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Chloride removal from industrial cooling water using a two-stage ultra-high lime with aluminum process

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ABSTRACT

This study evaluates the feasibility of chloride removal from industrial cooling water using a two-stage ultra-high lime with aluminum (UHLA) process. This two-stage UHLA process was employed to treat recycled cooling water collected from an industrial plant containing high concentrations of carbonate ions and suspended solids. The presence of anions such as carbonate and bicarbonate limits the removal of the desired ions, namely sulfate and chloride ions. The two-stage UHLA process was used in which lime is added at the first stage to remove carbonate ions, and both lime and sodium aluminate are added at the second stage to remove chloride and sulfate ions. Experimental results showed that chloride removal can be achieved at reasonable lime and sodium aluminate dosages. The results of equilibrium experiments indicate that the most cost-effective performance in the two-stage configuration occurred with lime dosages in the first and second stages equal to 50 mM and an aluminum dosage equal to 30 mM. These dosages achieved a 56% chloride removal.

Keywords: Chloride removal; Cooling water; Industrial wastewater; Recycling; Softening

1. Introduction

Cooling water is widely used in modern industries, and its function is critical to keep the temperatures of industrial processess stable. It works as a physical source of heat exchange extracting heat from high-temperature parts and dissipating it in the cooling tower through evaporation [1]. During circulation and evaporation, ions such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, SiO_2 and SO_4^{2-} become concentrated [2–5] and cause scaling and corrosion inside the heat exchanger and negatively affect the heat exchange rate [2]. A blowdown is a necessary process to discharge part of the cooling water, and fresh make-up water is added to balance water quantity and quality [2]. The presence of chloride ions is a particular problem in blowdown water treatment, when recycling the cooling water. Chlorine has a chemical number of 17, a chemical element belonging to the halogen and a major component of the salt [6]. Chloride salts such as sodium chloride are readily soluble in water, so they accumulate in solution [7]. The dissolved chloride ions increase electrical conductivity, thereby accelerating corrosion [3]. Consequently, it causes fouling that decreases the heat exchange and process efficiency [8].

Reverse osmosis and ion exchange can be used to remove chloride and sulfate ions [1,2,9]. The RO process can efficiently remove ionic substances, but pretreatment such

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as membrane or media filtration is required to prevent flux reduction by membrane fouling and scaling. Additionally, RO process generates a high volume of brine as a reject. Ion exchange is also effective for the removal of ionic substances, but there is also a problem of disposal or further treatment of the regenerant solution generated in the process of regenerating the resin.

Lime softening is a traditional method to remove hardness ions such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, and silica. The ultra-high lime with aluminum process (UHLA) is a modification of the conventional lime softening process in which aluminum is added to facilitate the removal of chloride and sulfate ions [3–5,10,11]. Chloride is precipitated as calcium chloroaluminate ($Ca_4Al_2Cl_2(OH)_{12}$), and sulfate is precipitated as calcium sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$) under conditions of high pH and in the presence of calcium and aluminum [3]. Solids formed in the UHLA process are called layered double hydroxides (LDH) [12]. This compounds is composed of layers of metal hydroxides which is containing two kinds of metallic cations and an interlayer with water molecules and anionic species [13,14]. When the solution contains multiple anions, inter-ionic exchange can occur between two or more phases because electrostatic forces loosely hold the interlayer anions. This exchange attains equilibrium, thereby producing solid solutions of varying compositions [15,16]. Such behavior means that the removal of anions in the UHLA process depends on the relative affinity of these anions for the solid phases, and solid solutions may form as a result of anion exchange.

The optimal range for removal of chloride in the UHLA process is 12±0.2 [3]. A large amount of lime is consumed to maintain the high pH range. One way to make the process economically attractive is to reduce reagent costs. This can be accomplished by using waste alum sludge from a water treatment plants as the source of the aluminum required for the process. UHLA process can effectively remove chloride ions [3–5,11], but there is limited data available to support its practical application in industries.

