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Use of Multi-Anionic Sodium Tripolyphosphate to Enhance Dispersion of Concentrated Kaolin Slurries in Seawater

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Abstract: This research aims to analyze the impact of sodium tripolyphosphate (STPP) as a rheological modifier of concentrated kaolin slurries in seawater at pH 8, which is characteristic of copper sulfide processing operations. The dispersion phenomenon was analyzed through chord length measurements using the focused beam reflectance measurement (FBRM) technique, complementing size distributions in unweighted and square-weighted modes. The reduction of the rheological properties was significant, decreasing from 231 Pa in a reagent-free environment to 80 Pa after the application of STPP. A frequency sweep in a linear viscoelastic regime indicated that by applying a characteristic dosage of 0.53 kg/t of STPP, the pulp before yielding increases its phase angle, which increases its liquid-like character. Measurements of the chord length verified the dispersion of particles, which showed an apparent increase in the proportion of fine particles and a reduction of the coarser aggregates when STPP was applied. Measurements of the zeta potential suggested that the high anionic charge of the reagent (pentavalent) increases the electrostatic repulsions between particles, overcoming the effect of cations in seawater. The results are relevant for the mining industry, especially when the deposits have high contents of complex gangues, such as clays, that increase the rheological properties. This increases the energy costs and water consumption needed for pumping the tailings from thickeners to the tailing storage facilities. The strategies that allow for the improvement of the fluidity and deformation of the tailings generate slack in order to maximize water recovery in the thickening stages.



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1. Introduction

The rheological behavior of thickened pulps is critical in mineral processing plants since they significantly affect the efficiency of solid–liquid separation operations, such as flotation, thickening, the pumping of concentrated slurries, and tailings deposits [1–4]. There is a direct relationship between the efficiency of water use in concentrator plants and the rheological properties of suspensions, mainly referring to tailings management operations [5,6]. Due to their large volumes, tailings management operations offer the most significant potential savings in water resources, being of great importance in regions with deposits located in arid zones, where water is scarce, putting the sustainability of operations at risk. In this context, industries are focused on improving water recycling to reduce consumption and reduce the environmental and social impacts caused by their activities.

Tailings are thickened in order to recover the water contained in the pulps and improve the deposit strategies in the tailing storage facilities. The pulps are exposed to chemical reagents in the thickener feedwell, generating massive and fast-settling aggregates that

settle to the bottom of the equipment and are discharged through a lower cone. When working with paste thickeners, the underflow can reach solid concentrations higher than 70 wt%, achieving attractive water recovery rates. However, pumping these slurries can be expensive, considering that rheological parameters rise exponentially with pulp density [7]. The direct use of seawater appears to be a promising alternative when the deposits are located close to the coastline. This strategy has been used in different plants worldwide, achieving sustainable results with an inexhaustible water source [8]. However, the use of seawater presents a series of operational challenges in the stages of flotation and thickening (although this last operation has been little investigated). The main problems arise when working at a highly alkaline pH of above pH 10.5, since the divalent cations precipitate, forming hydrophilic species that reduce the floatability of valuable minerals [9,10]. For this reason, the industries have chosen to work at a pH close to pH 8 and seek alternatives to depress pyrite, since, at this pH, it has a high tendency to float [11,12]. Besides, seawater modifies the rheological properties of suspensions compared to freshwater; for example, Reyes et al. [13] studied the rheological behavior of magnetite tailings with different combinations of seawater/process water. The authors found that the increase in salinity meant an increased yield stress, correlated with the zeta potential. This is because the counterions that are dissolved in the water compress the ionic cloud that surrounds the particles' surface, reducing the electrostatic repulsions. It has been found that quartz particles (the primary component in tailings) agglomerate in a saline medium, with cations that shield the electric charge and generate cationic bridges between surfaces. The phenomenon is intensified with fine particles and clays that produce higher values of yield stress, complex viscosity, and viscoelastic moduli [14,15].

Clays can be unaffected by gravity, but they interact with other particles through attractive or repulsive forces due to their colloidal size. Clay particles are positively charged at their edges in acidic and neutral pH ranges, and negatively charged at their faces due to isomorphic substitution, where the lower valence ions replace those of higher valence. This anisotropic characteristic leads to three aggregation modes: edge-to-face (EF), face-to-face (FF), and edge-to-edge (EE). The FF association forms structured laminar aggregates of an apparent low volume characterized by low yield stresses. Meanwhile, the associations EF and EE form a three-dimensional structure, known as a house of cards, that increases the fraction of apparent suspension volume [16]. What happens with the fine particles and clays is essential for mineral processing, considering that they have a relevant impact on solid–liquid separation and make the rheological behavior of concentrated slurries more complex [17–19].

