minerals

MDPI

Article

Technical Assessment of Secondary Sedimentation Process in Copper Sulphide Tailings with the Presence of Clays, in Continental and Sea Water

Catalina López-Espejo [1,2,*] and Christian F. Ihle [1,2,*]

[1] Advanced Mining Technology Center, Universidad de Chile, Tupper 2007, Santiago 8370451, Chile
[2] Laboratory for Rheology and Fluid Dynamics, Department of Mining Engineering, Universidad de Chile, Beauchef 850, Santiago 8370448, Chile
* Correspondence: clopezespejo@ing.uchile.cl (C.L.-E.); cihle@ing.uchile.cl (C.F.I.)

Abstract: Recovery of process water for recirculation is crucial, as the cost of adding additional fresh water is an economic constraint that is often prohibitive. Solid–liquid separation is a key process in the recovery of water resources. Therefore, research is needed to understand how fine particles, particularly quartz, kaolinite and sodium bentonite, impact the optimal separation process. In the present work, the effect of the presence of these clays in the solid–liquid separation of synthetic copper sulfide tailings is evaluated, quantifying the impact on the separation efficiency, considering the average settling rate and the turbidity of the supernatant. The physicochemical variables that control the suspension were monitored and the observed trends were explained by variations in properties such as zeta potential and pH. The characterization and quantification of the impact of the clays in the operation will allow us to lay the foundation for the development of a novel approach for the secondary treatment of the cloudy supernatant water of the thickeners. After the study, disparate effects on sedimentation efficiency could be distinguished depending on the type of clay and the water in which it is immersed. While in the case of tailings with the presence of kaolinite clays it is seen that the higher sedimentation efficiency occurs in the case of flocculation in distilled water, the salinity or presence of cationic coagulants is detrimental to it. In the case of tailings with the presence of bentonite clays, the sedimentation efficiency increases as there is a higher concentration of cationic salts (coagulation-synthetic sea water). In contrast, in the case of distilled water, the flocculation efficiency is very low, so it is recommended to add a cationic additive, which is supported by an associated low economic cost. In the case of tailings with the presence of ultrafine quartz content, a clear effect in the increase or decrease of sedimentation efficiency cannot be distinguished with the addition of flocculants, coagulants, or when working in sea water. Overall, the results suggest the convenience of splitting thickening and clarification as two distinct unit processes that may be treated using flocculant and salts, according to the fine mineral contents.

Keywords: tailings; clays; separation process

Citation: López-Espejo, C.; Ihle, C.F. Technical Assessment of Secondary Sedimentation Process in Copper Sulphide Tailings with the Presence of Clays, in Continental and Sea Water. *Minerals* **2022**, *12*, 257. https://doi.org/10.3390/min12020257

Academic Editor: Saeed Farrokhpay

Received: 3 November 2021
Accepted: 14 February 2022
Published: 17 February 2022

1. Introduction

The Chilean mineral processing industry faces two concurrent and independent challenges that somewhat force an evolution in future operational priorities: climate change and the progressive decay of ore grades. Climate change forces to reduce the use of water as much as possible [1,2], which is a challenge, not just due to the need for technology evolution to make the economically unfeasible feasible, but also because of the particular setup of mining operations [3]. On the other hand, the decrease of ore grades, which is associated with finer grinding [4], has been pushing energy consumption and material handling needs to unprecedented levels [5]. Higher residence times that promote the liberation of fine and ultrafine minerals such as clays represent a problem in various stages of the mineral process cycle [6].

An effect of reducing plant makeup is that water might be prone to accumulate salts, dissolved and suspended solids (due to increased recirculation), which might hinder valuable mineral recovery [6,7] and reduce the performance of thickeners [8]. The origin of water is key in the processing outcome. While the use of desalinated water is increasingly more widespread, the use of direct sea water is another operational option [9].

Physicochemical mechanisms that trigger settling (and, ultimately, gravitational separation) in suspensions have been established in pure clays as the result of electrostatic attractive forces that, depending on the pH and the surface charge distribution, form face-edge, edge-edge and face-face structures due to salt concentration and pH changes [10], and also to the intensity of mixing [11]. In the case of minerals, where the flocculation process is assisted by high-molecular-weight synthetic polymers, the resulting structures after flocculation addition resemble these effects, but are also strongly dependent on polymer molecular weight and dose [12]. Testing with kaolinite and using both anionic and cationic polyacrylamides, Nasser and James [12] observe an inverse correlation between turbidity and setting velocity. Using anionic flocculants, Zbik et al. [13] found that structures formed only in the presence of salt (prior the addition of flocculant) were not significantly affected by the flocculant addition regarding their shape, as the flocculant acts only as a densifying agent through polymer bridge formation between particles ([14,15], provide details relevant to mineral processing on this mechanism). Differently from previous studies, Ji et al. [16] used real tailings to assess the impact of salt and flocculant addition and found higher settling velocities in saline tailings than in freshwater tailings (however, it is to be noted that the reported uncertainty in saline tailings was considerably higher than in the freshwater samples). As in [12], they observed a negative correlation between settling velocity and supernatant turbidity in the case of the salt tailings, but a positive correlation (in the range 0–20 ppm flocculant concentration) in the fresh tailing sample using an anionic polymer (Magnafloc) was found. In their tests using the anionic polymer [16], they reported lower settling velocities in the case of saline tailings than those with freshwater tailings. The same trend was observed by Jeldres et al. [17] in the flocculation of kaolinite using an anionic polyacrylamide polymer (80 g/ton doses), and they explain the result by the screening of Na^+ cations of the anionic groups of the flocculant, thus inducing a coiling of the latter. The impact of hydrodynamics on flocculation reported by Mietta et al. [11] in pure clays has been confirmed more recently by Castillo et al. [8] with synthetic tailings. In the latter work, it was also found that the operational conditions that concurrently minimize turbidity and maximize settling velocity are not the same. More recently, using quartz–kaolinite blends under the presence of various salts as synthetic tailings, Ramos et al. [18] found a sharp increase of supernatant turbidity for pH values above a threshold value of ca. 10.3.

