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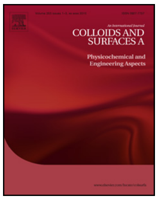

Impact of seawater salts on the viscoelastic behavior of flocculated mineral suspensions

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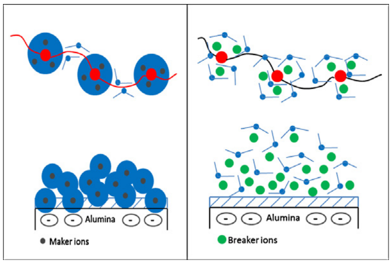
HIGHLIGHTS

- We study effects of salts on the viscoelastic behavior of flocculated suspensions.
- Small maker ions promote structured water layers around sites of solid–flocculant.
- Small counterions and similar water structure on surfaces lead to strong networks.
- Consequences are sediments with high yield stress.
- Compliance depends on applied stress revealing a non-linear viscoelastic behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of several electrolytes present in seawater on the rheological properties of flocculated alumina suspensions was assessed by using creep testing at pH conditions both above and below the isoelectric point. Flocculated suspensions were obtained by adding a high molecular weight anionic polymer flocculant to a cylinder of alumina suspension and aggregating the suspension using the plunger method. The suspension was allowed to sediment and the supernatant liquid decanted prior to tests of the viscoelastic properties of the resulting sediment. Salts analyzed were $MgCl_2$, $CaCl_2$ and NaCl, known as water structure makers, and KI and KCl, known as water structure breakers. A high salt concentration of 0.5 M was used to approach the ionic strength of seawater. For both pH's studied, the sediments demonstrated viscoelastic non-linear behavior observed as a non-linear relationship between yield strain and applied stress. In the absence of flocculant, it has been observed that the viscosity and yield stress of a suspension increase in the presence of structure maker salts for the case of both silica and alumina suspensions. In the presence of flocculant, new results are found: when the solid and flocculant were of opposite charge, the shear yield stress of the alumina suspensions increased with the breaker character of the salts, however when the solid and flocculant were of similar charge, then the yield stress is independent of the character of the salts. Similar water structures on the interacting surfaces lead to strong particle networks. The work demonstrates the importance of salt-surface interaction to the rheology of suspensions in the presence of polymer flocculants, as is typical of many mineral processing operations world-wide.

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1. Introduction

The sustainable development of many mining activity lies in the search for new water sources and a key alternative in some locations is the direct use of seawater. However, the high concentration and the variety of electrolytes in seawater represent a difficult challenge. Electrolytes change the interaction forces between particles and particle-additives as well as causing solvation and water structuring. This is attributed to differences between ions, where some are structure makers and others structure breakers [1]. These changes have direct impact on rheological parameters of suspensions such as the viscosity or yield stress [2–6].

Maker ions such as Li^+, Na^+, Mg^{2+}, and Ca^{2+} are small and thus have a strong electric field causing water molecules around these ions to become highly structured. Breaker ions such as Cs^+, K^+, Cl^- and I^- generally have a larger size than the maker ions and weaker electric fields. The field strength is considered insufficient to provide any structure to the water around these ions [7–10]. It is generally observed that the relative viscosity of a suspension increases in the presence of maker salts because of the strengthening of the water bonds. In contrast, the suspension viscosity in the presence of breaker salts generally decreases because the hydrogen bonds are weaker [11]. It is interesting to note that the viscosity of seawater is higher than for pure water for all temperatures, which could be postulated to be due to its structure maker salts Flocculation efficiency depends on the hydration layers of both solid and flocculant surface layers and the structure of water in such layers depends on the electrolyte present [6]. It is not hitherto obvious which of these contributions will dominate the viscosity of suspensions in the presence of polymer flocculants.

At low stresses, flocculated suspensions exhibit solid-like elastic behavior, whereas at high stresses they show fluid-like viscous behavior. The yielding transition from elastic to viscous is usually described as the yield stress. This stress depends on the strength of the particulate network structure and is defined as the force per unit area required to break the structure. The yield stress of particulate suspensions is typically related to particle shape and size distribution, solid concentration and surface chemistry [12–14], however more work is needed to improve current understanding of the contribution of network rigidity and strength to the yielding process. The yield point or yield stress is usually determined from a stress–strain plot as the point of transition between the linear and non-linear behavior (see for instance [15]). This transition usually occurs within a stress range rather than at a specific value and it is within this range that the suspension exhibits viscoelastic behavior [16–18].

