Inorganic Electrolytes on the Efficacy of a Carboxymethyl Cellulose as a Coagulant for Talc: Implications for Talc Depression in Flotation

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Abstract

Polymers such as polysaccharides are added into froth flotation circuits to render gangue or non-valuable minerals hydrophilic and these as a consequence are prevented from reporting to the concentrate. Recent flotation research on PGM ores suggests that changes in water quality, specifically inorganic electrolytes and their ionic strengths may affect the coagulative-flocculative nature of solid mineral particles in flotation pulps in the presence of polysaccharides such as carboxymethyl cellulose (CMC). This could well have considerable implications on the hydrophilicity of gangue minerals and therefore the concentrate grades owing to interactions between process water electrolytes, the polysaccharides and solid mineral particles. Thus this study considers the effect of ionic strength of process water and specific ions on the coagulation of talc particles using CMC. This investigation has shown that the settling time of talc particles decreased in increasing ionic strength of process water. It was shown that when talc particles were contained in Ca^{2+} and Mg^{2+} electrolyte solutions, their settling time was shorter compared to when they were present in Na+ electrolyte solutions. The reduction in settling time implies that there was an improvement in the hydrophilicity and coagulation of talc particles in concentrated electrolyte solutions.

Keywords: Coagulation, Electrolytes, Flotation, Polysaccharides, Water quality

Introduction

Polysaccharides such as carboxymethyl cellulose are widely used in water treatment clarifiers for the removal of solids from the water being treated such that water is recovered through the clarifier launders with less solid particles. This is achieved through CMC adsorption onto solid particles, forming larger flocs with the solid particles that are easy coagulate. These coagulated CMC-solid particles flocs settle down the bottoms of the clarifier and are removed as sludge through the clarifier underflow. Literature suggests that the efficacy of CMC adsorption onto solid particles is enhanced in waters containing Ca^{2+} and Mg^{2+} in high concentrations or ionic strengths. The same polymer finds its wide use in the froth flotation of talceous Cu-Ni-Pt sulfide bearing ores as a depressant for talc. The prevention of talc from reporting to the concentrate is an important aspect in the concentration of these ores as talc is naturally floatable. Its depression requires reagents such as CMC. Even in froth flotation, as is in the case in water treatment clarifiers, it is reported that to achieve a desired CMC-talc adsorption (and therefore depression), there needs to be polyvalent cations in solution. These polyvalent cations or oxyhydroxyl species act on the talc surface. This action of cationic inorganic electrolytes passivates talc since talc is naturally negatively charged. The highly negatively charged (CMC) then favourably adsorbs onto the passivated talc surface rendering it hydrophilic and in so doing prevent talc from attaching to air bubbles that move up the pulp phase. The scarcity of water in Cu-Ni-Pt concentrators has resulted in the use of recycled water with increased amounts of inorganic electrolytes. This introduces challenges and opportunities to understand how different physico-chemical aspects of flotation will behave when operating with process waters of high salinity. One such aspect is the depression of naturally floatable gangue which is generally accepted to be talc in sulfidic Cu-Ni-Pt ores (Corin et al., 2011). Previous research has shown that the adsorption density of CMC on talc is strongly affected by the ionic strength of the process water (Wiese et al., 2008). Laskowski et al. (2007) found that the depression of talc was enhanced in the presence of Ca2+ compared to K+. Furthermore, the presence of metal hydroxyl species resulted in a further improvement in talc depression because the metal hydroxyl species acted as bridges between CMC and the talc surface (Laskowski et al., 2007). Recent studies showed that the recovery of floatable gangue per g of water recovered decreased with increasing ionic strength of process water; this thus suggested that floatable gangue particles were more coagulated in high concentrations of inorganic electrolytes and hence their retarded floatability (Corin et al., 2011; Corin and Wiese, 2014; Manono et al., 2018, 2012). This thus suggested that there may well be interactions between the ions present in process water and CMC. Such interactions in turn affected the hydrophilicity of talc and the coagulative nature of talc particles and may well have important implications on the talc depression in flotation. However there is little evidence supporting the claims of a coagulative-flocculative phenomenon of talc particles in increased inorganic electrolytes in the presence of CMC although this phenomenon is well established in the removal of solids in water treatment clarifiers Chong et al. (2014). It is the basis of this paper that the application of the principles governing coagulation be explored to elucidate the speculation that there is an improvement in gangue depression upon the addition of CMC in saline waters in flotation. Water treatment clarifiers imitate the process of flotation since physico-chemical separation in these clarifiers occurs due to differences in surface properties of the particles except that there is no air injected into clarifiers or thickeners. Thus, some coagulative-flocculative behaviour of mineral particles should be observed in the pulp phase on flotation cells and this could potentially be responsible for the inhibition of bubble-particle attachment.