The present paper delves into the study of the sensitivity of settling velocity and supernatant turbidity in batch tests, and to salt and flocculant content, in various synthetic tailing configurations, produced similarly as in [8,19]. The main objective of this research is to evaluate the performance of clay-containing copper sulfide tailing physicochemical separation methods for different synthetic tailing conditions at constant pH of the sample. The general procedure is to achieve the grouping of particles by chemical agents, organic in the case of flocculation and inorganic salts in the case of coagulation. The analysis was carried out for distilled water and synthetic sea water.

2. Materials and Methods

2.1. Artificial Tailing Samples

The coarse material to be used was quartz, obtained from a local supplier. The fine material used for this study is composed of kaolinite, bentonite, and quartz. The first two were obtained directly by local suppliers, while the quartz was obtained ground from the coarse fraction in a ball-type equipment at the Laboratory of Mineral Processing, Mining Engineering Department, Univ. Chile.

The synthetic tailings prepared for this study respond to the following mass composition:

- A total of 80% in weight percentage of the tailings is composed of the coarse material of SiO_2, sieved through a # 140 mesh (more than 0.105 mm) three times, to ensure the minimum of fine components in it.
- The remaining 20% by weight is made from ultrafine or coarse clay fractions, corresponding to the same material as 80% of the mixture. The thick and clay-containing samples were named as shown in Table 1.

Table 1. Composition and name of the artificial tailings used in the study.

Sample Name	Fine Fraction Composition	Tailing Composition wt%
SF	No fines added	100% coarse
MM	100% bentonite	80% coarse 20% bentonite
KK	100% kaolinite	80% coarse 20% kaolinite
QQ	100% ultrafine quartz	80% coarse 20% ultrafine quartz
MK	50% bentonite 50% kaolinite	80% coarse 10% bentonite 10% kaolinite
MQ	50% bentonite 50% ultrafine quartz	80% coarse 10% bentonite 10% ultrafine quartz
KQ	50% ultrafine quartz 50% kaolinite	80% coarse 10% ultrafine quartz 10% kaolinite

As mentioned in the introduction, this type of synthetic tailing had already been used previously in [8,19].

Chemical composition of water: The experiments were carried out for both distilled water and synthetic sea water. Despite the fact distilled water does not represent real operation, it was chosen because the effects associated with the interactions of the ions present in the artificial tailings generated in the study can be controlled. The main characteristics of these are summarized in Table 2.

Table 2. Main characteristics of the water used in the study.

Property	Artificial Sea Water	Distilled Water
pH	7.16	5.76
Conductivity	5.04 mS/cm	0.67 mS/cm
Density	1.025 t/m^3	1.001 t/m^3

The synthetic sea water was made following the protocol proposed in [20]. The distilled water was provided by the Polymers Laboratory, Chemical Engineering Department, Univ. Chile.

2.2. Reagents

The flocculant used during the development of this research was SNF®704, an anionic polyacrylamide-type flocculant (PAM), supplied by SNF Chile S.A. A 0.10% by weight polymer solution was previously mixed on a magnetic stirrer at 300 rpm for 12 h.

For the coagulation tests, the cationic salts $CaCl_2$ and $MgCl_2$ were used. Because salts were used to assess coagulation, no significant difference in sedimentation rate, supernatant solids concentration, and zeta potential could be observed in the cases of synthetic sea water solutions. Consequently, this part of the study applies only to systems that operate with distilled water. A concentration of 500 mg/L of both coagulants was used, using a magnetic stirrer at 500 rpm for 12 h.

2.3. Characterization

Sedimentation rate and turbidity of the supernatant

To be able to compare the sedimentation processes of the different study conditions, the sedimentation rate and the solids concentration of the supernatant were estimated by means of test-tube sedimentation tests.

Here, the artificial tailings and the water sample were poured into a 500 mL cylinder, previously shaken on a magnetic stirrer for 15 min at 300 rpm to ensure homogeneity. Subsequently, the flocculant to be evaluated was added and the sample was slowly inverted 3 times, subsequently measuring the sedimentation rate. The variation in height with respect to time was measured by video analysis, which identifies the position of the supernatant–suspension interface every 0.5 s. The flocculated suspension was allowed to stand for 5 min and then 10 mL of the supernatant sample was withdrawn to measure turbidity (in Nephelometric Turbidity Unit, or NTU) using a Hach® 18900 turbidimeter (Hach, Loveland, CO, USA). The turbidity value was related to solids concentration in the supernatant. Solids concentration was fitted to turbidity through a linear fit for each type of artificial tailing and water used in the study.

Zeta potential

A Stabino® Particle Metrix instrument (Particle Metrix, Inning am Ammersee, Germany) was used for zeta potential measurements. Here, the supernatant from the sedimentation process was poured into the measurement cell and the zeta potential was calculated for 4 min with 5 s intervals. The value of this potential was considered as the average of the data of said measurement time, 2 min after its start, because one of the recommendations for the use of this equipment is to wait 120 s to stabilize measurements. It is important to note that a 100-micron separation piston was used, given the manufacturer's specifications for the measurement of the zeta potential of clays or ultrafine minerals.

Sedimentation efficiency parameters

To quantify the variation in the sedimentation efficiency of the artificial tailings, the optimal operating conditions were determined for the case of a synthetic tailing without the presence of clays (denoted here as SF). These values correspond to the solids content by weight (Cw) and the optimum dosage of flocculant, to achieve a maximum settling rate and a minimum concentration of solids in the supernatant (maximum percentage of solids removal in the supernatant). They were compared defining the following parameters:

- Sedimentation efficiency as a function of settling rate:

$$\eta_{S_R} = \frac{S_{R_{tailing}}}{S_{R_{opt}}} \tag{1}$$

where,
$S_{R_{tailing}}$: Settling rate of the artificial tailings evaluated.
$S_{R_{opt}}$: Settling rate of the operational optimum for the case of synthetic tailings without clays (SF).