2. Methods

Recycled cooling water from industrial processes was collected for this study. The quality of the sampled cooling water is shown in Table 1 in the following part. The concentration of chloride ion is 330 mg/L and bicarbonate ion is 1,048 mg/L. An expected challenge for applying UHLA to this water is that its chloride concentration is relatively low that can result in low chloride removal efficiency. Also it is expected that the presence of anions such as carbonate or bicarbonate hinders the removal of the desired ions such as sulfate and chloride. In order to achieve a reasonable chloride removal efficiency, the two-stage UHLA process is proposed as shown in Fig. 1; the first stage involves removing carbonate ions by precipitation as calcium carbonate using only lime, and the second stage involves removing chloride and sulfate ions using both lime and sodium aluminate as chemical reagents. Furthermore, the waste alum sludge was used as an alternative aluminum source to evaluate the possible reduction of chemicals.

Table 1
Composition of the representative water sample

Component	Concentration (mg/L)
Calcium (Ca^{2+})	26
Magnesium (Mg^{2+})	13
Sodium (Na^+)	688
Potassium (K^+)	26
Carbonate (CO_3^{2-})	0
Bicarbonate (HCO_3^-)	1,048
Sulfate (SO_4^{2-}-S)	453
Chloride (Cl^-)	330 (9.4 mM)
Nitrate-N (NO_3^--N)	< 0.01
Phosphorus(P)	0.26
pH	7.5
Total Dissolved Solids (TDS)	2,627

Table 1 gives the composition of the recycled cooling water sample containing high concentrations of bicarbonates, sulfate, chloride and dissolved solids.

Batch kinetic and equilibrium experiments were conducted in 250 mL polyethylene bottles (Nalgene). The plastic bottles were shaken for two days at room temperature (23–25°C) before sampling and analysis. The bottles were placed in a closed container with a CO_2 absorbent (Ascarite II, VWR) to avoid CO_2 contamination during the reaction time. Dry lime ($Ca(OH)_2$) and dry sodium aluminate ($NaAlO_2$) were added to the cooling water sample.

Two kinetic experiments were conducted to evaluate the time required to approach equilibrium for chloride removal. And then equilibrium experiments were conducted to evaluate chloride removal by the UHLA process. Nine sets of single-stage tests were conducted for three different lime doses and three different aluminum doses as shown in Table 2; then, eighteen sets of two-stage equilibrium experiments were conducted for two different lime doses in the first stage and three different lime and aluminum doses in the second stage as shown in Table 3. For the two-stage experiment, the reaction time was set to one day for each stage according to the kinetic test result shown in Fig. 2. After equilibrium was reached in the first stage of treatment, the solution was filtered to remove the precipitated solids. Then, the filtrate from the first stage was treated in the second stage by the addition of both lime and sodium aluminate. The pH was measured before filtration using a pH meter with a combination glass electrode that was standardized using two buffers (pH 10.00 and pH 12.45).

Recycle of the waste alum sludge was examined. The alum sludge was synthesized by precipitating aluminum hydroxide from aluminum sulfate according to the following equation.

$$Al_2(SO_4)_3 18H_2O + 6Na^+ + 6OH^- -> 2Al(OH)_3 + 6Na^+ + 3SO_4^{2-} \quad (1)$$

The solution containing $Al(OH)_3$ was filtered through a 0.45 µm membrane filter, and the wet solids were washed with deionized water twice to remove residual sulfate ions.

All the experiments were conducted in duplicate, and the data presented are average values with standard devi-

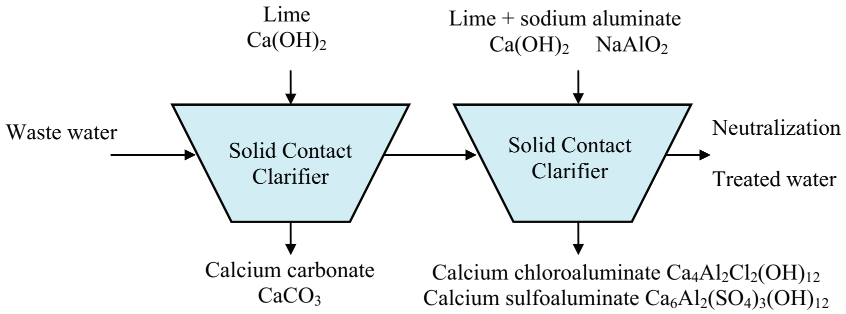


Fig. 1. Two-stage configuration for UHLA process.