Thus the purpose of this investigation was to provide experimental evidence to the speculation of a coagulative-flocculative behaviour of talc in the presence of CMC in highly concentrated electrolytes. Thus settling tests were performed on talc in synthetic plant water as well as single salt solutions of Ca^{2+}, Mg^{2+} and Na^{+} containing Cl^{-} in order to ascertain whether there are specific ion effects on talc coagulation. Zeta potential measurements were performed on talc suspensions in order to investigate the changes on the mineral surface with water quality. Furthermore, the microflotation of talc was investigated to ascertain the question of talc depression in degrading water quality.

Methods

The mineral used for settling tests was talc. 1 kg of talc was pulverised using a swing mill in small batches for approximately 15 seconds. Each pulverised batch was dry sieved through -160 µm, -75 µm and -38 µm consecutively. The oversized particles were re-pulverized until the -38 µm was achieved. The final product was split using a rotary splitter and stored in air tight bags. In order to satisfy the objectives of this study, coagulation tests, adsorption studies, zeta potential tests and microflotation tests were performed on talc in the presence of selected inorganic electrolytes shown in Table 1.

Coagulation Tests

Settling tests were performed on talc both in the presence and in the absence of CMC. Standard settling tests were performed to determine the settling time. For each settling test, 9 g of sample was added to 90 mL of the water type in a 100 mL beaker to make the mixture 10% solids. The mixture was adequately mixed for 1 minute using a magnetic stirrer, and then the pH adjusted to 9 using NaOH or HCl. The suspension was mixed at 500 rpm for 4 minutes to adequately disperse the mixture after pH adjustment. If the test was in the presence of CMC, 90 µL of CMC solution was added and conditioned for 3 minutes at 300 rpm. 3 minutes was chosen as the conditioning time as this was approximately the typical time for standard UCT batch flotation procedure. A lower speed of 300 rpm was used for uniform mixing and

Table 1 *Concentration of ions present in synthetic plant water (SPW) and single salts.*

Water type	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	NO_3^{-} (mg/L)	NO_2^{-} (mg/L)	CO_3^{2-} (mg/L)	TDS mg/L	Ionic Strength [mol/L]
1SPW	80	70	153	287	240	176	-	17	1023	0.0213
$CaCl_2$	285	-	-	503	-	-	-	-	788	0.0213
$MgCl_2$	-	173	-	503	-	-	-	-	676	0.0213
NaCl	-	-	490	755	-	-	-	-	1245	0.0213

to avoid breaking the flocs. After mixing, the slurry was carefully transferred to a 100 mL graduated cylinder and a stopwatch was started immediately thereafter. Measuring cylinders were used to determine the settling time instead of beakers as the longer length of the cylinders gave better visual representation of the extent of clearness of the mixtures and observing the extent of settling was improved thereby resulting in more accurate results. The cylinder was monitored until a clear supernatant liquid was observed against a clear background. A picture was taken, printed and stuck next to the working bench to serve as a basis for the clear supernatant liquid for the remaining tests.

Zeta Potential Tests

Firstly, synthetic plant water and single salt solutions under investigation were added into six test beakers, the pH solution was adjusted using dilute stock solutions of HCl and NaOH such that there existed a test beaker with a pH of 2, 4, 6, 8 and 10. Secondly, 0.0625 g of talc sample with a particle size of -25 µm were added onto each of the six test beakers. Thirdly, the suspension contained in a test beaker was placed on a magnetic stirrer for 15 minutes. The pH of the suspension was again measured and corrected as necessary. And finally, 1 mL of suspension was transferred into a Malvern Dip Cell and inserted into a Malvern Zetasizer for zeta potential measurements. All zeta potential measurements were performed in triplicate to ensure reproducibility and reliability of the test results. It is important to note that for each pH condition, the third step was performed just before zeta potential measuring so as to avoid any unnecessary time dependent reactions with the ions that would blind the comparability of the results from one pH to another.