- Sedimentation efficiency as a function of percentage of solids removal in the supernatant:

$$\eta_{C_S} = \frac{C_{S_{tailing}}}{C_{S_{opt}}} \tag{2}$$

where,
$C_{S_{tailing}}$: Percentage of solids removal in the supernatant of the artificial tailings evaluated.
$C_{S_{opt}}$: Percentage of solids removal in the supernatant of the operational optimum for the case of a synthetic tailing without clays (SF).

3. Results and Discussion

3.1. Linear Adjustment of Turbidity and Solids Concentration for Each Type of Tailing and Water Used in the Study

Tables 3 and 4 show the linear adjustment of turbidity and solids concentration for distilled water and synthetic sea water, respectively. Turbidity NTU was taken as the ordinate axis (y) and the concentration of solids in the mixture (mg/L) on the abscissa axis (x).

Table 3. Linear adjustment of turbidity (y, in NTU) and solids concentration (x, in mg/L) of synthetic tailings in distilled water.

Sample Name	Linear Adjustment	R^2
SF	$y = 143.85x - 15.15$	0.97
MM	$y = 0.0001x - 0.04$	0.99
KK	$y = 0.00097x - 0.039$	0.96
QQ	$y = 0.00097x - 0.053$	1.00
MK	$y = 0.0011x + 0.05$	0.86
MQ	$y = 0.0015x - 0.082$	0.97
KQ	$y = 0.001x - 0.019$	0.99

Table 4. Linear adjustment of turbidity (y, in NTU) and solids concentration (x, in mg/L) of synthetic tailings in artificial sea water.

Sample Name	Linear Adjustment	R^2
SF	$\mathrm{y} = 138.3x + 16.3$	0.98
MM	$y = 0.0015x - 0.015$	0.99
KK	$y = 0.001x + 0.006$	0.88
QQ	$y = 0.00124x + 0.0141$	1.00
MK	$y = 0.0011x - 0.037$	0.88
MQ	$y = 0.0017x - 0.14$	0.92
KQ	$y = 0.0011x + 0.041$	0.95

The adjustment was made for concentrations of 0.5 and 1 mg/L for the case of artificial tailings with the presence of ultrafine content. In the case of artificial tailings without the presence of clays (SF), the linear fit was made for concentrations between 0.1 and 5 mg/L. Below 0.1 mg/L, no further differences in turbidity were observed.

3.2. Operational Optimum for the Case of a Synthetic Tailing without the Presence of Clays (SF)

Settling rate: Settling rate was measured for different solids content by weight and flocculant dose for the case of distilled water and sea water. Results are shown in Table 5.

Table 5. Settling rates for tailings without fines at different solids content by weight and flocculant dosage in distilled water and synthetic sea water.

	Settling Rate (cm/s)					
Cw %	Distilled Water	Synthetic Sea Water	Distilled Water	Synthetic Sea Water	Distilled Water	Synthetic Sea Water
	12.5 g/Dry Ton		25 g/Dry Ton		50 g/Dry Ton	
8	<0.01	2.55 ± 0.26	3.88 ± 0.1	3.69 ± 0.2	3.44 ± 0.6	3.68 ± 0.5
10	4.33 ± 0.52	4.25 ±0.18	4.51 ± 0.1	4.98 ± 0.2	4.13 ± 0.2	4.23 ± 0.6
20	3.13 ± 0.65	3.5 ± 0.32	3.38 ± 0.5	4.33± 0.1	3.21 ± 0.5	3.19 ± 0.1

According to the information in Table 5, in all the cases evaluated, as the flocculant dose increases, the sedimentation rate reaches a maximum when the dose is 25 g/dry ton (lower settling velocities for flocculant doses above 25 g/dry ton). On the other hand, for a fixed dose of flocculant, the sedimentation rate reaches a maximum at Cw = 10% and then decreases as the solids concentration increases. It is important to note that these effects can be seen in both distilled water and synthetic sea water, and that the settling rate of the latter is higher in all cases compared to distilled water, so it can be deduced that there is a relationship between salinity, suspension concentration and type of flocculant used. The overall optimum obtained from the present experiments corresponds to the combination of Cw = 10% and a flocculant dose of 25 g/dry ton.

A highly saline medium, such as synthetic sea water, favors interactions between flocculant and quartz, which are less likely in the case of distilled water. In fact, the cations in solution protect the functionalities of the covalent bonds of SNF704 (HPAM) and in turn are adsorbed on the mineral surface, which allows a greater proportion of the functional groups of the flocculant that favor the sedimentation process. In the same way, this shielding of HPAM functionalities in synthetic sea water makes the size of the floc much smaller in solution and thus the settling velocity smaller, where the dependence of the diameter is, by virtue of the Stokes settling velocity expression, roughly proportional to the square of the diameter. There are numerical and experimental studies that verify this [18,21].

Comparing with [8,21], the unit consumption of flocculant per ton of treated mineral is 15 g/dry ton, for which an operational optimum was found that requires a greater mass of flocculant for treatment.

Percentage of solids removal in the supernatant: To obtain the percentage of solids removal after flocculation, the concentration of solids in the supernatant was measured 5 min after the start of flocculation and compared with the initial solids concentration. The corresponding results are shown in Table 6.

Table 6. Removal of solids percentage for tailings without fines at different solids content by weight and flocculant dosage in distilled water and synthetic sea water.