Table 2
Final concentration of chloride (mM) and removal efficiency (%) (single-stage)

Lime dose (mM)	Sodium aluminate dose (mM)			Sodium aluminate dose (mM)		
	30	60	90	30	60	90
50	8.54±0.14	8.55±0.18	8.55±0.10	6±1.5	6±1.9	6±1.0
100	6.29±0.20	6.77±0.08	7.36±0.34	32±2.2	27±0.9	19±3.7
150	6.12±0.17	3.53±0.12	2.37±0.28	34±1.8	62±1.3	73±3.0

Table 3
Final concentration of chloride (mM), removal efficiency (%), pH and ionic strength (two-stage)

Lime dose (mM)	Sodium aluminate dose (mM)			Sodium aluminate dose (mM)		
	30	60	90	30	60	90
Two-stage configuration with lime dose of 25 mM in the first stage						
	Final concentration of chloride (mM) removal efficiency (%)			pH ionic strength (M)		
50 (25+25)	8.07±0.41 13±4.4	7.73±0.11 17±1.2	7.87±0.11 15±1.2	12.34±0.14 0.18	12.41±0.10 0.21	12.55±0.0 0.24
100 (25+75)	5.30±0.53 43±5.6	3.30±0.24 64±2.6	4.29±0.06 54±0.2	12.44±0.01 0.33	12.49±0.07 0.36	12.62±0.01 0.39
150 (25+125)	5.16±0.06 44±0.7	2.48±0.30 73±3.2	2.57±0.77 72±8.2	12.42±0.01 0.48	12.53±0.01 0.51	12.62±0.01 0.54
Two-stage configuration with lime dose of 50 mM in the first stage						
	Final concentration of chloride (mM) removal efficiency (%)			pH Ionic strength (M)		
50 (50+0)	8.41±0.10 9±1.1	8.24±0.04 11±0.4	8.29±0.16 11±1.7	12.36±0.12 0.18	12.43±0.14 0.21	12.56±0.04 0.24
100 (50+50)	4.03±0.21 56±2.3	3.44±0.04 63±0.4	4.99±0.19 46±2.1	12.45±0.14 0.33	12.49±0.15 0.36	12.63±0.02 0.39
150 (50+100)	4.34±0.03 53±0.3	2.31±0.01 75±0.1	2.48±0.03 73±0.3	12.41±0.14 0.48	12.55±0.03 0.51	12.63±0.04 0.54

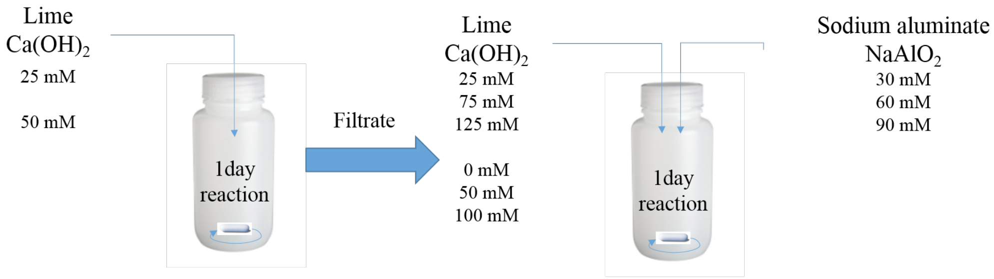
ation. Samples were collected and filtered through 0.45 μm membrane filters. Concentrations of chloride ion were measured using a Dionex 500 ion chromatograph equipped with a 4 mm Dionex AS–16 analytical and guard columns. The average recovery (accuracy) and the relative standard deviation (precision) of the concentration of chloride measurement were 99.7% and 1.97%, respectively. A method detection limit (MDL) was calculated as 1.00 mg/L.