Adsorption Tests

In order to investigate the extent to which CMC adsorbs onto talc in synthetic plant water, $CaCl_2$, $MgCl_2$ and NaCl, 90 mL of the particular synthetic plant water or single salt solution was measured into a conical flask and 270 µL of the 1% CMC stock solution was added to it. This was followed by the addition of 9 g of talc and thereafter the contents of the conical flask were conditioned in an Ecobath for 3 minutes (Mhlanga et al., 2012). This meant that the initial concentration of CMC in the conical flask was 30 mg.L^{-1} (equivalent to 300 g/t). Immediately after conditioning, the solution (supernatant) from the conical flask was filtered using a 0.22 µm Millipore syringe filter. The determination of CMC concentration in the filtrate was made possible through the use of the du Bois calorimetric method (du Bois et al., 1956). The amount of CMC adsorbed onto the mineral surface was calculated by deducting the concentration in the supernatant from the initial 30 mg/L. The experiments were conducted in triplicate for each synthetic plant water and single salt solution.

Microflotation Tests

Microflotation tests were performed using 3 g of talc at a size fraction of +38-106 µm. 50 mL of the either SPW, $CaCl_2$ or NaCl were added to the mineral sample; the mixture was then ultra-sonicated for 5 minutes to allow for good dispersion of the mineral mixture. The suspension was then transferred to a UCT Microflotation Cell and the pulp was circulated by a peristaltic pump set at 90 rpm. 90 µL (300 g/t) of 1% CMC solution was then added to the cell and conditioned for 1 minute. The cell was then topped up with the particular inorganic electrolyte solution to the 250 mL mark. Through a microsyringe, air was introduced at the base of the cell at

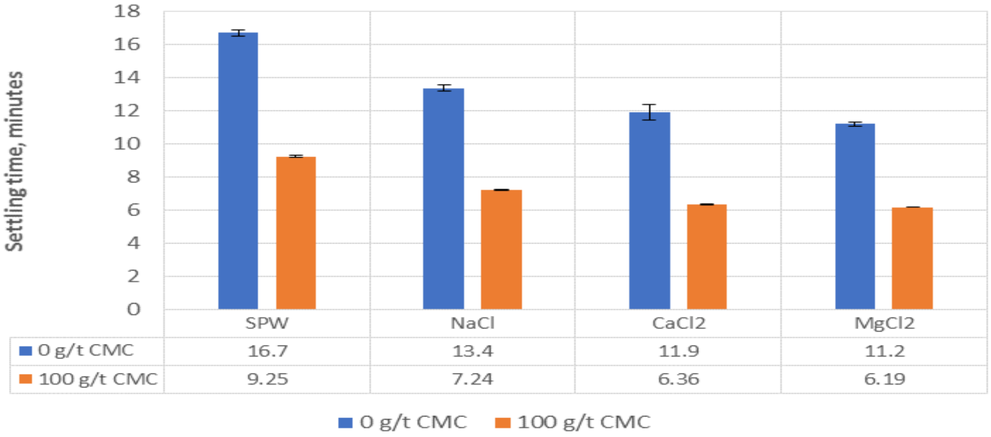


Figure 1 *Settling time of talc particles in various inorganic electrolytes.*

a flow rate of 7 mL/min. Concentrates were then collected at 2, 6, 12 and 20 minutes of flotation and a tailings sample was taken after the collection of the last concentrate. The concentrates and tailings were filtered, dried and weighed. The procedure was repeated for the selected inorganic electrolyte solutions and all tests were done in duplicate to minimise experimental error.

Figure 1 shows the settling time of talc particles in various inorganic electrolytes. Figure 1 demonstrates that the settling time of talc decreased in the order of SPW>NaCl>$CaCl_2$>$MgCl_2$ in both the absence and presence of CMC. There was a further decrease in the settling time of talc particles in the presence of CMC compared to when there was no CMC in the system. The decrease in the settling time of talc particles with the divalent Ca^{2+} and Mg^{2+} compared to Na+ is said to be a result of an increase in the hydration layers around on the talc surface. This could also be a result of the stronger $CaOH^+$ and $MgOH^+$ species which may have formed on the surface of talc and thus leading to a more coagulated pulp (Laskowski et al., 2007). It is known that the presence of divalent cations in talc containing systems, where oxyhydroxyl species may form on the surface of talc, promotes the adsorption of the negatively charged CMC ligand onto the passivated talc surface. The enhanced talc-CMC adsorption in turn results in the formation of larger flocs which are easy to coagulate.

