JOURNAL OF MATERIALS SCIENCE 31 (1996) 5665–5669

Surface-charge density and potential of coal–liquid mixtures and control of their stability and fluidity

T. HAMIEH
Centre de Recherches sur la Physico-Chimie des Surfaces Solides (CNRS-CRPCSS), 24, Avenue du Président Kennedy, 68200 Mulhouse, France

The preparation conditions of concentrated (>70%) aqueous suspensions of coal were optimized, as were the surface charge density and the surface potential of the coal–water suspensions. The theoretical study showed that (1–3) or (2–3) electrolytes such as Na_2SO_4 or $Na_5P_3O_{10}$, greatly increase the surface charge density and the surface potential of the coal particles in water. This study has led to the interesting result that thinners and stabilizing agents of concentrated clay suspensions, such as lignosulphonates, tripolyphosphates, polynaphtalene sulphonates, etc., must also be good thinners and stabilizing agents for ground coal–water suspensions. Two parameters were controlled: the stability and the fluidity of the suspensions. A penetrometry technique revealed the importance of the resistance coefficient, C_r that can be used as a criterion for the evaluation of coal–water mixture stability and fluidity. Concentrated coal suspensions (about 75% of solid by weight) were prepared in water by using different additives, for instance sodium tripolyphosphate (NaTPP) and surfactants like lignosulphonates (by coupling of the dispersion and stabilizing effects) with the optimum concentration ratio of these two products equal to 1.9. The stability of the suspensions was then greater than 2 months and the viscosity was 1900 cP.

1. Introduction

There has been significant interest in recent years in the development of domestic fuels which could displace those presently imported by certain countries for industry. Because of the large quantity of fuel consumed by the electric power generation industry, much of this interest has focused on fuels to replace oil and gas combusted in existing utility boilers. Many of these efforts have focused on the use of coal as the replacement fuel, because it is the World's most abundant fossil fuel [1].

It has been suggested [2] that concentrated coal-water slurries can be utilized as an economical means for the transportation of coal over long distances or as a substitute fuel for oil or coal–oil mixtures for electric power generation.

The growing importance of coal–oil mixtures and coal–water mixtures as alternate fuels to replace oil in industrial boilers and furnaces has been demonstrated in recent years. The symposia on coal slurry combustion and technology have brought together a large number of workers interested in the various methods of preparation and handling of coal–oil mixtures (COM) and coal–water mixtures (CWM), their rheology and stability, their combustion characteristics and other aspects of this technology [3].

Because coal is a complicated mixture of carbonaceous and inorganic matters, the physico-chemical properties of each coal must be understood in order to optimize the rheology and the stability of the slurries.

The purpose of this work was to optimize the preparation conditions of concentrated (> 70%) aqueous suspensions of coal that would be stable and fluid enough to replace a conventional fuel in existing systems of transportation, storage and combustion. To do this, it was imperative that two parameters be controlled: the stability and the fluidity of the suspensions. The high percentage (up to 30%) of mineral impurities in the coal may have a considerable effect on the charge and surface potential of the coal particles, and consequently on the stability of the suspensions. The choice of stabilizers and thinners then depends directly on the nature and quantity of these impurities [4].

2. Optimization of the surface-charge density and surface potential of coal–water suspensions

To estimate the physico-chemical interactions between dispersed particles and the stability of the suspension, it is necessary to appreciate their surface charge and surface potential [5]. This electrical double layer displays a fundamental role in the field of colloidal phenomena like, for instance, stability, electrokinetics, micelle formation, electroadsorption, flotation and polyelectrolyte properties. To estimate the

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influence of physico-chemical interactions between particles and a dispersive medium on the stability of suspensions, it is necessary to know the surface charge and potential of solids. Of course, these parameters alone are insufficient to represent both the nature and whole of the interactions. Nevertheless, surface charge and potential constitute very important parameters in studying attraction phenomena between solid surfaces. Dispersion stability is characterized by zeta potential measurements of dispersed solid particles [6].

Unfortunately, there is no exact analytical solution to the Poisson–Boltzmann (P–B) equation for a charged particle. Many numerical solutions have been proposed by Muller and Hoskin [7, 8] using electronic calculation techniques. More recently, Loeb *e t al.* [9] proposed tables giving the surface potential as a function of distance for a variety of electrolytes at different concentrations.

All these theories, useful as they are, lack clarity. Indeed, they do not propose simple mathematical functions for the surface potential and charge. In this section, we have gone back to the primitive model of the classical P–B equation in the case of spherical particles in assuming the same classical approximations. The ion is simply treated as a point charge.