3. Results and discussion

3.1. Kinetics of chloride precipitation

A kinetic study was conducted using lime (200 mM) and sodium aluminate (100 mM). Eq. (2) shows the chemical reaction. Lime and sodium aluminate were added more than the stoichiometric amount required as the water included other anions such as sulfate and bicarbonate. Fig. 3 shows

(a) Single-stage UHLA Equilibrium experiment



(b) Two-stage UHLA Equilibrium experiment

Fig. 2. Schematic procedure diagram for equilibrium experiments.

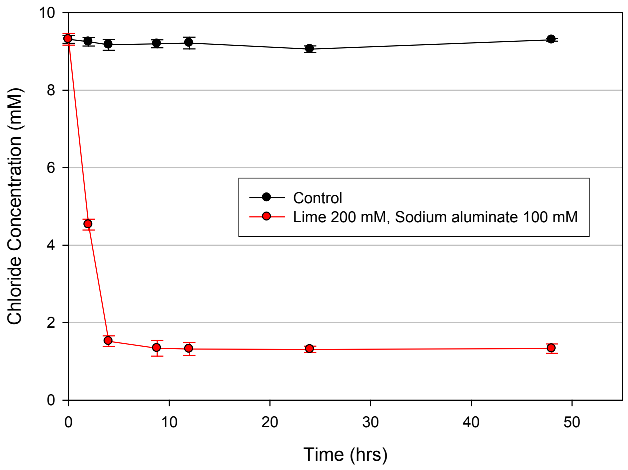


Fig. 3. Chloride concentration as a function of time in the kinetic experiment.

the results of the kinetic experiment. These results indicate that chloride concentration decreased with time until four hours, and after that, chloride removal was negligible. This indicates that kinetics should not be a limitation for applying the UHLA process for chloride removal and that batch experiments will approach equilibrium after four hours.

$$4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4OH^- \rightarrow Ca_4Al_2Cl_2(OH)_{12}(s) \qquad (2)$$

3.2. Effect of chemical doses on chloride removal

Equilibrium experiments were conducted to evaluate the effects of lime and sodium aluminate doses on chloride removal using the single-stage UHLA process. Figs. 4–6 show the results of the lime dosage on chloride removal at sodium aluminate doses of 30, 60, and 90 mM, respectively. Table 2 provides the numerical values of the final chloride concentrations along with chloride removal efficiencies at different lime and sodium aluminate doses. Figs. 4–6 show that chloride concentrations decrease with increasing dosages of lime and sodium aluminate. Chloride removal efficiency was at 62% with a lime dose of 150 mM and sodium aluminate dose of 60 mM, and it was at 73% with a lime dose of 150 mM and a sodium aluminate dose of 90 mM.

The industrial cooling water used in this study contains relatively high concentrations of bicarbonate and sulfate ions compared to chloride ions. These bicarbonate and sulfate ions compete with chloride ions for the solid phase due to the relative affinities. Higher doses of lime and aluminum are required to achieve the same level of chloride removal compared to a sample containing less amount of carbonate and sulfate. This problem can be eliminated by removing carbonate ions before precipitation of chloride ions.

The two-stage configuration as shown in Fig. 1, was examined to reduce the chemical consumptions. Two sets of equilibrium experiments were conducted using the same initial conditions as in the single-stage experiment (total lime doses of 50, 100, and 150 mM and total sodium aluminate doses of 30, 60, and 90 mM) but with the lime doses divided between the two stages. In the first set of equilibrium experiments, the first-stage lime dose was 25 mM; in the second set, the first-stage lime dose was 50 mM. Table 3 lists the experimental conditions, final chloride concentrations, and chloride removal efficiencies for these sets of experiments.