Figure 2 shows how the zeta potential of talc changed with pH under various inorganic electrolyte solutions. It can be seen that the potential of talc particles was more negative in synthetic plant water compared to the rest of the inorganic electrolyte solutions with MgCl2 resulting in the most positive zeta potential compared to all the tested single salt solutions across the given pH range. It can also be seen that the divalent Ca^{2+} and Mg^{2+} containing single salt solutions resulted in a more positive zeta potential compared to the monovalent Na+ containing single salt solution. Between pH 4 and pH 12, the zeta potential increased with increasing pH for $CaCl_2$ and $MgCl_2$ whilst an opposite trend was observed for SPW and NaCl in that the zeta potential decreased with increasing pH. At pH 2, all tested inorganic electrolyte solutions resulted in the same zeta potential. It is also interesting to note that for the divalent cations, a zeta potential of 0 mV was achieved at about pH 4 and pH 8. The less negative zeta potential in Ca^{2+} and Mg^{2+} single salt solutions could be explained by the presence of stronger oxyhydroxyl species such as $CaOH^+$ which are said to passivate the talc surface. The phenomenon of a passivation of talc particles is in agreement with the decrease in settling time in the presence of Ca^{2+} and Mg^{2+}. This potentially explains the stronger talc coagulation in divalent cation single salt solutions compared to the monovalent cation single salt solution.

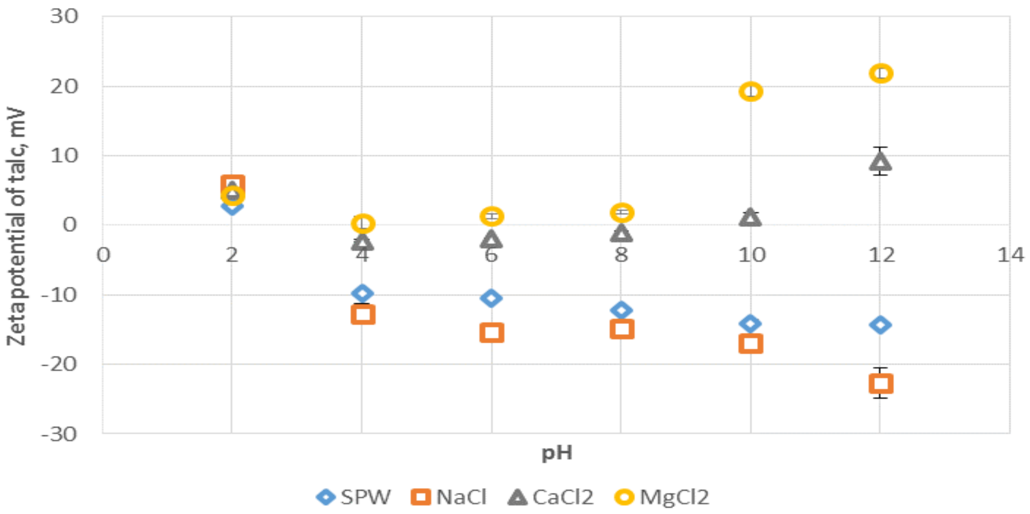


Figure 2 *The zeta potential of talc in various inorganic electrolytes.*

Figure 3 shows that the adsorbed concentration of CMC onto talc particles increased in the order of SPW<NaCl<$CaCl_2$<$MgCl_2$ though the difference between the single salts is very minimal. There is however a trend of an increase in CMC absorption with the divalent cations compared to the monovalent cations. The difference in the adsorbed concentration of CMC onto talc particles may be due to the changes seen in the zeta potential of talc, in that the presence of Ca^{2+}, Mg^{2+} and oxyhydroxyl species create a conducive environment for CMC adsorption onto talc (Burdukova et al., 2008).

Figure 4 illustrates the effect of selected inorganic electrolytes on the floatability of talc without CMC. It can be seen that rate of recovery was higher in $CaCl_2$ compared to NaCl and that synthetic plant water resulted in the least rate of recovery. It is however worth noting that the final recovery of talc was the same for all tested inorganic electrolytes.

Figure 5 illustrates the effect of selected inorganic electrolytes on the floatability of talc in the presence of CMC. NaCl resulted in the highest rate of recovery compared to $CaCl_2$ and SPW.