The influence of certain physico-chemical parameters, such as the ion valence in the case of disymmetrical electrolytes has never been seriously studied. We proposed previously [10] a more realistic solution of the non-linear P–B equation using the spherical coordinates, gave the equations of the electrostatic potential $\Psi(r)$ in the case of 1–1, 1–2 and 2–1 electrolytes, and established the exact expression for the surface charge density, σ_0, of a charged sphere for different electrolytes 1–2, 2–1, 1–3, 3–1, 2–3 and 3–2. This theoretical study allowed us to classify the different electrolytes with decreasing order of charge density. $\sigma_{0(2-3)} > \sigma_{0(1-3)} > \sigma_{0(3-2)} > \sigma_{0(1-2)} > \sigma_{0(3-1)} > \sigma_{0(2-1)} > \sigma_{0(1-1)}$. To obtain more stable suspensions of negatively charged solid particles in water, when preparing it, one must chose electrolytes (1–3) or (2–3) which greatly increase the electrostatic repulsion between particles.

These theoretical results were confirmed by an experiment in studying the surface charge and potential of the suspensions of coal in water in the presence of different disymmetrical electrolytes such as Na_2SO_4, $Na_5P_3O_{10}$, $CaCl_2$, Na_3PO_4 and NaCl. This study showed that electrolytes (1–3) or (2–3), such as Na_2SO_4 or $Na_5P_3O_{10}$, greatly increase the surface charge density and the surface potential of the coal particles in water.

Finally, we have shown that the surface potential and charge of the coal–water suspension are interdependent.

3. Interaction energy between particles of coal in water

The most important physical property of colloidal dispersions is the tendency of particles to agglomerate. The encounters between particles in a dispersed medium are frequent as a result of the Brownian motion, and the stability of the dispersion results from the interaction between particles during these encounters. The principal cause of aggregation is the attractive force of Van der Waals (VDW) between particles while the stability against aggregation is a consequence of the repulsive forces between the double electrical layers of particles of identical charges and also the particle–solvent affinity [11].

The Deryaguin Landau Verwey and Overbeek (DLVO) theory [12, 13] only takes into account the interaction between particles having a double electrical layer. This theory is applied, in principle, to dispersions in an aqueous medium and used for an estimation of the relative values of the attractive and repulsive forces.

The interaction energy of VDW is given by

$$V_A = -\frac{A}{6}\left[\frac{2a^2}{H^2+4aH} + \frac{2a^2}{H+2a^2} + \log\left(\frac{H^2+4aH}{H+2a^2}\right)\right] \qquad (1)$$

where A is the Hamaker constant of the system, a the radius of the particles, and H the separation distance between the particles.

The repulsive electrostatic energy, V_E, between two particles is equal to

$$V_E = \pi\varepsilon a\Psi^2\left\{\log\left[\frac{1+\exp(\kappa H)}{1-\exp(\kappa H)}\right] + \log\left[1-\exp(-2\kappa H)\right]\right\} \qquad (2)$$

where Ψ is the electrical potential of the surface, ε the permittivity of the medium, κ the Debye–Hückel constant, k Boltzmann's constant and T the absolute temperature.

The total potential energy of interaction, V_T, between two particles in the DLVO theory is given by

$$V_T = V_A + V_E \qquad (3)$$

Therefore, V_T depends upon five parameters: a, A, ϕ, κ and H.

We tried to apply this theory in order to understand the stability of highly concentrated coal–water suspensions.

The conclusions of this complete analysis indicate that a stable suspension may be obtained with an ionic strength equal to or below 5×10^{-3} mol dm^{-3}, a surface potential, ϕ, higher than 1501 mV and a particle radius settled between 1 and 5 μm. A small A value also contributes to a good stabilization.

Experimentally, we can act upon the surface potential, Ψ (zeta potential), by modifying the pH of the medium, the agitation time of the suspension and the ionic strength, κ. With ϕ and κ optimized, only the size of the particles, a, and the Hamaker constant can be changed. For economic considerations, we have to grind coal within a range of 0–300 μm. The radius a is therefore fixed by Gaussian distribution within the interval [0;300] μm. Finally, to modify the Hamaker constant, we introduce some polymeric dispersants or some polyelectrolytes in the medium. In this case, new repulsive energies appear and overcome the attractive Van der Waals energy, which will stabilize the suspension by a steric effect.

It should also be remembered that the surface potential may be increased by using some ionic dispersants, such as polynaphtalene sulphonates and lignosulphonates, which also allow the Hamaker constant to be lowered.

A study of the evolution of the surface potential for coal suspensions versus the pH with or without an electrolyte has been undertaken using zetametry with the help of a Laser Pen Kem zetameter (model 500), which enables the zeta potential of colloidal particles to be determined from measurement of their speed of displacement in an electrical field.