Common strategies used in the plant to deal with highly rheological tailings consider generally inefficient methods, such as dilution with water or pH modifications, which possess uncertainties when the complex gangues do not present monotonous behaviors with the pH. Another alternative is to use chemical reagents that modify the physicochemical properties of the mineral surface. This is based on promoting the dispersion of particles mainly through electrostatic and/or steric repulsions. Zhou et al., who analyzed the yield stress of fine silica suspensions flocculated with cationic polymers at different dosages, reported interesting results. The authors found a direct relationship between the rheological properties of concentrated slurries of silica with the adhesive forces between the particles' surfaces. These measurements were performed on an atomic force microscope (AFM) using a colloidal probe technique. Cement, paint, paper, cosmetic, and pharmaceutical industries use bentonite as a thickening agent, while the ceramic processing and paper coating industries require liquefaction. For this, they use rheological modifiers such as polyelectrolytes, polymers, or surfactants under various chemical conditions in order to achieve the required rheological performance in the final product [20–22].

Interestingly, Sjöberg et al. [23] found that salts with multivalent anions such as sulfates and phosphates increased the critical coagulation concentration of clay dispersions, preventing their coagulation. Penner and Lagaly [24] studied the effects of potassium phosphates with different amounts of hydrogen molecules on the rheological properties of

kaolin suspensions. The hydrogen molecule-free phosphate compound, K_3PO_4 , was the dispersant that decreased the viscosity of the suspensions the most. Sahnoun et al. [25] showed that sodium polyphosphate provides greater efficiency as a dispersing agent for kaolin suspensions than sodium tripolyphosphate. It promotes lower viscosity values associated with the oligomeric nature of the polyphosphate, giving rise to a dispersion mechanism through electrostatic repulsion as steric stabilization. Other studies include Na-Hexametaphosphate [26–28]. For example, Rubio-Hernández et al. [26] showed that a small concentration of this dispersant (<0.5 wt%) caused a great reduction in the yield stress of kaolin suspension in distilled water. Although no study reports the use of this type of reagent in saline medium, it is expected that multi-anionic salts may help to generate the repulsion and dispersion of clay particles in seawater, where the ionic strength is around 0.6 M [8]; therefore, the objective of the present study is to analyze the dispersing ability of sodium tripolyphosphate salt, STPP, since once it is dissolved in water, the reagent has a pentavalent anionic charge. The results are analyzed as a function of the dose on kaolinite slurries prepared in seawater. For this, a rheological analysis was developed, considering the yielding and viscoelastic properties. Then, the dispersion was evaluated through the chord length particle distribution before and after the reagent addition. Zeta potential measurements deduced the dispersion mechanism.

2. Methodology

The pulps were prepared with kaolin particles purchased from Ward's Science. Its composition was determined by X-ray diffraction (XRD) analysis on a Bruker, D8 Advance X-ray diffractometer (Bruker, Billerica, MA, USA) using the Powder Diffraction File of ICDD (International Center for Diffraction Data) software TOPAS (version 5, Bruker, Billerica, MA, USA). The spectra show a majority (over 10%) of halite and kaolinite and a minority (1–10%) of SiO_2 (Figure 1). The seawater was obtained from the coast of Antofagasta (Chile) and later filtered by an ultraviolet filter to remove algae and micro-organic species. The ion concentration of seawater was determined by atomic absorption spectrophotometry, presenting 11,480 mg/L of Na^+ , 1410 mg/L of Mg^{2+} , and 405 mg/L of Ca^{2+} . The Cl^- concentration was 18,770 mg/L, determined by the argentometric method. The rheological modifying reagent provided by Manuchar Chile S.A. was sodium tripolyphosphate (STPP), with the chemical formula $Na_5P_3O_{10}$, and a molecular weight of 367.9 g/mol. The slurries are deflocculated in order to isolate the effect of STPP in seawater.