The effects of both lime and aluminum doses on chloride removal for both the single-stage and two-stage are examined and results are shown in Figs. 4–6, respectively. These figures and a table show that higher levels of chlo-

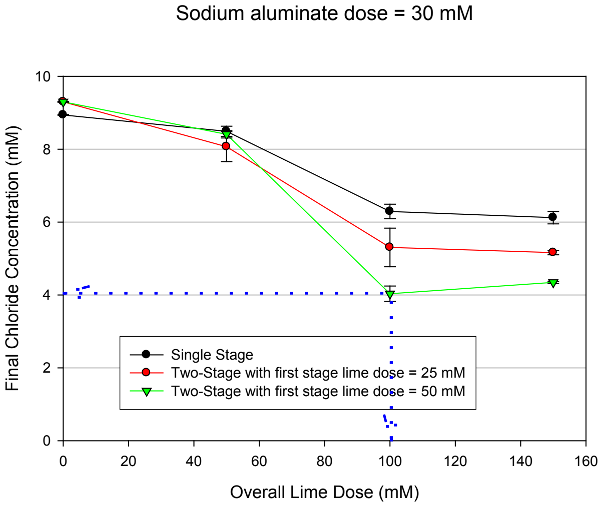


Fig. 4. Effects of the lime dosage on chloride removal at a sodium aluminate dose of 30 mM.

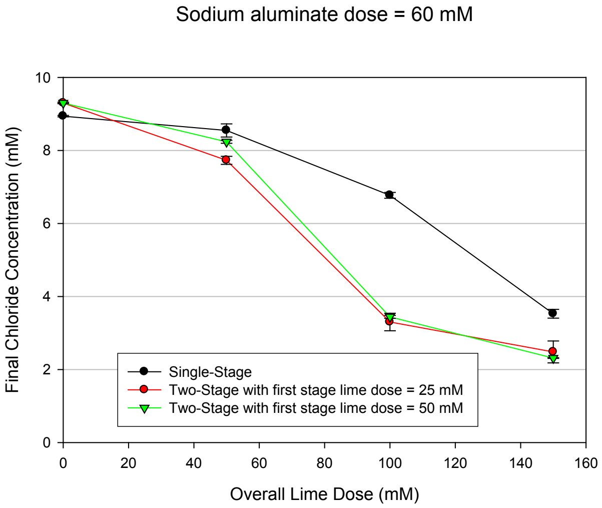


Fig. 5. Effects of the lime dosage on chloride removal at a sodium aluminate dose of 60 mM.

ride removal were achieved in the two-stage configuration than that in the single-stage configuration when the same amount of lime and sodium aluminate were dosed.

A comparison of chemical consumption and chloride removal efficiencies in the two configurations indicated that the best performance was observed in the two-stage configuration with a first-stage lime dose of 50 mM. The most cost-effective lime and aluminum doses were 100 mM and 30 mM respectively. These doses achieved a chloride removal efficiency of 56%. Higher chloride removal efficiencies can be achieved by using higher chemical doses, as seen in Table 3. Based on the market prices of lime ($50~150/ton, US Lime and Minerals) and sodium aluminate ($500~560/ton, 43% solids, USALCO), the chemical cost to achieve this removal efficiency (56%), normalized by the concentration removed, is about $0.45/mM. If waste alum sludge from water treatment plants is used as an aluminum source, then the normalized treatment cost is expected to be reduced to less than $0.2/mM.

