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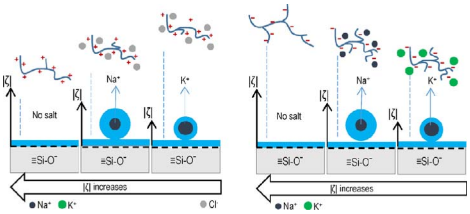
Research Paper

Zeta potential and viscosity of colloidal silica suspensions: Effect of seawater salts, pH, flocculant, and shear rate

Cristian P. Romero[a], Ricardo I. Jeldres[b], Gonzalo R. Quezada[a], Fernando Concha[c], Pedro G. Toledo[a,*]

[a] Chemical Engineering Department and Surface Analysis Laboratory (ASIF), University of Concepción, PO Box 160-C, Correo 3, Concepción, Chile
[b] Department of Chemical Engineering and Mineral Process, University of Antofagasta, PO Box 170, Antofagasta, Chile
[c] Department of Metallurgical Engineering, University of Concepción, PO Box 160-C, Correo 3, Concepción, Chile

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of various seawater electrolytes on the zeta potential and viscosity of silica suspensions has been studied as a function of electrolyte concentration, pH, flocculant and shear rate. Salts were alkali and alkaline-earth metal chlorides. The magnitude of the negative zeta potential of silica as a function of pH for monovalent cations follows $Li^+ > Na^+ > K^+ > Cs^+$ implying that adsorption follows $Cs^+ > K^+ > Na^+ > Li^+$. In the presence of divalent cations, the magnitude of the negative zeta potential as a function of pH decreases greatly following $Mg^{2+} > Ca^{2+}$, implying that adsorption follows $Ca^{2+} > Mg^{2+}$. Regarding the flocculant in solution, molecular simulations indicate that repulsion between anionic acrylate units causes the polymer to adopt expanded tertiary conformations, however with cations this repulsion is shielded causing the polymer to fold into balled-up conformations. The adsorption of cations on anionic flocculant chains follows inverse series than silica, i.e., $Li^+ > Na^+ > K^+ > Cs^+$ and $Mg^{2+} < Ca^{2+}$. The different ability of silica and flocculant to adsorb cations leads to force fields that create three-dimensional networks of particles with resistance depending on the cation. The viscosity of silica suspensions formulated at 0.5 M salt and pH 7 in anionic flocculant follows $KI > KCl > NaCl > MgCl_2 >$ water, and in cationic flocculant follows $KI < KCl < NaCl < MgCl_2 <$ water. In anionic flocculant, the counterion is the same for silica and flocculant leading to strong particle-flocculant interaction and suspensions with high viscosity. The resistance of the particle networks formed are weakened only slightly as the shear stress increases In cationic flocculant, the cation is the counterion of silica while the anion is the counterion of flocculant, their ionic atmospheres are different giving rise to weak particle-flocculant interaction and low viscosity suspensions. The resistance of such networks is increasingly weakened as the shear rate increases. The higher the pH, the higher the repulsion, and the lower the viscosities of the suspensions formulated with either flocculant.

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[*] Corresponding author.
E-mail address: petoledo@udec.cl (P.G. Toledo).

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1. Introduction

The use of seawater or partially desalinated seawater to process metal ores is becoming the only sustainable solution in regions with severe aridity [1–5]. The mining industry continues to make great efforts to close the water cycle, however water lost to tailings often exceeds 0.75 m^3 for each ton of ore processed. The use of water with varying degrees of salinity requires improving current understanding of the impact of salts on large thickeners where water is separated from silica-rich solids, particularly on the yield stress and viscosity of the suspensions involved. At first glance, the use of seawater may seem advantageous since its cations could act by shielding the negative charges on the surface of the silica particles thus facilitating the formation of dense flocs which readily precipitate leaving a clarified supernatant water. However, sediments must be transported to tailings ponds for final disposal and therefore the flocs formed must be spongy and flexible to facilitate the clarification operation and also the transport. In the absence of salts there is a technology based on flocculants to accelerate thickening [6], however in the presence of salts it is not easy to anticipate the efficiency of traditional flocculants and ultimately their usefulness. For example, Wang et al. [7] and Jeldres et al. [8] showed that the settling performance of flocculated kaolinite slurries is reduced in high salt solutions, however Ji et al. [9] have shown that on the contrary the sedimentation rate of mining tailings improves when salinity is increased. Seawater ions have different degrees of hydration, in the presence of silica particles some of these ions are adsorbed completely hydrated, others only partly and others completely dehydrated, making any prediction of their impact on coagulation and flocculation processes very difficult. The literature on flocculation studies is extensive [10–25], however, a systematic study is lacking on the effect of seawater ions on the flocculation of silica particles in the presence of either cationic or anionic flocculant. It is useful to order seawater cations according to the Hofmeister series [26,27], from poorly hydrated cations such as Cs^+ to strongly hydrated cations such as Mg^{2+}, that is, $Cs^+ > K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The listing is partial and limited to cations of seawater studied here. Early members of the series increase solvent surface tension, decrease the solubility of non-polar molecules (“salting out” effect) and decrease the local order of water, they are known as water structure breakers, on the contrary later members of the series increase the solubility of polar molecules (“salting in” effect) and increase the local order of water, they are known as water structure makers [28–31]. In this work, we study the viscous behavior of silica suspensions as a function of the concentration of flocculant, either anionic or cationic, in the presence of seawater cations, water-structure makers and breakers, at concentrations as high as 0.5 M to approximate the ionic strength of seawater. Based on measurements of the zeta potential of silica particles and conformation of the flocculant in saltwater, the flocculation quality, the governing mechanism, and the resulting viscosity are determined.