Figure 6 shows the total recovery of talc in the presence of selected inorganic electrolytes with and without CMC. It can be seen that in the absence of CMC, $CaCl_2$ resulted in the highest recovery compared to NaCl whilst SPW resulted in the smallest recovery. Figure 6 also shows that the presence of CMC led to a substantial decrease in talc recovery in each

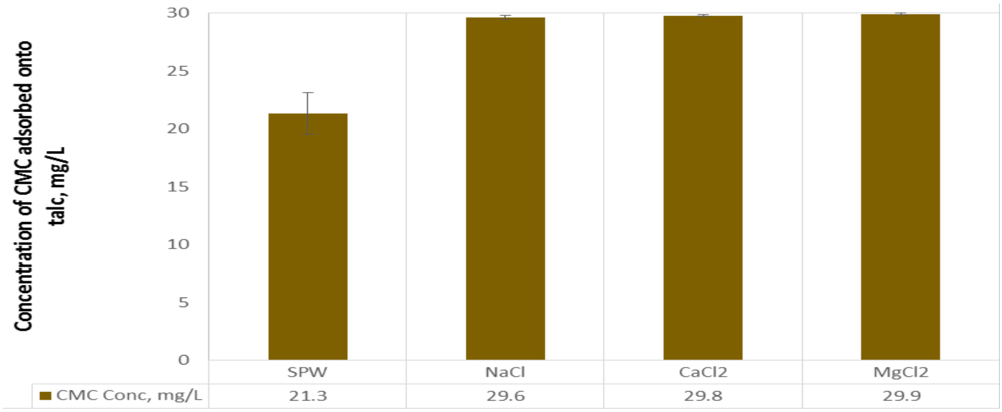


Figure 3 *The concentration of CMC absorbed onto talc particles in various inorganic electrolytes.*

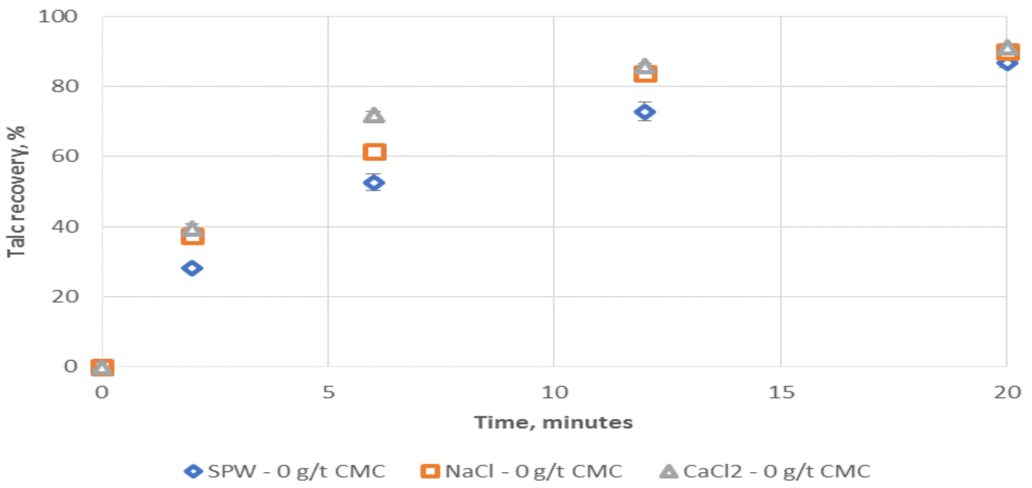
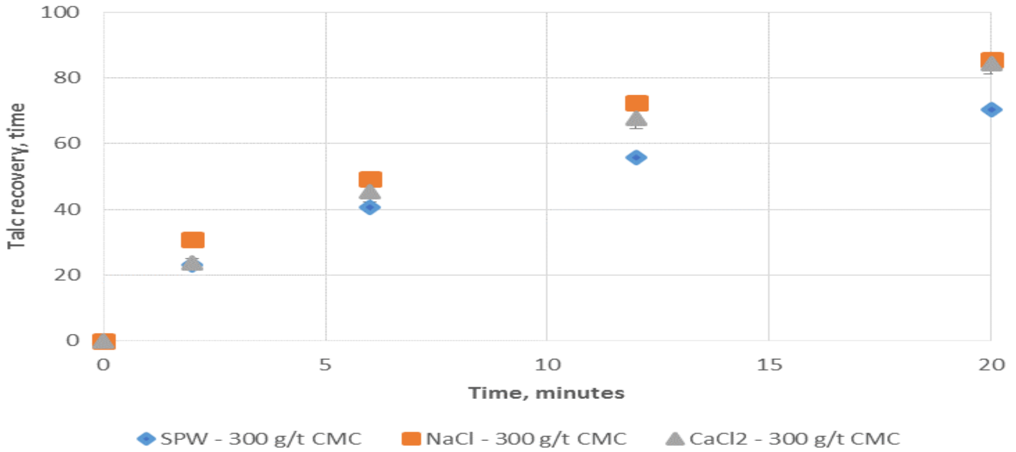
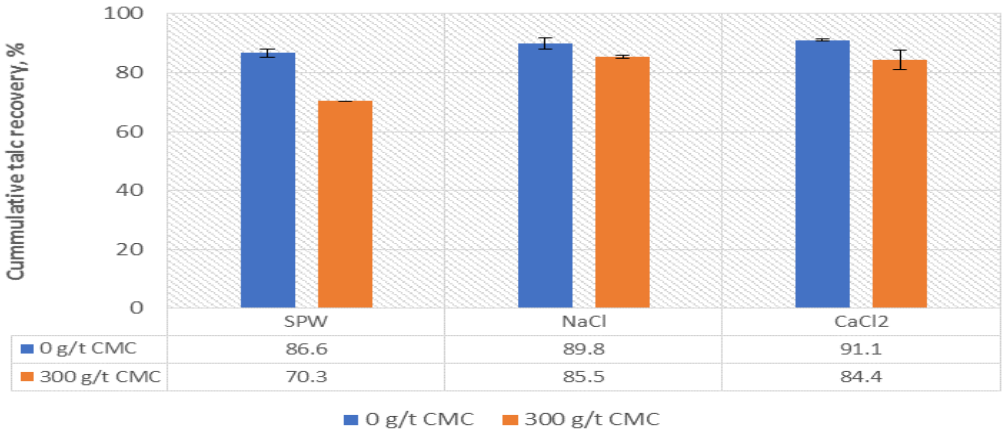