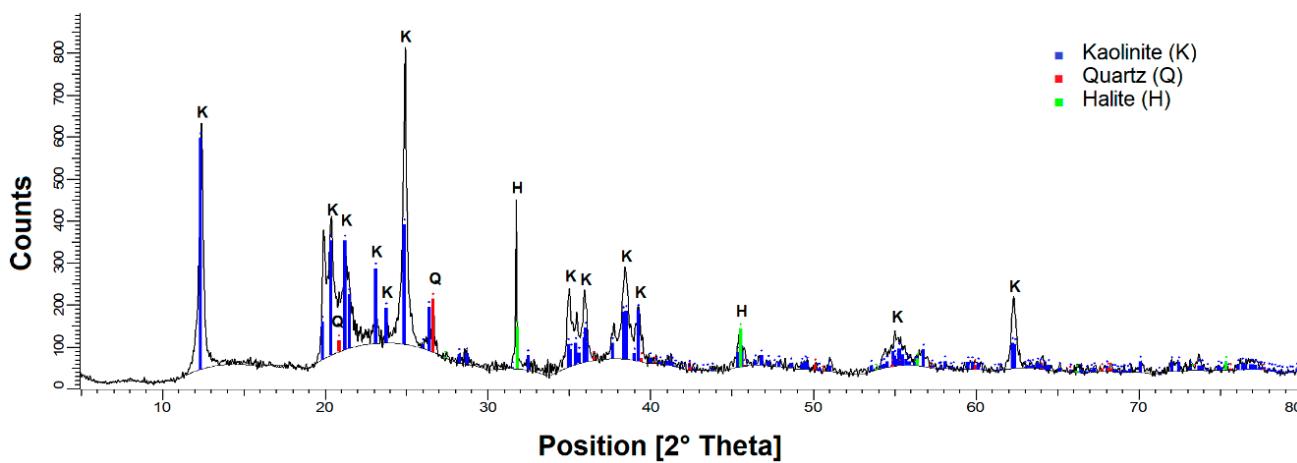


Figure 1. X-ray diffraction spectrum of kaolin particles.

Figures 2 and 3 show the FTIR spectra of kaolin and STPP, respectively. The bands between the wavenumber range $3600\text{--}3700\text{ cm}^{-1}$ correspond to the OH^- groups located in the octahedral sheet for kaolin. In the ranges of $500\text{--}1200\text{ cm}^{-1}$, it is possible to find the bands that identify the bonds of the typical elements that characterize kaolin: Si-O, Al-OH,

and Si-O-Al. For the STPP, the characteristic bands are found at (i) 1215 cm^{-1} , where a P=O stretch is located, (ii) 1126 cm^{-1} and 1089 cm^{-1} , where symmetric and antisymmetric stretch vibrations are located in the PO_2 and PO_3 groups, respectively, and (iii) 882 cm^{-1} , where an antisymmetric stretching of the P-O-P bridge occurs.

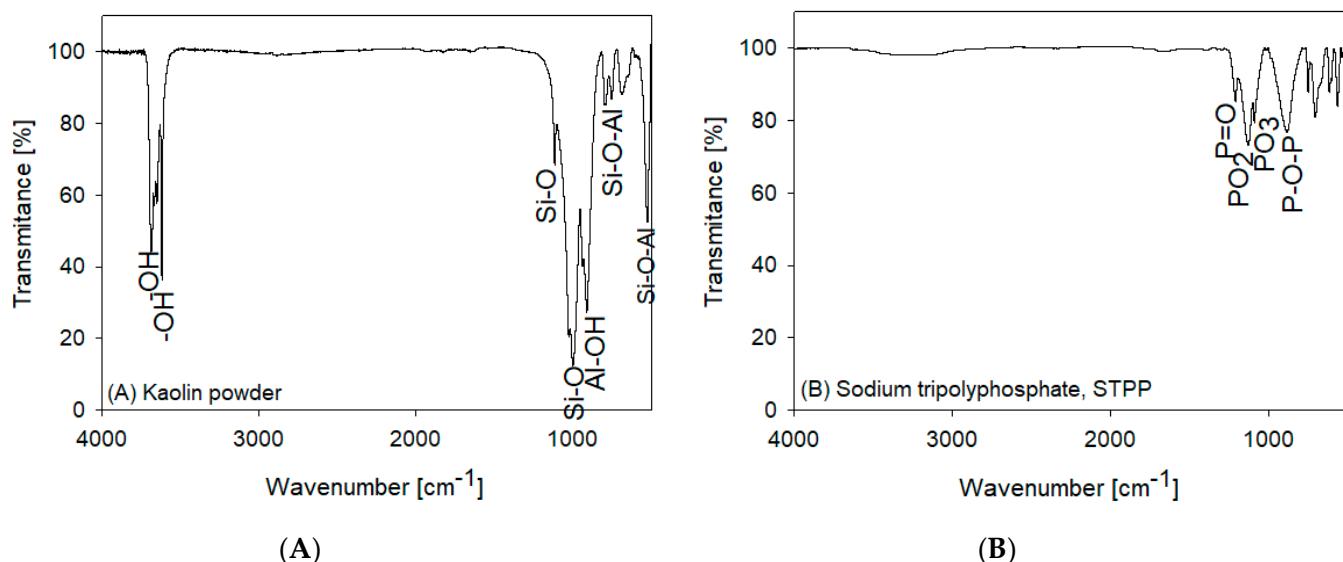


Figure 2. Fourier-transform infrared spectroscopy (FTIR) for: (A) kaolin powder; (B) sodium tripolyphosphate, STPP.