2. Experimental

2.1. Materials

The silica particles used in this study were ground quartz (Sigma Aldrich), about 99% pure, and particle size 0.5–10 mm (approx. 80% between 1 and 5 μm). Milli-Q water was used in all experiments. In order to prepare suspensions with high ionic strength, close to that of seawater, salt was added until reaching 0.5 M a maximum limit in concentration. Two polyacrylamide copolymers were used independently for the rheological tests, an anionic with branched structure and high molecular weight (SNF 60430), donated by Centinela Copper Mine (Antofagasta, Chile) and a cationic with linear structure and low molecular weight, donated by BO Paper Bio Bio (San Pedro de la Paz, Chile). Flocculant dosages ranged from 0 to 700 g/ton of dry mass of solid. For the anionic flocculant the intrinsic viscosity was 357 dL/g and the cationic at pH 5.5 was 1905 meq/g. For the cationic flocculant the intrinsic viscosity and ionic demand were 4.3 dL/g and 1838.4 meq/g at pH 5, 3.0 dL/g and 1290.3 meq/g at pH 7, 2.3 dL/g and 590 meq/g at pH 9 and 1.8 dL/g and 980 meq/g at pH 11. It should be noticed that the flocculant changed from cationic to anionic at pH 11. The intrinsic viscosity is used as a molecular weight indicator and the ionic demand as a measurement of the charge density of the flocculant. The intrinsic viscosity of the flocculants was measured with a Cannon-Fenske capillary viscometer at 23C, for details see Jeldres et al. [8]. Flocculant charge was determined by potentiometric titration using particle charge detector PCD 03 (Mütek). The cationic polymer Poli-DADMAC was used to determine the charge of the anionic flocculant and the anionic polymer PVSK was used for the cationic flocculant. The pH of the resulting suspensions was adjusted using HCl (Merck) to achieve pH 7 or NaOH, CsOH, LiOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$ (Merck) to reach pH 9 in suspensions with NaCl, CsCl, LiCl, KCl-KI, $MgCl_2$ and $CaCl_2$ (Merck) respectively.

2.2. Methods

The zeta potential measurements of silica suspensions in saline solutions were performed with a ZetaCompact Zeta9000 (CAD Instruments), a zetameter using the technique of micro-electrophoresis. The measurements were carried out according to the concentration and type of salt dissolved, at pH 7 and 9, with 0.05% by weight of silica. Salts used were $MgCl_2$, $CaCl_2$, LiCl, NaCl, KCl, KI and CsCl at 0.03, 0.1 and 0.3 M.

Shear viscosity was measured with a Haake RV 20 viscometer with a cylindrical Searle type measuring device (Haake Co). The silica suspensions were formulated at 40% by weight with the addition of salt to a concentration of 0.5 M. The pH was adjusted to 7 and 9 to retain the anionic and cationic condition of each flocculant. The assays were performed independently using $MgCl_2$, KCl, KI and NaCl salts. After adjusting the pH, an increasing amount of flocculant was added in the range 0–470 g/ton in most of the cases studied. For this, a stock solution with 0.1 g/L of flocculant was initially prepared. Before measurement, each mixture was stirred for a defined time of 40 s to promote flocculation. The viscometer delivers flow curves (stress vs. shear rate) and viscosity (viscosity vs. shear velocity) for a range of velocities between 0 and 400 s^{-1}. The results reported here are for 150, 200 and 320 s^{-1} to embrace the typical shear rate of pumps used in mining operations to drive the pulps [32].

The flocculant conformation was determined by light microscopy with a Motorized System Microscope BX61 (Olympus) in 50 mL samples of the initial solution of flocculant prepared at 0.1 g/L, at pH 2, 7 and 11, in pure water and in NaCl 0.03 M solutions.

3. Results and discussion

3.1. Silica zeta potential

Silica is a solid with uncharged silanol groups (≡Si−OH) and charged silicic acid groups (≡Si−O^-) on its surface. The negative surface charge of silica above its isoelectric point (iep ~ 2 [24]) is determined by the dissociated silanol groups. Fig. 1 shows that ions of positive charge as those from the monovalent alkali metal series Cs^+, K^+, Na^+ and Li^+ act as counter ions on the anionic silica surface, adsorbing on the surface-dominating negative sites and thus decreasing the absolute value of the zeta potential. The figure also shows that the higher the cation concentration the lower the absolute value of the zeta potential which in agreement with Franks [24] applies to any given cation (see also [29–31]). The results here also agree with those obtained in the experimental determination of the critical concentration of coagulation since ions that decrease the magnitude of the zeta potential of silica particles more significantly favor the coagulation and subsequent sedimentation of the particles [13]. The concentration to