	Removal of Solids %							
Cw %	**Distilled Water**	**Synthetic Sea Water**	**Distilled Water**	**Synthetic Sea Water**	**Distilled Water**	**Synthetic Sea Water**	**Distilled Water**	**Synthetic Sea Water**
	5 g/Dry Ton		**12.5 g/Dry Ton**		**25 g/Dry Ton**		**50 g/Dry Ton**	
8	52.5 ± 0.09	64.2 ± 0.042	68.7 ± 0.01	83 ± 0.052	77.7 ± 0.25	89.7 ± 0.002	83.4 ± 0.08	92.9 ± 0.011
10	43.2 ± 0.045	19.4 ± 0.083	58.2 ± 0.044	75.2 ± 0.026	72.4 ± 0.026	82.4 ± 0.038	77.8 ± 0.018	88.2 ± 0.082
20	55.1 ± 0.014	12 ± 0.068	74.9 ± 0.031	64.3 ± 0.067	82.3 ± 0.014	79.1 ± 0.042	87.4 ± 0.082	92.7 ± 0.074

Regardless of the type of water, the concentration of solids in the supernatant responds in a similar way: as in the case of samples in distilled water, the higher the percentage of initial solids (Cw), the higher the concentration of solids in the supernatant after the sedimentation process. Along with this, above a flocculant dose of 25 g/dry ton, the concentration of solids in the supernatant does not decrease noticeably.

A comparison of the solids concentration in the supernatant between distilled water and sea water reveals that in the latter case the lowest concentration of solids is found. This can be attributed to the fact that the salts present in the mixture of sea water favor sedimentation, as deduced by [13].

Zeta potential: Table 7 summarizes the values of zeta potential of the supernatant for each configuration Cw/flocculant dose evaluated in distilled water.

All the zeta potential results are negative, which supports previous studies which indicate that quartz has a zeta potential less than zero [22]. It is justified that the variations in the zeta potential of the minerals with pH are due to the acids used to adjust the pH of the solution: the addition of H+ in the form of HCl to the water to achieve a lower pH generates an increase of the concentration of these ions that, after an adsorption process in the quartz mineral, compress the double electrical layer, generating negative values and lower zeta potential.

Table 7. Zeta potential of the supernatant for tailings without fines at different solids content by weight and flocculant dosage in distilled water.

Cw %	Zeta Potential mV	pH	Zeta Potential mV	pH	Zeta Potential mV	pH
	12.5 g/Dry Ton		25 g/Dry Ton		50 g/Dry Ton	
8	−6.5 ± 0.5	5.81	−5.0 ± 0.5	6.01	−3.7 ± 0.9	5.97
10	−6.7 ± 0.5	5.67	−5.5 ± 0.8	5.73	−5.2 ± 0.8	6.04
20	−10.9 ± 1.0	5.78	−8.2 ± 0.7	5.88	−6.7 ± 0.5	6.07

As the flocculant dose increases, for the same Cw, the value of the zeta potential increases, decreasing in absolute value. Likewise, for the same dose of flocculant, the higher the Cw, the lower the value of the zeta potential. It is important to note that the differences between the different zeta potential values are not significant, so it can be inferred that it is not a determining factor when choosing a Cw/flocculant dose configuration in the absence of fines. Along with this, most of the absolute values are numbers less than 10 mV, corresponding to stable dispersions [23], so there is a tendency for solids immersed in the supernatant to precipitate [24].

A set of measurements of flocculation in synthetic sea water was made. Results are summarized in Table 8.

Table 8. Zeta potential of the supernatant for tailings without fines at different solids content by weight and flocculant dosage in artificial sea water.

Cw (%)	Zeta Potential mV	pH	Zeta Potential mV	pH	Zeta Potential mV	pH
	12.5 g/Dry Ton		25 g/Dry Ton		50 g/Dry Ton	
8	−2.4 ± 0.5	7.78	−2.5 ± 0.5	7.85	−3.6 ± 0.5	7.92
10	−2.6 ± 0.5	7.81	−2.7 ± 1.0	7.92	−2.9 ± 1.5	7.80
20	−2.8 ± 1.5	7.79	−3.1 ± 0.5	7.86	−3.7 ± 0.5	7.78

The same effect mentioned in the part of distilled water in most cases was observed: at higher Cw, for a fixed dose of flocculant, the value of the zeta potential decreases (in this case, it becomes more negative). At the same time, for a fixed Cw, the higher the flocculant dosage, the zeta potential decreases. Likewise, there is not a great difference between the values of the different cases, so, like the study with distilled water, it is not a determining factor when choosing the optimal configuration of Cw/flocculant dose. The difference between the values of the zeta potential between the cases of distilled and sea water is explained by the presence of ions (monovalent and bivalent) in synthetic sea water, which increase the negativity of the solution [25]. However, when analyzing the stability of the supernatant solution, the solids present in the solution tend to precipitate, as deduced by [24].

In sea water, high salinity makes the zeta potential less than certain at any pH. The existence of ions in sea water, specifically calcium and magnesium (divalent ions), compresses the double electrical layer that surrounds mineral surfaces, significantly reducing the range and magnitude of the zeta potential [23].

Sedimentation efficiency: According to the definitions given in the methodology, the parameters with which the sedimentation efficiency will be compared are:

- Settling rate: 4.51 cm/s for distilled water and 4.98 cm/s for synthetic sea water.
- Percentage of solids removal in the supernatant: 71.5% for distilled water and 85.2% for synthetic sea water.

A pH scan between 2 and 12 was performed for both samples and the zeta potential was measured in sea water and distilled water. The result can be seen in Figure 1.