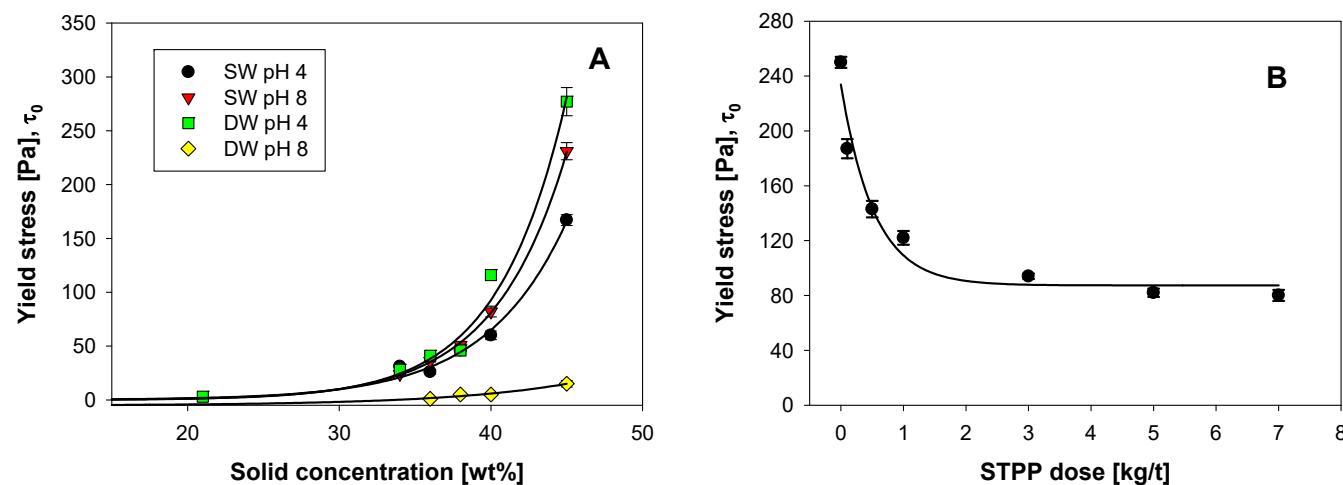


Figure 3. (A) Yield stress of kaolin slurries prepared in seawater (SW) and distilled water (DW); (B) effect of sodium tripolyphosphate (STPP) on yield stress of kaolin slurries in seawater at pH 8.

2.1. Rheological Characterization

For each measurement, a 400 mL kaolin pulp was prepared in seawater at 45 wt%. The multi-anionic salts were added to the stock slurry according to the required dose and mixed by mechanical stirring. Then a 120 mL aliquot was taken for characterization. Measurements were made in an Anton Paar MCR 102 rheometer (ANAMIN Group, Santiago, Chile) using a vane-in-cup configuration, with a 2.2 and 4.2 cm diameter, respectively. The measured data were processed using the Rheocompass TM Light software (ANAMIN Group, Santiago, Chile). The yield stress was detected in the logarithmic representation of the deformation (γ) over the shear stress (τ). Up to specific shear stress, the relationship between γ and τ is constant, representing the range of elastic deformation [29]. At the end of this range, irreversible deformation occurs with increasing shear stress, resulting

in sample flow and a steeper curve slope. To determine the elastic limit in the $\log \gamma / \log \tau$ diagram, the bend in the measurement curve was analyzed with the help of two tangents applied on the two slopes. The slurries were also subjected to oscillatory rheological trials with and without STPP at the corresponding characteristic dosage obtained from yield stress measurements (see Equation (1)). The usual test measures the dependence on the oscillation frequency of the storage G' and loss G'' moduli in the linear viscoelastic regime. The oscillatory tests here comprised a frequency range of 1–100 rad/s. A constant strain of 0.1% was maintained, previously selected using an amplitude sweep to ensure a linear viscoelastic behavior. The amplitude sweep test was set at 6.28 rad/s. Deformations were generally low to preserve the structure of the pulps.