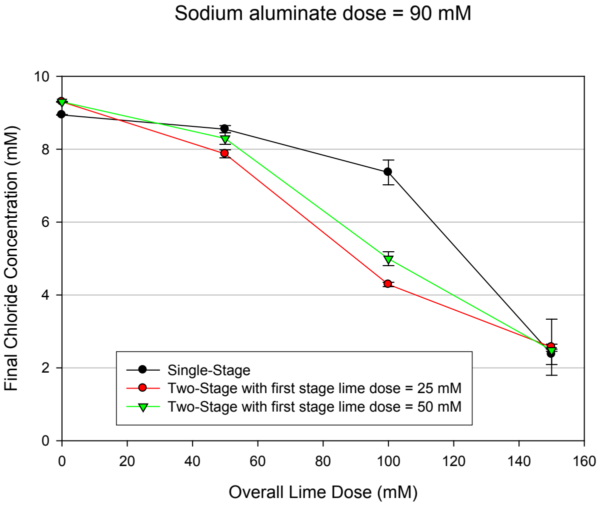


Fig. 6. Effects of the lime dosage on chloride removal at a sodium aluminate dose of 90 mM.

3.3. *Evaluation of an alternative aluminum source*

This experiment was conducted to evaluate the possibility of an alternative aluminum source. The experimental conditions and results is shown in Table 4. At the first stage, 50 mM of $Ca(OH)_2$ was added, and the same dose of $Ca(OH)_2$ and 10~60 mM of alum sludge ($Al(OH)_3$)were added at the second stage. Fig. 7 depicts the chloride removal efficiency of different $Al(OH)_3$ doses. When the aluminum concentration was 30 mM, the removal efficiency was optimum to remove 44% of chloride ions, inidcating the alum sludge could be used as an alternative alum source.

4. Conclusions

Chloride removal from cooling water blowdown was carried out using single-stage and two-stage UHLA processes. Experimental results showed that reasonable chloride removal efficiency could be achieved with lime and sodium aluminate doses. The results of equilibrium experiments indicated that, for the treatment configurations and chemical doses investigated, the two-stage configuration with lime doses in the first and second stages equal 50 mM each and an aluminum dose equal 30 mM is the most cost-effective treatment condition. This system achieved a chloride removal efficiency of 56% with chemical costs, normalized to the concentration of chloride removed, amounting to $0.45/mM. In tests for assessing the potential of alternative aluminum sources, 44% of chloride ion was removed when 30 mM of aluminum was added in the second stage, and it showed possibility of recycling of alum sludge. Our results demonstrate chemical precipitation of chloride with lime and aluminum doses in the recycled cooling water. Also, we anticipate that UHLA is one of chloride treatment options in the industrial wastewater in which membrane process such

Table 4
Final concentration of chloride (mM), removal efficiency (C/C_0) and pH

1st stage lime dose (mM)	2nd stage lime dose (mM)	Lime with $Al(OH)_3$ dose(mM)	Chloride conc. (mM)	C/C_0	pH
50	50	10	8.96±0.14	0.97±0.018	12.06±0.20
		20	7.02±0.24	0.76±0.031	12.02±0.13
		30	5.14±0.14	0.56±0.017	11.89±0.07
		40	6.61±0.54	0.72±0.061	11.70±0.05
		60	7.87±0.16	0.85±0.014	11.57±0.03

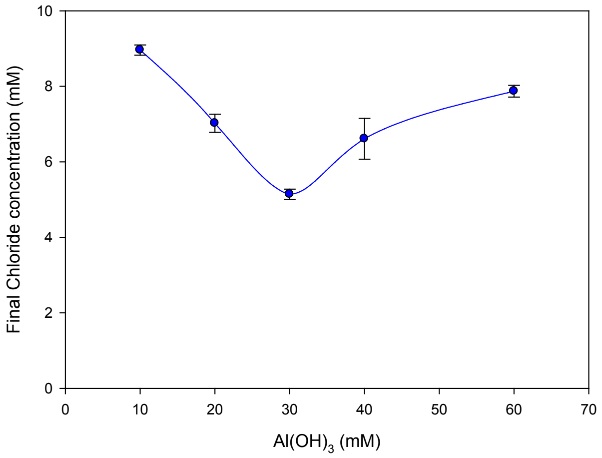


Fig. 7. Chloride removal using an alternative aluminum source ($Al(OH)_3$).

as reverse osmosis (RO) and nanofiltration (NF) are limited due to high scaling potential or brine treatment.

Acknowledgements

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