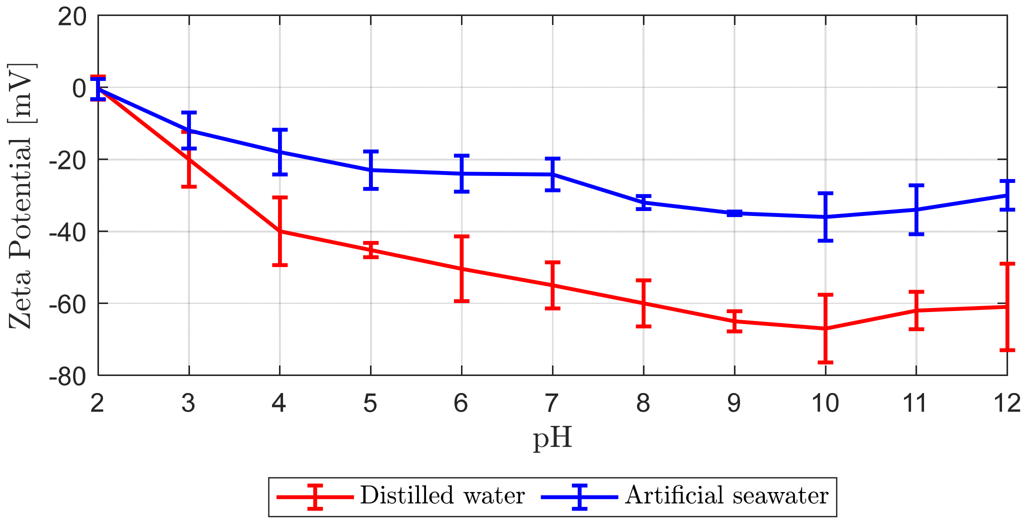

Figure 1. Zeta potential at different pH of endless synthetic tailings solution, with Cp = 10% and a flocculant dose of 25 g/dry ton.

It can be observed that the zeta potential is negative at all values of pH and that it decreases progressively until a pH of 9. As the pH increases from this point, an increase in this potential occurs, mainly due to the interaction between the OH^- ions and the SiO_2 structure. In distilled water, it is possible to see that the zeta potential is low compared to the zeta potential in synthetic sea water. This is because the interaction of cationic ions in sea water alters the characteristics of the solution, mitigating the effect. This result can be contrasted with that found by [26], where an increase in the zeta potential of quartz can also be seen once a pH greater than 9 is reached. As the zeta potential is negative, by 'lower' it is implied 'greater in absolute value'. An explanation of this trend, which has also been observed in [26,27], is related to the adsorption of cations (in the case of sea water, Ca^{2+} and Mg^{2+}) on the surface of negatively charged particles that tend to saturate, increasing salt concentration.

3.3. Sedimentation of Synthetic Tailings with Presence of Clay, without Additives

Table 9 shows the sedimentation efficiency for synthetic tailings with clays and without additives, both with sea water and distilled water.

Table 9. Sedimentation efficiency value of synthetic tailings with presence of clays, without additives with respect to tailings without the presence of clays.

Tailing Name	Distilled Water		Sea Water	
	η_{S_R}	η_{C_S}	η_{S_R}	η_{C_S}
MM	0.0%	5.50%	2.2%	48.50%
MK	2.9%	16.00%	2.9%	12.00%
KQ	9.5%	59.00%	4.7%	22.50%
MQ	4.3%	49.00%	6.0%	31.50%
KK	7.4%	61.00%	2.3%	49.50%
QQ	11.1%	55.50%	7.4%	38.50%
SF	43.2%	69.50%	45.1%	74.00%

As expected, sedimentation without fines has the highest sedimentation efficiency in both sea water and distilled water. For tailings containing bentonite minerals (MM, MK and MQ), the higher the proportion of bentonite, the higher the concentration of solids in the supernatant. When the same mineral mixtures were put in sea water, sedimentation efficiency increased, mainly due to the existence of cationic salts in sea water, which generate covalent bonds that facilitate the sedimentation of montmorillonite and kaolinite (this behavior has also been observed in [18]). Noteworthy, the presence of bentonite in the flotation process can be mitigated when working with sea water, since the Mg^{2+} and Ca^{2+} ions favor the covalent bond and subsequent sedimentation of the clay. In the case of artificial tailings whose compositions have kaolinite and quartz, main components of Chilean tailings [18], it can be observed that the sedimentation efficiency is reduced in the presence of sea water. One of the possible causes is that the presence of Mg^{2+} and Ca^{2+} complexes reduce the magnitude of the zeta potential of the particles, reducing the tendency for precipitation. This effect is described below considering the impact of flocculation with an anionic polymer and is complemented by the results of [12,13].

3.4. Synthetic Tailings Flocculation with the Presence of Clays

According to Table 10, in the case of distilled water, the highest sedimentation efficiencies are observed when kaolinite, ultrafine quartz and/or a combination of these are present. In contrast, considerably lower efficiencies are observed under the presence of bentonite. This is because bentonite has a high weight percentage of sodium montmorillonite, which can swell in contact with water and produce a viscous gel-like structure, making it difficult to settle [28].

Table 10. Sedimentation efficiency value of synthetic tailings flocculation with and without the presence of clay.

	Distilled Water		**Sea Water**	
	η_{S_R}	η_{C_S}	η_{S_R}	η_{C_S}
MM	5.3%	25.0%	6.2%	73.5%
MK	18.4%	52.5%	20.3%	64.5%
KQ	63.0%	92.5%	27.7%	40.5%
MQ	8.4%	39.5%	26.5%	69.5%
KK	51.7%	91.0%	18.4%	22.0%
QQ	56.9%	87.0%	72.1%	63.0%
SF	5.3%	25.0%	6.2%	73.5%

On the other hand, in the case of sea water, the settling rate of tailings with the presence of kaolinite decreases markedly. This observation was also found in the literature, where it is explained that kaolinite can generate less dense flocs in high salinity water due to the presence of calcium ions and the complex structure of kaolinite [29].