2.2. Particle Size Distribution

The particle size distributions (PSD) were studied by a particle tracking system using focused beam reflectance measurement (FBRM) technology (ParticleTrack G400, Metter-Toledo, Columbus, OH, USA). This instrument scans a highly focused laser beam through suspended particles at a fixed speed (2 m/s tangential velocities) and measures the time duration of the backscattered light from these particles. This length of time is multiplied by the fixed speed of the laser and results in a characteristic measurement of the particle's geometry, known as the chord length, collecting thousands of measurements per second. This produces a histogram classified in several bins in the range of 0.5 to 1000 or 2000 μm .

An aliquot of the stock solution was diluted with seawater to 5 wt%, ensuring that the FBRM response was not affected by the solid fraction, and the pH was adjusted to 8. The FBRM probe was introduced directly into the suspension for 3 min. The iC FBRMTM software (Mettler Toledo, Ohio, USA) recorded the chord length distribution every 2 s. Five equidistant distributions were chosen for data analysis, and the data were averaged to ensure statistical validity.

2.3. Zeta Potential

An aliquot of the stock suspension was taken and diluted with seawater until reaching 1 g/L. A volume of 10 mL was extracted, which was used for its zeta potential measurement on a Stabino® instrument (Colloid Metrix, Meerbusch, Germany). The core of the Stabino is a cylindrical PTFE measuring beaker and piston. The sample is added to the beaker, and the piston oscillates at a constant frequency during measurement. Particles become immobilized on the beaker and piston's surface, allowing for the fluid stream created by the moving piston to shift the mobile ion cloud around each particle up and down, creating an oscillating frequency. The potential created is detected and measured by the two electrodes as a streaming potential. From this, the zeta potential is calculated after five measurements for each sample.

3. Results and Discussions

3.1. Yield Stress of Kaolin Slurries

Figure 3A shows how the liquid medium influences the rheological behavior of kaolin pulps. Four systems were analyzed: distilled water and seawater each at pH 4 and pH 8. There is a substantial change in yield stress when moving the pH distilled water. This phenomenon has been explained in the literature [30–32] and responds to the electrostatic changes in the clay surfaces. At pH 4, the faces are expected to present anionic charges while the edges are cationic, producing a strong agglomeration, mainly due to face-to-edge bonds. The bond's strength is high and leads to a yield stress of 277 Pa (45 wt%). As the pH rises, the edges change their electrical character. At pH 8, there is no electrostatic attraction, and the pulp stabilizes. This leads to a sharp drop in yield stress, reaching a value of 15 Pa (45 wt%).

The highly saline environment of seawater changes the nature of electrostatic forces, where counter ions screen the electrical charges on the particle's faces and edges. This reduces the electrostatic attraction at pH 4, and thus the yield stress fell to 167 Pa (45 wt%).

By raising the pH from pH 4 to pH 8, the cations of seawater, mainly magnesium, calcium, and sodium, help the union of kaolin particles through cationic bridges. As a consequence, the yield stress increased from 167 to 231 Pa (45 wt%). In this context, it is interesting to compare what happens at pH 8 since it is a relevant condition of what happens in the mining industry. It is shown that seawater can create rheological problems in clay pulps, which is a detriment to the mineral processing operations [14,19,33]. Rheological modifiers may be applied in order to reduce the value of the rheological parameters, which is achieved through reagents that stabilize the pulp. In this case, STPP is proposed, considering it is a pentavalent anion when dissolved. With this, it is expected that the electrostatic shielding caused by seawater ions will be overcome.

Figure 3B effectively shows that with the addition of STPP, the yield stress of the kaolin pulp in seawater decreased in the form of exponential decay, from 231 Pa until reaching a limit value, close to 80 Pa. That is, the value can be reduced by approximately 65%. This behavior is similar to that obtained by Jeldres et al. [34], who analyzed the impact of sodium polyacrylate on the rheological properties of synthetic tailings, composed of mixtures of quartz and clays (kaolin and sodium montmorillonite). The authors found that the relationship between the yield stress and the reagent dosage can be represented by a pseudo-first-order equation (Equation (1)).

$$\tau_c = \tau_{max} - a \left(1 - \exp \left(-\frac{d}{d_c} \right) \right) \quad (1)$$