On the other hand, a high negative charge of coal in an acid medium is often observed, while in this pH region, the adsorption of protons should rather favour the creation of a positive surface charge. For instance, the zeta potential reaches -20 mV at pH values around 3. At this pH, Cl^- ions should be neutralized by H^+. Otherwise coal particles are still wet by water at this pH, while they normally should be hydrophobic in an acid medium because the ionization of superficial groups (–OH, –COOH, etc.) being very weak.

In fact, wetting by water is due to the mineral impurities in the coal, such as aluminosilicates which set the high negative surface charge of the coal. This hypothesis has been confirmed by studying the influence of the demineralization upon the surface charge, and points out, without any doubt, the influence of mineral impurities upon the surface potential of coal. This has led to the interesting result that thinners and stabilizing agents of concentrated clay suspensions, such as lignosulphonates, tripolyphosphates, polynaphtalene sulphonates, etc., must also be good thinners and stabilizing agents for ground coal–water.

These findings led us to study the evolution of zeta potential versus the pH in the presence of TPPNa (sodium tripolyphosphate). It can be observed that the zeta potential increases to reach -75 mV for a TPPNa concentration of 10^{-3} M, hence an excellent stability for the suspension. This result then confirms the theoretical model discussed in Section 2.

This very important result should allow coal–water suspensions to be prepared which are definitely stable in the presence of TPPNa and lignosulphonates.

4. Static stability test: application to highly concentrated coal–water suspensions

The stability of concentrated coal–water suspensions is of vital importance for bulk transportation, as opposed to pipeline transportation and for storage. It is imperative that a slurry can be produced which will remain in suspension for extended periods of time.

Stability is directly dependent upon the yield stress of the fluid which depends, in turn, on the reactions between the colloidal fraction of the particle-size distribution and the chemistry of the system. A stable slurry, therefore, demands a compromise using a size distribution for maximum packing efficiency but containing a colloidal fraction sufficient to react to the chemistry for acceptable stability [14].

The stability of the suspension depends on the following factors: the densities of the coal and liquid, viscosity of liquid, the surface properties of coal (its relative hydrophilic nature, its zeta potential and its morphology). At very low concentrations, free settling occurs according to the Stokes equation. The concentration of coal increases, and the stability becomes a complex phenomenon. There are many particle–particle interactions taking place which will hinder settling. The particles may also adhere to each other to form clusters (flocs or coagula). Depending on the state in the suspension, the suspension can be broadly classified in three types: aggregatively stable suspension, flocculated suspension and coagulated suspension in which the sediment formed might be compact and difficult to break [15].

Another popular method of measuring stability in glass containers is a rod penetration test. A glass container filled with slurry is allowed to stand for a period of time, after which a glass rod of specific weight and diameter is dropped into the slurry and allowed to penetrate through it. The time it takes for the rod to travel from the surface of the slurry to the bottom of the container is measured: the shorter the time of travel the more stable is the system [16].

We intend in this section to compare the two techniques used to obtain information both on the stability and the fluidity of highly concentrated coal in water slurries: the techniques are penetrometry and viscosimetry.

The penetrometry technique consists in the dropping, with no initial speed, of a glass rod with known dimensions (length L and diameter d) into the suspension, installed in a graduated test tube. The rod is submitted to its weight, P (gravity), and the viscous forces, f, of the suspension. The fundamental principle of dynamics gives the equation

$$m\frac{d\mathbf{v}}{dt} = \mathbf{f} + \mathbf{P} + \mathbf{F}_A \qquad (4)$$

Now, Equation 4 can be written

$$m\frac{dv}{dt} + \frac{C_r s \rho}{2} v^2 = mg - V_x \rho g \qquad (5)$$

where x is the displacement of the rod, and g the gravitational acceleration. $V_x = sx = m(t)/\rho_s$ (the volume of the rod sunken into the suspension). ρ and ρ_s are the volumic masses of the glass and the suspension respectively, $m(t)$ is the buoyancy of the sunken part of the rod at time t, v the instantaneous speed of the rod, s the rod section area and C_r the viscous resistance coefficient.

Solution of Equation 5 is generally very complicated; however, if we use the experimental data, we obtain

$$v = \frac{dx}{dt} = \frac{418.342}{C_r}\left(1 + C_r - \frac{C_r}{89.2}x\right)^{1/2} \qquad (6)$$

x is expressed in cm and v in cm s^{-1}.