In all cases, a good sedimentation efficiency is observed after 5 min of flocculation. The sedimentation efficiency of the removal of solids in the supernatant (η_{C_S}) is also lower when compared to the case of distilled water and sea water for the samples with kaolinite content (KQ and KK). Likewise, the sedimentation efficiency in the cases with the presence of bentonite (MM, MQ and MK) is higher in sea water than in distilled water.

Regarding ultrafine quartz, it is observed that in mixtures of quartz with kaolinite or bentonite, the sedimentation efficiency is improved, considering the 'pure' case (that is, only with quartz as ultrafine content). This can be due to two possible behaviors: acting as inert, where the increase in the settling rate is explained by the presence of more flocculating bonds available, or because the flocculation effect is enhanced. It is worth noting in this study that ultrafine quartz, QQ, has lower concentrations of solids in the distilled water supernatant than in sea water. This could be explained by the presence of salt particles rather than by the presence of quartz. In addition, in the QQ instance, it can be observed that in mixtures of quartz with kaolinite or bentonite, the sedimentation efficiency is improved, compared to the 'pure' case (QQ). To verify some of these assumptions, Figure 2 shows the variation in the settling rate of the MQ and KQ cases for different doses of flocculant.

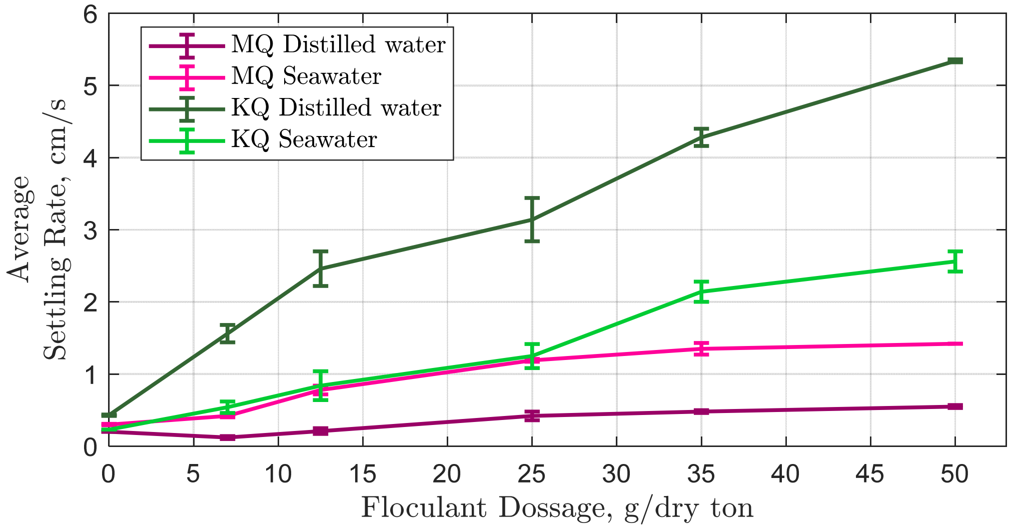

Figure 2. Variation in the settling rate of the MQ and KQ cases for different doses of flocculant.

According to Figure 2, the mean settling rate increases as a function of the flocculant dose to a certain extent, so the existence of ultrafine quartz could respond more to the behavior of an inert within the synthetic tailings mixture.

3.5. Coagulation of Synthetic Tailings with Presence of Clays

The settling rate of the two coagulants used was compared: $MgCl_2$ and $CaCl_2$ at 500 mg/L following the suggestion of [30]. The height of the solid was measured in 1 min intervals, since there are no notable differences in the range of seconds because coagulation is a slower process compared to flocculation [31].

The turbidity of the supernatant was measured 30 min after the coagulant was added. To be able to relate this result to the solids concentration of the supernatant, the calibrations for distilled water were used. It is important to mention that before the study, the following turbidity of the coagulants used was measured:

- $MgCl_2$ (500 mg/L): 72.8 NTU.
- $CaCl_2$ (500 mg/L): 81.4 NTU.

Table 11 shows the summary of the efficiencies as a function of the average settling rates and removal of solids in the supernatant for both cases. It is noted that the performance in terms of settling rate using exclusively inorganic salt type coagulants is very low. In particular, the best results were given in mixtures of quartz and bentonite for magnesium chloride, and for the case of calcium chloride, ultrafine quartz results are the best.

Results from Table 11 also reveal that the sedimentation efficiency as a function of the removal of solids in the supernatant is high when compared with the same value as a function of the settling rate. In general terms, we can see the removal efficiency is slightly higher for the case of $MgCl_2$ compared to $CaCl_2$.

Table 11. Sedimentation efficiency value of synthetic tailings flocculation with presence of clay, with respect to tailings without the presence of clays.

	$MgCl_2$		**$CaCl_2$**	
	η_{S_R}(%)	η_{C_S}(%)	η_{S_R}(%)	η_{C_S}(%)
MM	0.59%	99.89%	0.44%	99.65%
MK	0.39%	99.96%	0.31%	99.70%
KQ	0.42%	99.85%	0.46%	99.47%
MQ	0.62%	99.22%	0.02%	99.44%
KK	0.20%	99.58%	0.18%	99.20%
QQ	0.64%	99.99%	0.74%	99.82%

3.6. Flocculation-Coagulation of Tailings under the Presence of Clays

The study of the effect of flocculation-coagulation of tailings under the presence of clays was limited to the case of distilled water, due to that with the presence of the salts used for coagulation it is already implicitly considered in the case of synthetic sea water.

In addition, this analysis was carried out for those combinations where there is the presence of bentonite, that is, MM, MQ and MK. The reason these settings were chosen is because, in the case of distilled water, the sedimentation efficiency is low for these samples, both as a function of the settling rate and the concentration of solids in the supernatant.