It has been suggested that the material yielding transition is determined by a critical strain, the yield strain, or strain energy rather than by a critical stress [19,20]. The yielding transition is far from being understood and this is particularly the case with flocculated suspensions. However, the viscoelastic behavior of flocculated mineral suspensions can be determined by using the creep test. This test measures the strain when a constant stress is applied and is used to determine the material compliance, which is a measure of the particle network strength and its viscoelastic behavior. This is particularly relevant for mineral suspensions in separation processes such as thickening where excessive addition of polymer flocculant is observed to cause higher yield stresses and changes in the network behavior at yield. This has consequential effects on flow start-up and cessation in pipe flow and tailings disposal, for example.

Appropriate fluidity properties of slurries require careful control of the rheological properties, set by interaction forces defining the particle network. The viscosity and yield stress of suspensions have been routinely measured and several authors have explored the relationship of these properties with the interaction potential between particles (for examples see [21–26]). Electrolytes are pivotal to determining the strength and range of these forces. Little is known about such forces in suspensions with concentrated salts and seawater. For example, controlling the inter-particle interactions through chemistry, Velamakanni et al. [27] increased the viscosity of dispersed alumina suspensions over 4 orders of magnitude at pH < point of zero charge (PZC) through weak aggregation with certain indifferent electrolytes containing hydrolyzable anions. According to these authors a combination of short-range repulsive (lubricating) hydration force and long-range attractive van der Waals force explain the observed viscosity-consolidation behavior of the slurries, especially in the presence of excess salt. It was postulated that hydration layers are formed on the positively charged alumina particles at low pH when hydrated anions interact with the positive surface sites on the alumina. At the PZC, the anions in the slurry do not form a hydration layer for flocculated slurries but when the salt content in coagulated slurries exceeds the critical coagulation concentration (CCC), the depth of the hydration minimum increases with increasing salt concentration, resulting in coagulated slurries with increased viscosity.

In a series of works to quantify the formation and properties of hydration layers and the range and magnitude of the repulsive forces that result [28–32], the authors found that the interaction between molecularly smooth mica surfaces in very dilute electrolyte solutions (10^{-4} M) obeys the DLVO theory. However at higher concentrations ($\geq 10^{-3}$ M), specific to each electrolyte, more hydrated cations bind to the negatively charged mica surfaces giving rise to an additional short-range repulsive hydration force below ~5 nm. The hydration force increases with the hydration number of the cation, i.e. the average number of water molecules in the first shell, in the order $Mg^{2+} > Ca^{2+} > Na^+ > Li^+ > K^+ > Cs^+$. It is believed that this force is due to the energy needed to dehydrate the bound cations. The reverse result was found by Chapel [33] for the hydration force between silica surfaces in a range of electrolyte concentration (from 10^{-4} to 10^{-1} M). It was postulated that hydroxyl groups present on the silica surface dominated the water structure. Thus, the strength and range of the hydration force is observed to increase with the hydration number of counterions for mica but decreases for silica.

Later, Colic et al. [34] studied the effect of counterion size on short-range repulsive forces for alumina slurries at high pH (>PZC) and at high ionic strengths. Their results contradicted the hydration force model of Pashley [31] and Pashley and Israelachvili [32] that had been used by Velamakanni et al. [27] to explain their results with alumina at low pH (<PZC). According to Colic et al. [34] the range of the repulsive forces correlates well with the size of the unhydrated ions; smaller counterions (maker ions) penetrate deeper into the hydration layer of the alumina surfaces than large counterions (breaker ions) producing inter-particle pair potentials with deeper potential wells and thus stronger particle networks as rheological measurements show. These results were confirmed later by Colic et al. [35] for silica slurries at various pHs (see also [36–40]) and supported by reference-hypernetted chain statistical models describing the interaction of ions with solvated surfaces. More recently, Acuña and Toledo [41,42] found that the AFM force between glass surfaces and between mica and silica surfaces has universal character in the short range, less than ~1 nm or about 3–4 water molecules, independent of solution conditions, i.e. electrolyte ion size, charge and concentration ($<10^{-2}$), and pH.

The goal here is to study the impact of different seawater salts, structure makers and breakers, on the rheological properties of flocculated alumina sediments by using creep testing and to relate the rheological behavior to the hydration number of the counterions and their effect on short-range repulsive forces.