TABLE I Values of limiting speed, resistance coefficient, theoretical and experimental viscosities as a function of settling time

Settling time (day)	Limiting speed, v_l ($\mathrm{cm\,s^{-1}}$)	C_r	Theoretical viscosity, η(cP)	Experimental viscosity, η(cP)
20	0.200	4.4×10^6	1800	1950
40	0.083	2.5×10^7	4300	4500
60	0.067	3.9×10^7	5400	5500
80	0.025	2.8×10^8	14000	Not measurable
90	0.013	9.8×10^8	27000	Not measurable

By integration, we obtain $x(t)$ and $v(t)$ as a function of time t

$$x(t) = \frac{89.2}{C_r}\left[4.690\left(1 + C_r\right)^{1/2} t - 5.499\, t^2\right] \tag{7}$$

$$v(t) = \left[\frac{418.342}{C_r}\left(1 + C_r\right)^{1/2} - \frac{981}{C_r}\, t\right] \tag{8}$$

The viscous forces are highly dependent on C_r and decrease as a function of the time t. The limiting speed, v_l, of the rod decreases as a function of the resistance coefficient, C_r. This last parameter can be related to the viscosity, η (the theoretical viscosity), of the suspension by a semi-empirical relationship

$$\eta = \frac{1}{24}\frac{C_r}{1000}\rho\, v_l d \tag{9}$$

Information on the stability of these suspensions was obtained by using the previously described penetrometry technique. A suspension is considered to be "stable" and its stability equal to S days, if the rod entirely penetrates in less than 6 min after a setting of S days.

Certain rheological properties of the suspensions, for instance the limiting speed v_l, the resistance coefficient C_r and the viscosity η, were obtained (Table I) by pplying the theory previously developed in the presence of certain surfactants and additives like the sodium polynaphtalene methane sulphonate and ammonia with ammonium sulphate.

There is a good correlation between calculations and experimental data. It can be observed that in order to obtain a fluid suspension, the resistance coefficient, C_r, must be lower than 10^7 and the limiting speed, v_l, higher than $0.1\ \mathrm{m\,s^{-1}}$. The uncertainty between calculated and measured viscosities is less than 10%.

This study reveals the importance of the resistance coefficient, C_r, that can be used as a criterion for the evaluation of CWM stability and fluidity.

The "fluidity" of the suspensions is only obtained after addition of stabilizers and dispersing agents. It was measured by determining the viscosity of the suspensions (containing 75% solids) with a Rotovisco RV3 viscosimeter made by Haake. The testing of the slurries was accomplished by steadily increasing the shear rate to which the sample was subjected from zero to approximately $300\ \mathrm{s^{-1}}$, steadily decreasing γ back to zero, and then repeating the cycle. Experimental viscosity of the CWM was determined at $100\ \mathrm{s^{-1}}$ from the initial and equilibrium flow curves. Results obtained show that there is a good correlation between viscosity of our concentrated suspensions measured by the penetrometry technique and that obtained by a viscosimeter (Rotovisco MV II).

5. Conclusion: preparation of concentrated, stable and fluid suspensions

According to the above findings, we were able to affirm that the thinners and stabilizers of concentrated clay (aluminosilicates), such as the lignosulphonates and polyphosphates used as thinners in drilling muds, should also be good thinners and stabilizers in suspensions of ground coal in water, because the surface charge depends on the silicate content. Following this hypothesis, we admit that the stability is due to the electrical repulsion of the charged particles. If the charge on the particles is high (zeta potential > 60 mV), the particles repel each other and the suspension is stable. If the zeta potential is less than ± 20 mV, the Brownian movement of the particles promotes their collision and attachment to each other, and there will be lumping and flocculation (DLVO theory).

Intensive research has been undertaken over the past decade in the analysis and production of coal suspensions in oil and in water. This research is generally described in the form of patents. But the effect of the surface charge and of various additives on the charge is never approached systematically.

This investigation allowed us to analyse systematically variation of the zeta potential as well as charge, as a function of pH, in the presence of the different dispersants and additives at different concentrations.

Concentrated coal suspensions (about 75% of solid by weight) were prepared in water by using different additives, for instance sodium tripolyphosphate (NaTPP) and surfactants like the Surfaron (S1520N100: sodium polynaphtalene methane sulphonate) and lignosulphonates (by coupling of the dispersion and stabilizing effects) with the optimum concentrations of these two products.

The results of the penetrometry technique also reveal that the concentration ratio $C_{\mathrm{NaTPP}}/C_{\mathrm{lignosulphonate}}$ must be higher than 2, in order to obtain fluid and stable concentrated suspensions (75% in coal). The stability of the suspensions was then greater than 2 months, but with a viscosity of 1900 cP.

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Received 31 May 1995
and accepted 24 April 1996