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Modifying the Surface Charge of Kaolin and Cristobalite Particles by Adding Cations

Materials

KEYWORDS : Agglomeration, zeta potential, rheology, surface charge.

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ABSTRACT

Some chemical reagents are normally used to promote either the agglomeration or dispersion of fine particles by knowing their surface charge through zeta potential (ζ) measurements. These ζ measurements are useful through a wide range of applications, i.e., to control the viscosity of a mineral pulp during its processing.

In this work the ζ of powders of kaolinite and cristobalite were measured in a pH from 2 to 12, alone, and adding separately salts containing K^+, Cu^{2+}, and Al^{3+} cations, in order to modify or manipulate the magnitude of the surface charge of the cristobalite and kaolinite species.

Experimental results indicate that both cristobalite and kaolinite observe similar pH- ζ relationships in presence of K^+, Cu^{2+}, and Al^{3+} cations. The pH, cation valence, and ionic strength reverse the original zeta potential value of both mineral species.

1. Introduction

As mentioned in the literature [1-4], the rheological behaviour of a suspension depends on the hydrodynamics effects, solid-liquid interactions, and the attractive and repulsive forces acting between particles. Although more attention has been focused on the hydrodynamics, volume fraction of solids in the slurry, and particle size distribution, the effect of the electrical surface charge of particles on viscosity is not taken into consideration.

According to the mathematical expression developed by Smoluchowski the viscosity of the suspension (η_s) is proportional to the zeta potential of particles (ζ), in such a way that the presence of electrical surface charge on a particle increases the viscosity of the suspension.

$$\eta_s = \eta \left[1 + 0.25\,\phi \left\{1 + \frac{D\,\xi^2}{2\,\pi\,\lambda\,\eta\,r^2}\right\}\right] \qquad (1)$$

being ϕ, the aggregate volume of spheres in unit volume of suspension; r, the radius of the particle; D, the dielectric constant; λ, the specific conductivity of the liquid, and η, the viscosity of the suspending liquid.

On the other hand, it is well known that zeta potential (ζ, mV) is a measure of the magnitude of the repulsion or attraction between particles. The measure of this parameter is extremely useful through a wide range of applications such as pharmaceuticals, mineral processing, water treatment, and ceramics (pouring readily during slip casting), among others [2].

The zeta potential is an "apparent" superficial charge measured in the proximity of a particle, in a zone occupied by the counter-ions called "diffuse layer". Depending on the magnitude of the electrical charge of the particle, the diffuse layer expands (highly charged particle) or contracts (slightly charged particle) [5-8]. From the above, the zeta potential value can be manipulated by changing the pH of the media, since the H^+ or $(OH)^-$ ions (called counter-ions) modify the extent of the diffuse layer (see Figure 1).

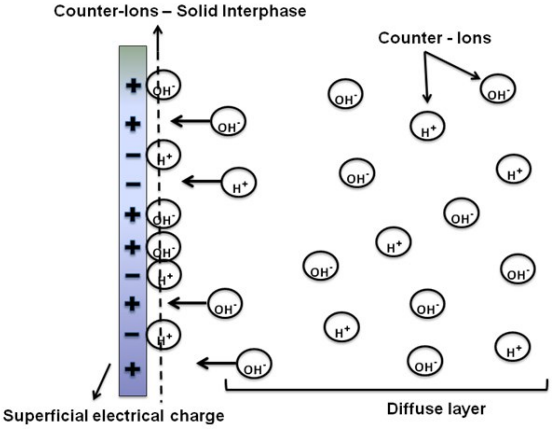


Figure 1.- Schematic representation of the electrical double layer model for measuring the zeta potential parameter.

The objective of the present work is to establish the pH, ionic strength, and cation valence effect on the zeta potential of two powder minerals: cristobalite and kaolinite.

2. Experimental procedure

The present study was applied to a mineral from a kaolin deposit located in a province of Michoacan, Mexico. The first step was to separate cristobalite from Kaolinite for a further electrochemical study. All the mineralogical species contained in every sample and for all the experimental steps, were identified by means of X-ray diffraction (XRD Siemens D5000).

2.1. Separating Kaolinite and Cristobalite

The mineral, as extracted from the deposit was qualitatively characterized according its mineralogical components. The mineral was milled until reaching a d80 equal to -45μm in order to liberate the cristobalite and the Kaolinite from the bulk sample. The new sample was washed several times with distilled water until it had evidence of separation of kaolinite and cristobalite. The washed particles (kaolinite powder with d80 -5μm), were separated and dried at 90°C during 24 hours.