Figure 4 The effect of various inorganic electrolytes on the microflotation of talc in the absence of CMC.





	SPW	NaCl	CaCl2
0 g/t CMC	86.6	89.8	91.1
300 g/t CMC	70.3	85.5	84.4

Figure 5 The effect of various inorganic electrolytes on the microflotation of talc in the presence of CMC.

Figure 6 The total recovery of talc in selected inorganic electrolytes.

water type. In the absence of CMC, the Ca^{2+} ion gave the highest recovery of talc, followed by Na^+ and SPW. This finding is in line with literature as it is expected that monovalent cations would result in lower amounts of solids recovered as floatability is improved with higher valency of electrolytes owing to an improved bubble particle attachment (Craig et al., 1993). In the presence of CMC, the opposite trend was observed as Na+ with the least depressive resulted in the highest recovery. This finding is in line with literature in that, divalent cations such as Ca^{2+} reduce the natural flotation of talc more compared to monovalent cations such as Na^+ (Parolis et al., 2008; Shortridge et al., 2000). This is explained by the fact that hydroxo species, particularly those of calcium, selectively adsorb onto gangue minerals. Such species enhance the depressive action of carboxymethyl cellulose (CMC) onto gangue via an acid-base interaction between the positively charged mineral surface (talc) and the negatively charged CMC molecule (Burdukova et al., 2008; Laskowski and Castro, 2015; Laskowski et al., 2007). The Na^+ salt is said to be unable to form hydroxide complexes which are known to be the drivers of cation adsorption on mineral surfaces (Ansari and Pawlik, 2007). The floatability findings of this work are in line with the zeta potential results which showed that in Ca^{2+}, the mineral surface is more passivated, creating a conducive environment for CMC adsorption which in turn results in a coagulated pulp as shown by the lower settling time in Ca^{2+} and Mg^{2+}.

Conclusions

The coagulation of talc particles was enhanced in the presence of divalent cations. The zeta potential results showed that the mineral surface was more passivated in the presence of divalent cations compared to monovalent cations. The increase in the zeta potential suggested a conducive environment for CMC to adsorb onto talc as shown by the higher CMC adsorption. This in turn led to coagulated talc particles. This result could explain the decrease in the floatability of talc in Ca^{2+} and CMC containing systems.

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