In a stable dispersion, coarse particles settle faster than fine ones. In the artificial tailings studied in this work, this effect could be seen in the artificial tailings and bentonite solutions (MM, MQ, MK). For this case, it was decided to destabilize the dispersion using coagulants, in this case Mg^{2+} and Ca^{2+}. In a suspension subjected to a coagulation process, a clear layer develops after a while, with a defined boundary below it. This limit falls rapidly at the beginning and then more slowly in the consolidation stage, approaching a limit sediment volume, which is greater than that formed without the existence of coagulation [32].

At the same time, it can be observed that in the case of tailings with the presence of kaolinite (KK and KQ) the presence of inorganic salts is detrimental to the quality of sedimentation. The addition methodology was:

1. The coagulant dose is added to the already prepared sample and allowed to act for 30 s.
2. Subsequently, the flocculant dose is added and mixed.
3. The settling rate is measured after the addition of the flocculant and the solids concentration of the supernatant, and the zeta potential is calculated after 5 min from the end of the process.

Table 12 summarizes sedimentation efficiencies as a function of the rate of sedimentation and solids removal in the supernatant for the selected coagulants and artificial tailings.

Table 12. Sedimentation efficiency value of synthetic tailings coagulation-flocculation process with the presence of bentonite clays.

	$MgCl_2$		**$CaCl_2$**	
	η_{S_R}(%)	η_{C_S}(%)	η_{S_R}(%)	η_{C_S}(%)
MM	94.85%	99.97%	80.76%	99.83%
MK	79.47%	99.85%	81.19%	99.75%
MQ	100%	99.19%	100%	99.16%

Noting that ultrafine quartz is inert in this set of artificial tailings, the lower the bentonite concentration, the better the sedimentation efficiency using this coagulation-flocculation process. When compared with the results obtained in the separate processes, we can notice an improvement in the efficiency as a function of the settling rate (that is, there are higher settling rates) and a smaller, but existing, increase in the percentage of solids in the supernatant.

In the case of clays with kaolinite and bentonite, there is a substantial increase in both efficiency indices. However, it is lower compared to the case of bentonite or pure kaolinite. Both types of clays present opposite effects regarding the use of one methodology or the other: artificial tailings with kaolinitic clays present better efficiency in environments free of cationic ions, while those of bentonite are more efficient in highly saline environments.

4. Conclusions

The present work shows that both sedimentation efficiencies depend strongly on the type of water, flocculant dose and kind of blend of fine minerals used. While kaolinite settling in distilled water (interpreted herein as an idealized case of salt-free water) decreases with salinity, in the case of bentonite clays settling is enhanced with cationic salt content and, on the other hand, flocculation is poor in distilled water. These strongly divergent results complement the observation that when using bentonite–kaolinite blends, the resulting sedimentation efficiency is between the value of the sedimentation efficiencies of bentonite and pure kaolinite, thus implying the hindrance effect that bentonite effects on kaolinite separation.

Importantly, the differing result that is obtained either considering the sedimentation efficiency based on the settling velocity, giving a direct indication of the thickening capacity, or the definition based on the supernatant solids content, related to recirculated water quality, suggests that thickening and clarification can be improved with two separate processes. In particular, the separate use of flocculant and salt to enhance sedimentation and clarification, respectively, seems like a path to follow to fine-tune such overall combined efficiency improvement and to enable a cost-effective reduction of additive traces in overflow water. Based on the present results, future work should seek for technical-economical optimal models for sequential thickening and clarification.

Author Contributions: Conceptualization, C.L.-E. and C.F.I.; methodology, C.L.-E.; validation, C.F.I.; formal analysis, C.L.-E.; investigation, C.L.-E.; writing—original draft preparation, C.L.-E. and C.F.I.; writing—review and editing, C.L.-E. and C.F.I.; visualization, C.L.-E.; supervision, C.F.I.; project administration, C.F.I.; funding acquisition, C.F.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Chilean National Agency for Research and Development grant number AFB180004 and Fondecyt Project 1211044. C.F.I. also acknowledges support from the Vice-rectory of Research and Development of the University of Chile, project code 253 ENL11/20.

Data Availability Statement: The data for this publication can be found in Catalina López Espejo's Magister's Thesis, "Estudio experimental de procesos de sedimentación secundaria de ultrafinos de relaves mineros chilenos". (In Spanish).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Boger, D.V. Rheology and the resource industries. *Chem. Eng. Sci.* **2009**, *64*, 4525–4536. [CrossRef]
2. Edraki, M.; Baumgartl, T.; Manlapig, E.; Bradshaw, D.; Franks, D.M.; Moran, C.J. Designing mine tailings for better environmental, social and economic outcomes: A review of alternative approaches. *J. Clean. Prod.* **2014**, *84*, 411–420. [CrossRef]
3. Ihle, C.F.; Kracht, W. The relevance of water recirculation in large scale mineral processing plants with a remote water supply. *J. Clean. Prod.* **2018**, *177*, 34–51. [CrossRef]
4. Northey, S.; Mohr, S.; Mudd, G.M.; Weng, Z.; Giurco, D. Modelling future copper ore grade decline based on a detailed assessment of copper resources and mining. *Resour. Conserv. Recycl.* **2014**, *83*, 190–201. [CrossRef]
5. Calvo, G.; Mudd, G.; Valero, A.; Valero, A. Decreasing ore grades in global metallic mining: A theoretical issue or a global reality? *Resources* **2016**, *5*, 36. [CrossRef]
6. Connelly, D. High clay ores a mineral processing nightmare. *Aust. J. Min.* **2011**, *24*, 28–29.
7. Forbes, E.; Davey, K.J.; Smith, L. Decoupling rehology and slime coatings effect on the natural flotability of chalcopyrite in a clay-rich flotation pulp. *Miner. Eng.* **2014**, *56*, 136–144. [CrossRef]
8. Castillo, C.; Ihle, C.F.; Jeldres, R.I. Chemometric optimisation of a copper sulphide tailings flocculation process in the presence of clays. *Minerals* **2019**, *9*, 582. [CrossRef]
9. Cisternas, L.A.; Gálvez, E.D. The use of sea water in mining. *Miner. Process. Extr. Metall. Rev.* **2018**, *39*, 18–33. [CrossRef]
10. Rand, B.; Pekenć, E.; Goodwin, J.W.; Smith, R.W. Investigation into the existence of edge—face coagulated structures in Na-montmorillonite suspensions. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1980**, *76*, 225–235. [CrossRef]
11. Mietta, F.; Chassagne, C.; Winterwerp, J.C. Shear-induced flocculation of a suspension of kaolinite as function of pH and salt concentration. *J. Colloid Interface Sci.* **2009**, *336*, 134–141. [CrossRef] [PubMed]
12. Nasser, M.S.; James, A.E. The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions. *Sep. Purif. Technol.* **2006**, *52*, 241–252. [CrossRef]
13. Zbik, M.S.; Smart, R.S.C.; Morris, G.E. Kaolinite flocculation structure. *J. Colloid Interface Sci.* **2008**, *328*, 73–80. [CrossRef] [PubMed]
14. Wang, C.; Harbottle, D.; Liu, Q.; Xu, Z. Current state of fine mineral tailings treatment: A critical review on theory and practice. *Miner. Eng.* **2014**, *58*, 113–131. [CrossRef]
15. Qi, C.; Fourie, A. Cemented paste backfill for mineral tailings management: Review and future perspectives. *Miner. Eng.* **2019**, *144*, 106025. [CrossRef]