This equation considers three fitting parameters; τ_{max} is the yield stress without applying the reagent, a is the difference between the minimum and maximum yield stress, and d_c is the characteristic dosage. This last term can be used to indicate the dosage required to reduce rheological properties, and its value was 0.53 kg/t for STPP. The dispersant is anionic from charged phosphate groups, which can adhere to anionic particles through cationic bridges with Na^+ , Mg^{2+} , and Ca^{2+} ions found in seawater. The optimum dose can be justified with a surface saturation limit, where higher reagent dosages do not increase stabilization. Even Rubio-Hernández et al. [26] showed that high dosages of a polyvalent reagent such as Na-Hexametaphosphate increase the yield stress of kaolin suspensions. It should be noted that polyphosphates are negatively charged chains of phosphorus and oxygen that increase in pH. Therefore, the sodium hydroxide required to reach pH 8 decreased when the reagent dose increased (Table 1). In this case, the sodium hydroxide in seawater pulp of 45 wt% kaolin was 2.19 kg/t. However, after applying 0.53 kg/t of STPP, the amount of NaOH required to reach pH 8 was 1.24 kg/t.

Table 1. Sodium hydroxide required to achieve pH 8 in kaolin pulps 45 wt% according to the sodium tripolyphosphate (STPP) dose.

STPP Dose (kg/t)	NaOH (kg/t)
0	2.19
0.10	1.65
0.53	1.24
1.00	1.03
3.00	0.69
5.00	0.56
7.00	0.27

3.2. Viscoelasticity by Oscillatory Rheology

For the oscillatory tests, small sinusoidal stress is applied, and then the resulting strain is measured. The stress used for the frequency sweep is small enough (shear strain 0.1%) to ensure that the sample responds in the linear viscoelastic range, where the viscoelastic moduli have physical meaning. Figure 4A shows that, in general, G' is greater than G'' , as in solid-like viscoelastic materials, both moduli are relatively independent of the oscillation frequency within the range studied, which is typical of a gel-like behavior [35]. When

0.53 g/t of STPP was added, a change appeared in the gel structure of the suspension, where both moduli decreased, and the elastic modulus was greater than the viscous modulus, but the difference between both was reduced. This is noted when comparing the phase angle (Figure 4B), defined as:

$$\delta = \arctan\left(\frac{G''}{G'}\right) \quad (2)$$

where δ is the phase angle, G'' is the viscous modulus, and G' is the elastic modulus. The phase angle increases with the addition of the reagent. An increase in the phase angle establishes that the pulp increases its viscous character compared with its elastic character. A similar analysis was developed by Lin et al. [36], who evaluated the effect of solids concentration on the gel structure of kaolin suspensions. The authors found that the gels formed by kaolin suspensions were more liquid-like when the concentration of solids increased, as suggested by the increase in the phase angle obtained from a frequency sweep in a linear viscoelastic regime. On the other hand, Jeldres et al. [15] performed oscillatory rheology tests to analyze the rheological properties of flocculated kaolin suspensions in a saline environment. The authors found a strong impact of salinity, finding that the gels formed were more solid-like at low salinity and more liquid-like when salinity increased.

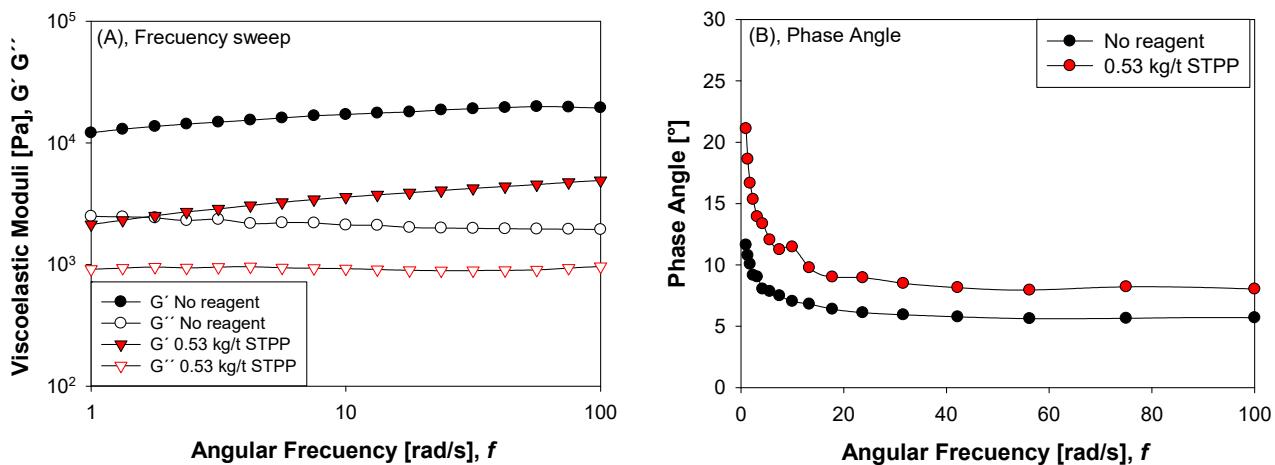


Figure 4. Effect of sodium tripolyphosphate (STPP) on viscoelasticity of kaolin slurries in seawater: (A) sweep-frequency test; (B) phase angle.