2.2. Zeta Potential (ζ) measurements

Suspensions composed of 20 ml of distilled water and 0.011 g of either, kaolinite or cristobalite powder were mixed; the pH of the media was varied from 2 to 12 by using HCl, and NH_4OH. The salts added to the water to provide cations to the system were NaCl, $CuCl_2$, KCl, and $AlCl_3$ ($1X10^{-3}$ M). All reagents were provided by Sigma-Aldrich.

Zeta potential measurements were carried out in every suspension by using a ZetaMeter (Zetasizer, Model Malvern 300 HSA), for each pH value five readings of zeta potential were taken and averaged for the values reported.

3. Results and discusion

Figure 2 shows the XRD results and can be observed that both species cristobalite and Kaolinite were perfectly separated from the original ore sample.

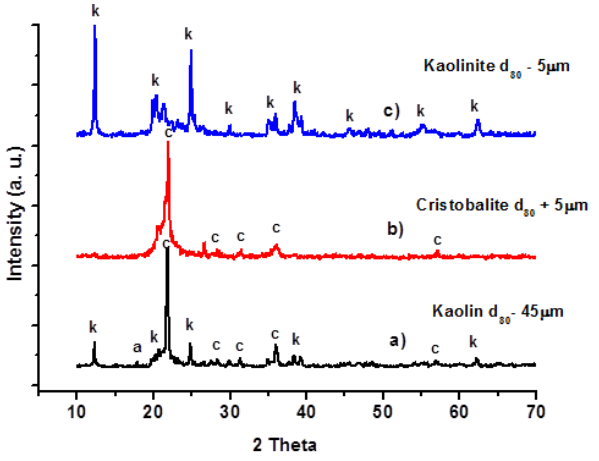


Figure 2.- XRD results from powder samples: a) Kaolin ore with d_{80} -45 µm, b) cristobalite particles, c, with d_{80} +10 µm, and c) kaolinite particles, k, with d_{80} -5 µm.

3.1. pH effect on zeta potential

The zeta potential-pH curves of kaolinite and cristobalite are shown in Figure 3. At pH 2 and up to 12 the cristobalite observes only negative surface charge, going from -1 to -36 mV; according to the literature the quartz, as another allotropic specie of silica and with similar electrical charge behaviour like cristobalite, observes an isoelectric point (IEP) at pH lower than 2[9]). On the other hand, kaolinite shows a different behaviour where the ζ value is 24 mV at pH 2, and -18 mV at pH 12. In this case, the IEP appears around pH 3.9. Another study reports that the IEP of kaolinite occurs at a pH between 4 and 5 [10, 11]; this difference is may be due to the chemical association of the corresponding minerals.

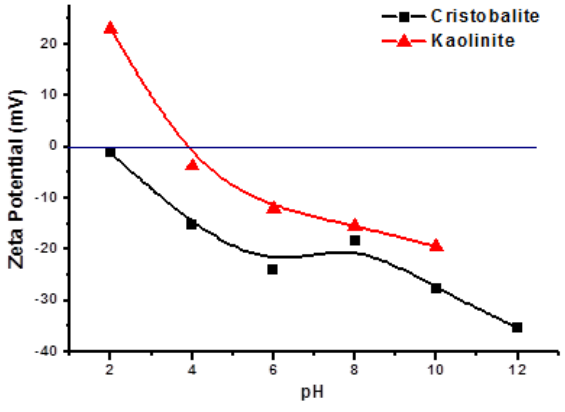


Figure 3.- Effect of pH on the estimated zeta potential values of kaolinite and cristobalite particles.

From figure 3, the negative zeta potential of kaolinite increases with pH, since adsorption of OH^- ions on the mineral surface results in a large diffuse electrical double layer and a more negative zeta potential value.

From the ζ values, and at pH 2 (positive and negative, respectively), can be established the great possibility to form agglomerates since one solid specie will attract the other, causing changes on the rheology of the slurry.

Figure 4 shows the evidence of the agglomeration phenomena in the slurry containing both kaolinite and cristobalite particles, at pH 2.

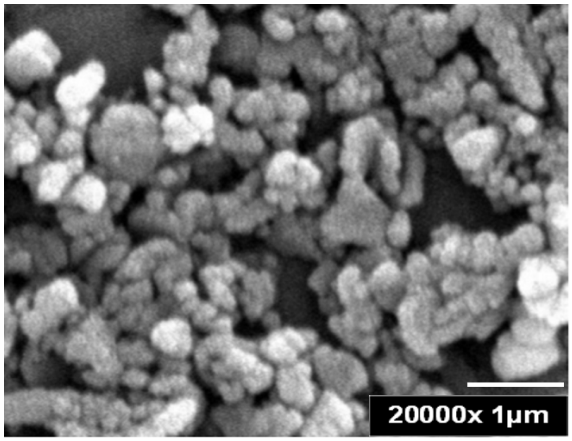


Figure 4.- Photomicrograph from SEM of aggregated solids from a slurry with cristobalite and kaolinite particles, and for pH 2.