16. Ji, Y.; Lu, Q.; Liu, Q.; Zeng, H. Effect of solution salinity on settling of mineral tailings by polymer flocculants. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *430*, 29–38. [CrossRef]
17. Jeldres, R.I.; Arancibia-Bravo, M.P.; Reyes, A.; Aguirre, C.E.; Cortes, L.; Cisternas, L.A. The impact of sea water with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores. *Miner. Eng.* **2017**, *109*, 10–13. [CrossRef]
18. Ramos, J.J.; Leiva, W.H.; Castillo, C.N.; Ihle, C.F.; Fawell, P.D.; Jeldres, R.I. Sea water flocculation of clay-based mining tailings: Impact of calcium and magnesium precipitation. *Miner. Eng.* **2020**, *154*, 106417. [CrossRef]
19. Contreras, S.; Castillo, C.; Olivera-Nappa, Á.; Townley, B.; Ihle, C.F. A new statistically-based methodology for variability assessment of rheological parameters in mineral processing. *Miner. Eng.* **2020**, *156*, 106494. [CrossRef]
20. Bidwell, J.P.; Spotte, S. *Artificial Sea Waters: Formulas and Methods*; Jones and Bartlett Publishers: Boston, MA, USA, 1985.
21. Quezada, G.R.; Jeldres, R.I.; Fawell, P.D.; Toledo, P.G. Use of molecular dynamics to study the conformation of an anionic polyelectrolyte in saline medium and its adsorption on a quartz surface. *Miner. Eng.* **2018**, *129*, 102–105. [CrossRef]
22. Kaya, A.; Yukselen, Y. Zeta potential of clay minerals and quartz contaminated by heavy metals. *Can. Geotech. J.* **2005**, *42*, 1280–1289. [CrossRef]
23. Vallar, S.; Houivet, D.; El Fallah, J.; Kervadec, D.; Haussonne, J.M. Oxide slurries stability and powders dispersion: Optimization with zeta potential and rheological measurements. *J. Eur. Ceram. Soc.* **1999**, *19*, 1017–1021. [CrossRef]
24. Clogston, J.D.; Patri, A.K. Zeta potential measurement. *Methods Mol. Biol.* **2011**, *697*, 63–70. [CrossRef] [PubMed]
25. Shehata, A.M.; Nasr-El-Din, H.A. Zeta Potential Measurements: Impact of Salinity on Sandstone Minerals. Presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, TX, USA, 13–15 April 2015. [CrossRef]
26. Khangaonkar, P.; Bala Subramani, K. Flocculation of hematite fines by anionic polyacrylamide polymers. *Miner. Eng.* **1993**, *6*, 765–774. [CrossRef]
27. Reyes, C.; Álvarez, M.; Ihle, C.F.; Contreras, M.; Kracht, W. The influence of sea water on magnetite tailing rheology. *Miner. Eng.* **2019**, *131*, 363–369. [CrossRef]
28. Owen, A.; Fawell, P.; Swift, J.; Farrow, J. The impact of polyacrylamide flocculant solution age on flocculation performance. *Int. J. Miner. Process.* **2002**, *67*, 123–144. [CrossRef]
29. Jeldres, R.I.; Forbes, L.; Cisternas, L.A. Effect of Sea water on Sulfide Ore Flotation: A Review. *Miner. Processing Extr. Metall. Rev.* **2016**, *37*, 369–384. [CrossRef]
30. Wang, Y.; Peng, Y.; Nicholson, T.; Lauten, R.A. The role of cations in copper flotation in the presence of bentonite. *Miner. Eng.* **2016**, *96–97*, 108–112. [CrossRef]
31. Dontsova, K.; Norton, L.D. Effects of exchangeable Ca: Mg ratio on soil clay flocculation, infiltration and erosion", Sustaining the global Farm. In Proceedings of the 10th International Soil Conservation Organization Meeting, West Lafayette, IN, USA, 24–29 May 1999; pp. 580–585.
32. Kitchener, J.A. Flocculation in Mineral Processing. In *The Scientific Basis of Flocculation. NATO Advanced Study Institutes Series; Series E*; Applied Science; Ives, K.J., Ed.; Springer: Dordrecht, The Netherlands, 1978; Volume 27. [CrossRef]