3.3. Chord Length Distribution

The FBRM tool allowed us to study the aggregation/dispersion phenomenon through the chord length distribution of the kaolin particles, choosing a system without a reagent and another with STPP at the characteristic dosage. Chord length is presented as unweighted (UW) and square-weighted (SW) distribution. UW gives the count of chord lengths of each of the intervals (0.25–1000 μm) without considering the magnitude of the lengths, making it sensitive to changes in the region of the fine particles, while the SW is used to analyze the distribution of the largest size particles specifically. Average chord lengths (unweighted and square-weighted) can be expressed mathematically as:

$$L_{mean} = \frac{\sum_{1 \leq i \leq M} f(i)l_i}{\sum_{1 \leq i \leq M} f(i)} \quad (3)$$

$$L_{mean}^2 = \frac{\sum_{1 \leq i \leq M} f(i)l_i^3}{\sum_{1 \leq i \leq M} f(i)l_i^2} \quad (4)$$

where M is the number of intervals, l_i is the center of the interval i , and $f(i)$ is the probability of measuring a chord included in the interval i .

Figure 5A shows that without STPP, the maximum counts occurred at the size of $21\text{ }\mu\text{m}$, with a height of 1300 s^{-1} . However, the peak was less evident after adding the reagent, with broadband to the left of $20\text{ }\mu\text{m}$ appearing. It also increased the chord length values, an indicator of the dispersion of fine particles, which initially agglomerated when the pulp did not present the reagent. The square-weighted CLD (Figure 5B) shows that the coarse particles were strongly altered by the STPP, decreasing their size and quantity. Without reagent, the peak appeared at $53.1\text{ }\mu\text{m}$ with a height of 21 s^{-1} , but when adding 0.53 kg/t of STPP, the peak moved to $46.2\text{ }\mu\text{m}$, with 17 s^{-1} . This dispersion of the particles and stabilization of the pulp was induced by reducing the particle–particle bonds. It is directly related to the reduction of rheological properties.

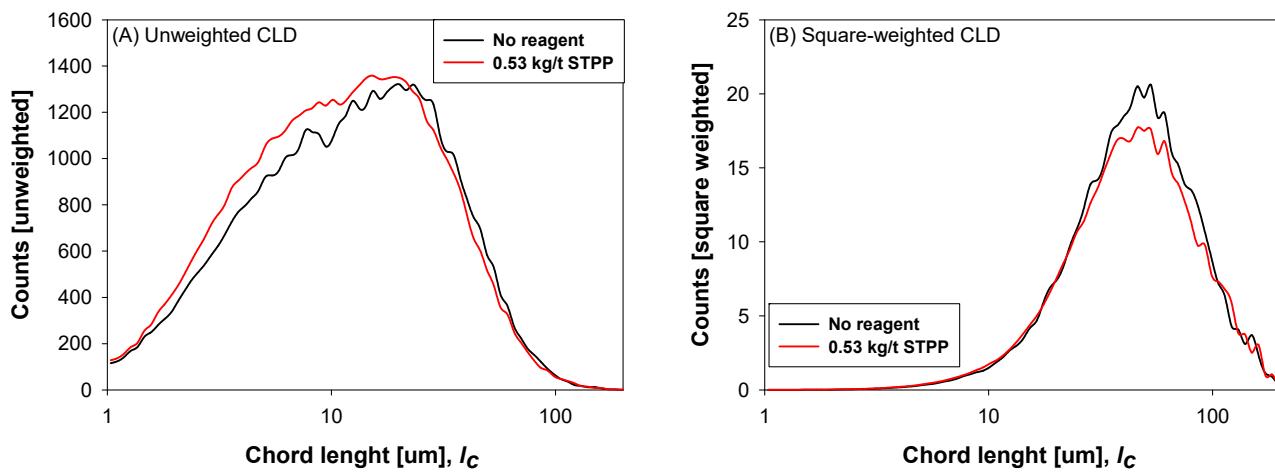


Figure 5. Effect of sodium tripolyphosphate on chord-length distribution of kaolin slurries: (A) unweighted chord-length distribution; (B) square-weighted chord-length distribution.

