Çan coal, the electrolyte concentration may have changed due to the high mineral content and dissociation of ionogenic groups on the coal surface.

In contrast to KCl and CaCl_2 , AlCl_3 causes some unusual effects. As seen in Figure 4, a reduction in the magnitude of the zeta potential of particles is observed in the presence of 1×10^{-1} mol/L AlCl_3 . Then, in the 1×10^{-3} M concentration of AlCl_3 solution, the particle becomes more positively charged. The results in Figure 4 clearly show the marked effect of the Al ions on the zeta potential of the coal particles. Al^{3+} (the predominant species) particles remain with a negative or zero charge at low AlCl_3 concentration. Thus, the zeta potential of particles becomes less negative and eventually becomes positive above a certain concentration, which, according to the experimental data, occurs between 1×10^{-1} and 1×10^{-5} mol/L AlCl_3 . The charge reversal on coal particles is attributed to the adsorption of Al^{3+} ions at the particle-liquid interface.

Effect of Anionic Ions on the Surface Charge of Coal Particles

The effects of the NaNO_3 , Na_2SO_4 , and Na_2CO_3 electrolytes (same cation and different anion) on the zeta potential at different particle sizes of both sink and float coal samples are shown in Figures 5-7, respectively, as a function of electrolyte concentration.

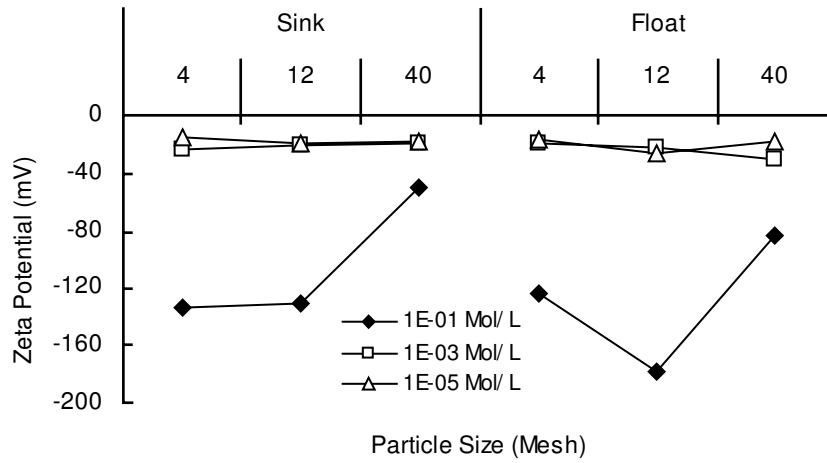


Figure 5. The effect of Na₂SO₄ concentration on the zeta potential of both sink and float coal samples as a function of particle size.

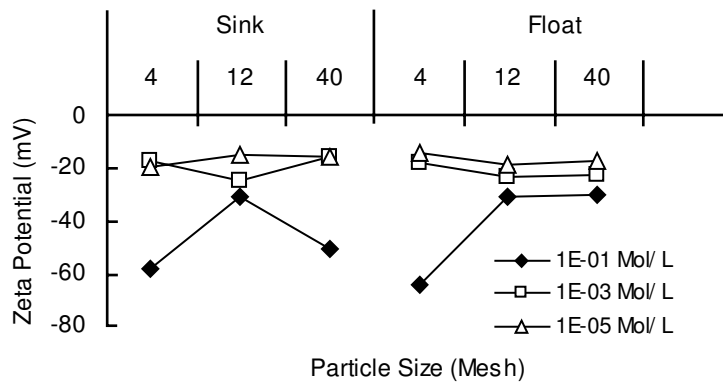


Figure 6. The effect of NaNO₃ concentration on the zeta potential of both sink and float coal samples as a function of particle size.

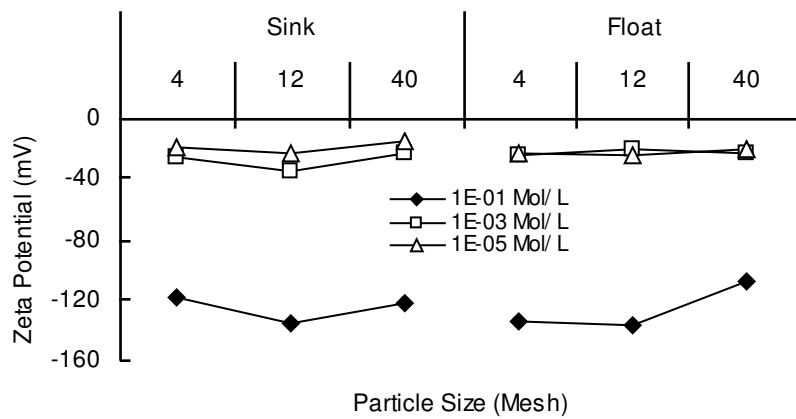


Figure 7. The effect of Na₂CO₃ concentration on the zeta potential of both sink and float coal samples as a function of particle size.

Coal particles exhibit a strong negative zeta potential in 1×10^{-1} M solutions of SO_4^{2-} and CO_3^{2-} ions, but not in the solution of the NO_3^- ion. The reason for this is its greater charge compared to coal, apparently due to greater adsorption of SO_4^{2-} and CO_3^{2-} ions. The zeta potential of particles in 1×10^{-3} and 1×10^{-5} M solutions of these ions became less negative near the critical micelle concentration. This could have been due to higher anionic effect on the electrophoretic mobility of the coal particles during the measurement.^{19,20}

Conclusions

This study has clearly shown that the surface charge of coal particles can vary in different types and concentrations of electrolytes, as well as in solutions of different pH. Cationic ions such as K^+ and Ca^{2+} , and anionic ions such as NO_3^- had minor effects on the observed zeta potential on the surface of coal particles; however, ions such as cationic Al^{3+} , and anionic SO_4^{2-} and CO_3^{2-} had a significant effect on the observed zeta potential on the surface of coal particles. The effect was positive for cations and negative for anions. It is possible to improve the separation of brown coal and related mineral matter by changing their surface properties, which can be characterized by measurement of the zeta potential. The zeta potential of the coal particles in all figures (except Figure 1) reached their maximum in 1×10^{-1} M solutions of both cationic and anionic electrolytes.

In conclusion, the surface charge of coal particles will be useful for separating various minerals from coal and in coal preparation processes, such as froth flotation, oil agglomeration, selective coagulation and fluxing, and wastewater treatment.

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