3.2. Effect of the ionic strength on the zeta potential

The measured zeta potential values depend on a great extent of the chemical reagents used to adjust the pH of the media. For instance, the concentration of H^+ ions increases with the amount of HCl in the water, since the pH decreases.

From figure 5, the effect of the ionic strength on the zeta potential is observed. For liquid-liquid, and solid-liquid systems, the interaction between species is ruled by the following expression:

$$I = \frac{1}{2}\sum m_i z_i^2 \qquad (2)$$

Where **I** is the ionic strength, which is a measure of the intensity of the electric field in the system[12,13]; **m** is the molality of **i**; and **z** is the valence of the corresponding ion **i**. As the concentration of $CuCl_2$ increases, the zeta potential of cristobalite is more positive; on the other hand, when the concentration of KCl_2 increases from $1x10^{-3}$ to $1x10^{-2}$ M, the zeta potential of kaolinite becomes less negative.

From the above, by increasing the ionic strength (ionic concentration) of the liquid media, the electrical diffuse layer compresses resulting in a zeta potential values near to the IEP, which will enhance the agglomeration phenomena and will be reflected, for example, in a higher viscosity of a given slurry.

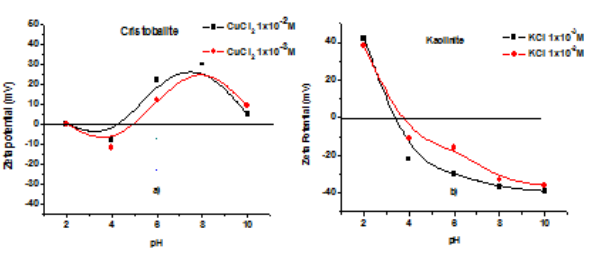


Figure 5.- Effect of the ionic strength on the zeta potential values in suspensions containing kaolinite or cristobalite, and by adding $CuCl_2$ and KCl.

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3.3. Cation valence effect on zeta potential

Figure 6 shows the effect of cation valence on the zeta potential values for suspensions containing cristobalite and kaolinite. As can be appreciated, as the cation valence increases the zeta potential becomes more positive (or less negative depending on the pH), and the corresponding IEP is moving to higher pH values.

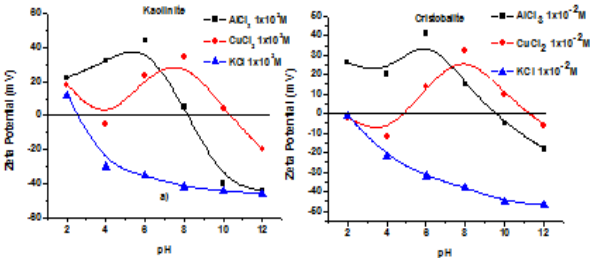


Figure 6.- Effect of the cation valence on zeta potential for slurries containing kaolinite or cristobalite.

From the above figures, the monovalent K^+ yields more negative zeta potential values than the divalent cation Cu^{2+}. This divalent cation compresses the diffuse double layer as regards the K^+ cation. This fact is supported by the zeta potential curve built when adding the Al^{3+} cation in the range of pH from 2 to 7; nevertheless, additional research must be carried out in order to explain clearly the behavior of the zeta potential curve for pH larger than 7, which shows a different trend, despite the fact that a cation with larger valence was added.

As mentioned above for slip casting the viscosity of the slurry must be minimized. From figure 6 by manipulating the pH of the slurry the repulsive forces between particles can be increased and then, the viscosity can be minimized.

4. Conclusions

From the experimental work carried out in order to establish the pH, ionic strength, and cation valence effect on the zeta potential of two minerals (powders of cristobalite and kaolinite), by adding KCl, $CuCl_2$, and $AlCl_3$, the following conclusions are drawn:

Both cristobalite and kaolinite observe similar pH- zeta potential relationships in presence of K^+, Cu^{2+}, and Al^{3+} cations. The pH, cation valence, and ionic strength reverse the zeta potential value of both mineral species: kaolinite and cristobalite.

By manipulating the pH, cation valence, and ionic strength in the liquid media, the viscosity of the slurry can be yield to a minimum, improving its handling during the slip casting for production of ceramic ware, or during the unit operations of mineral processing.

Acknowledgment

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