3.4. Zeta Potential

Figure 6 shows the zeta potential of kaolin suspensions in seawater at pH 8, with different dosages of STPP. The cations Na^+ (11,480 ppm), Mg^{2+} (1410 ppm), and Ca^{2+} (405 ppm) reduced the thickness of the electrical double layer, generating a low value of zeta potential (-5.4 mV); this is compared with -30.4 mV obtained in distilled water at pH 8. As there is no dominant electrostatic repulsion, the particles aggregate by van der Waals attractions and cationic bridging, generating rheological properties that are significantly higher than in a salt-free environment (see Figure 3). The addition of STPP increased the electrostatic repulsion of the particles, achieving values close to -15 mV (0.53 kg/t of STPP). When the STPP molecule dissociates in water, it is left with a pentavalent charge, with phosphate charged groups that adsorb on the particle surfaces by cationic bridges, with the ions present in the medium. This counteracts the electrostatic screening and intensifies the electrical repulsion that promotes dispersion. This mechanism differs from previous studies where sodium polyacrylate was used to improve the dispersion in kaolin slurries in seawater [34,37]. In those works, no relevant change in the zeta potential was observed after sodium polyacrylate was applied. However, being a low molecular weight polymer, a steric stabilization of the clay particles occurred, reducing the pulp's yield stress.

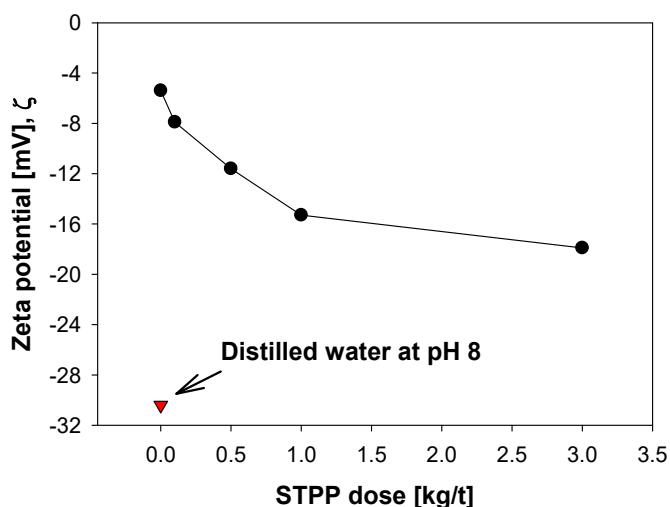


Figure 6. Effect of sodium tripolyphosphate (STPP) on zeta potential of kaolin slurries (5 wt%) in seawater at pH 8. Zeta potential in distilled water at pH 8 is -30.4 mV .

4. Conclusions

Kaolin pulps at pH 8 in freshwater do not have high rheological properties, since the electrostatic repulsions between the particles generate a stable suspension. However, seawater produces a drastic increase in yield stress. The highly saline environment changes the nature of the electrostatic interactions and allows for an increase in the particle–particle bonds, mediated by the cationic bridges with the Na^+ , Mg^{2+} , and Ca^{2+} ions. The addition of STPP caused a significant reduction in yield stress, which exponentially decayed from 231 Pa to 80 Pa. A pseudo-first-order model was adjusted, obtaining the characteristic dosage (0.53 kg/t) as a fitting parameter. Through a frequency sweep (1–100 Hz) in a linear viscoelastic regime, both the elastic and viscous moduli were relatively independent of the oscillation frequency within the range studied, which is typical of a gel-like behavior. The elastic modulus was higher than the viscous modulus, but the phase angle increased when STPP was added, increasing its liquid-like character before yielding.

The results were related with a follow-up on the chord length, presented as an unweighted and square-weighted distribution. After the reagent application, a large number of fine particles initially formed as agglomerates were released. This led to a decrease in the size and quantity of coarse agglomerates. When dispersed in water, the STPP molecule exhibits a pentavalent anionic charge caused by negatively charged oxygen and phosphorus chains. The adsorption of this molecule to the kaolin particles provides an increase in the electrical charge on the surfaces, reflected in the reduction of zeta potential from -5.4 mV to -15 mV . This is when applying the characteristic dosage at pH 8. This increase in electrostatic repulsions explains the dispersion of particles and the reduction of rheological parameters.

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