REMOVAL OF CHLORIDE FROM WASTEWATER BY ADVANCED SOFTENING PROCESS USING ELECTROCHEMICALLY GENERATED ALUMINUM HYDROXIDE

A Thesis

by

SYED FAISAL MUSTAFA

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Chair of Committee,	Ahmed Abdel-Wahab
Committee Members,	Mohamed Nounou
	Mahmood Amani
Head of Department,	M. Nazmul Karim

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ABSTRACT

Wastewater recycle and reuse is limited in many cases by high concentrations of dissolved solids. The majority of dissolved solids can be removed by precipitation. However, chloride is among ionic species that is difficult to remove due to its high solubility. Chloride can be removed from water and wastewater by precipitation as calcium chloroaluminate using advanced softening process. This research was conducted to evaluate chloride removal using electrochemically generated aluminum hydroxide and lime. Kinetics of chloride removal was investigated and the system reached equilibrium within two hours of reaction time indicating that removal kinetics is suitable for practical application of the process. Equilibrium characteristics of chloride removal were characterized. Good chloride removal was obtained at reasonable ranges of lime and aluminum doses. However, the stoichiometry of chloride removal deviated from the theoretical stoichiometry of calcium chloroaluminate precipitation. Analysis of experimental data indicated that this deviation was due to the formation of other solid phases such as tricalcium hydroxyaluminate and tetracalcium hydroxyaluminate. This research obtained the optimum doses of electrochemically produced aluminum hydroxide and lime which achieved maximum chloride removal. An attempt to regenerate and recycles precipitated solids was also investigated.

DEDICATION

To my parents

ACKNOWLEDGEMENTS

I am sincerely grateful to my advisor and chair of my committee, Professor Ahmed Abdel-Wahab, who has not only provided guidance in my research work but has helped me through.my tough times in life. His calm and disciplined attitude inspires me. I am fortunate to have him as my supervisor during my MS study. I would also like to acknowledge my committee members: Dr. Mohamed Nounou and Dr. Mahmood Amani. I want to thank Dr. Angela without whose help in the laboratory, it would have never been possible.

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1. INTRODUCTION

Qatar is among a few countries in the world with least availability of water resources. This scarcity of water is going to become an even greater problem over the coming years due to population growth. Adding to the difficulty, climate changes will potentially cause precipitation to be more uncertain and variable. This problem is more prevalent in arid and coastal regions. Situation gets even worse owing to the huge addition of wastewater every day in this region due to its oil and petroleum industry.

Conservation of water resources and reuse of wastewater is key issue, this region faces. Among different inorganic salts, chloride is found to be present in abundance in groundwater and wastewater [1]. Seawater is one of the major causes of infiltration of chloride salts in water.

As per the regulatory bodies, threshold limit of chloride is kept at 250 mg/L for drinking water [2]. Different wastewaters have different concentration of chloride with produced water having too high concentrations, however wastewater from mining industry or other similar industry have an average chloride concentration of 1000 mg/L[3].

The increased level of chloride in natural water have their implications on the aquatic life and environment [4]. The high content of chloride in the wastewater poses major problem in treatment systems particularly in biological units [5]. It gives rise to the corrosion in pipes and also damage the crops if the chloride-containing wastewater is discharged to the agricultural land [5].

Chloride ions also have negative effect during the electrolysis process for the production of electrolytic zinc. Chloride concentration above 100 mg/L has the ability to corrode the electrode and significantly decrease the useful life of the electrode. It also increases the electricity consumption and debases the electrolytic zinc quality due to increase of lead content. Furthermore chloride ions can be oxidized to chlorine gas by potassium permanganate in the acidic environment which could make the workplace very risky [6].

In addition to the above direct effect of chloride, it is also found that it has long lasting induced effect on buildings, concrete, sculptures if unchecked chloride concentration is put in to the construction process. Salt induced corrosion of passive reinforcing steel is common problem especially where deicing salts, chloride-containing admixtures or chloride-contaminated aggregate are added to the concrete [5]. Decay of porous materials used in construction is prominent cause of the damage of the buildings and sculptures. Historical buildings, monuments, sculptures and frescoes are the main site which suffers the material weathering due to induced decay. As chloride salts are found in abundance in nature, it along with other salts is largely believed to be responsible for the weathering processes in buildings and sculptures. Laboratory analysis of the salt contaminated masonry also shows similar results [7] and it is known that compared to sulfate, chloride is three times more active in pitting the metals with 10 mg/L as the concentration above which it starts corroding iron surface.

Depending upon the concentration and the medium where chloride is present, several processes have been employed in removing chloride from water and wastewater.

Among these processes are reverse osmosis and electrodialysis [8]. However these technologies are nonselective and expensive. They also produce brine, which has disposal issue attached to it [9].

There are some other processes which use different reaction mechanism to remove chloride from water. One of such process is recovery of the chloride ions from the aqueous solution by calcined MgAl-CO_3 layered double hydroxides (LDH) [5]. There is another similar method where layered double hydroxides (LDH) containing nitrate as the inter layer anion (ZnAl-NO_3) is used in removing chloride from aqueous solution [10]. In this process anion exchange takes place and chloride is removed from the aqueous solution. In both the above processes, the reaction mechanism is based on anion exchange and are complex, furthermore, chloride is removed at the expense of addition of another anion.

Work has also been done where magnesium aluminum oxide was used as a neutralizer when mineral acid was treated with it [11]. The similar mechanism was further used to remove chloride from calcium chloride by magnesium aluminum oxide. It was found that both calcium and chloride was considerably removed from the solution.

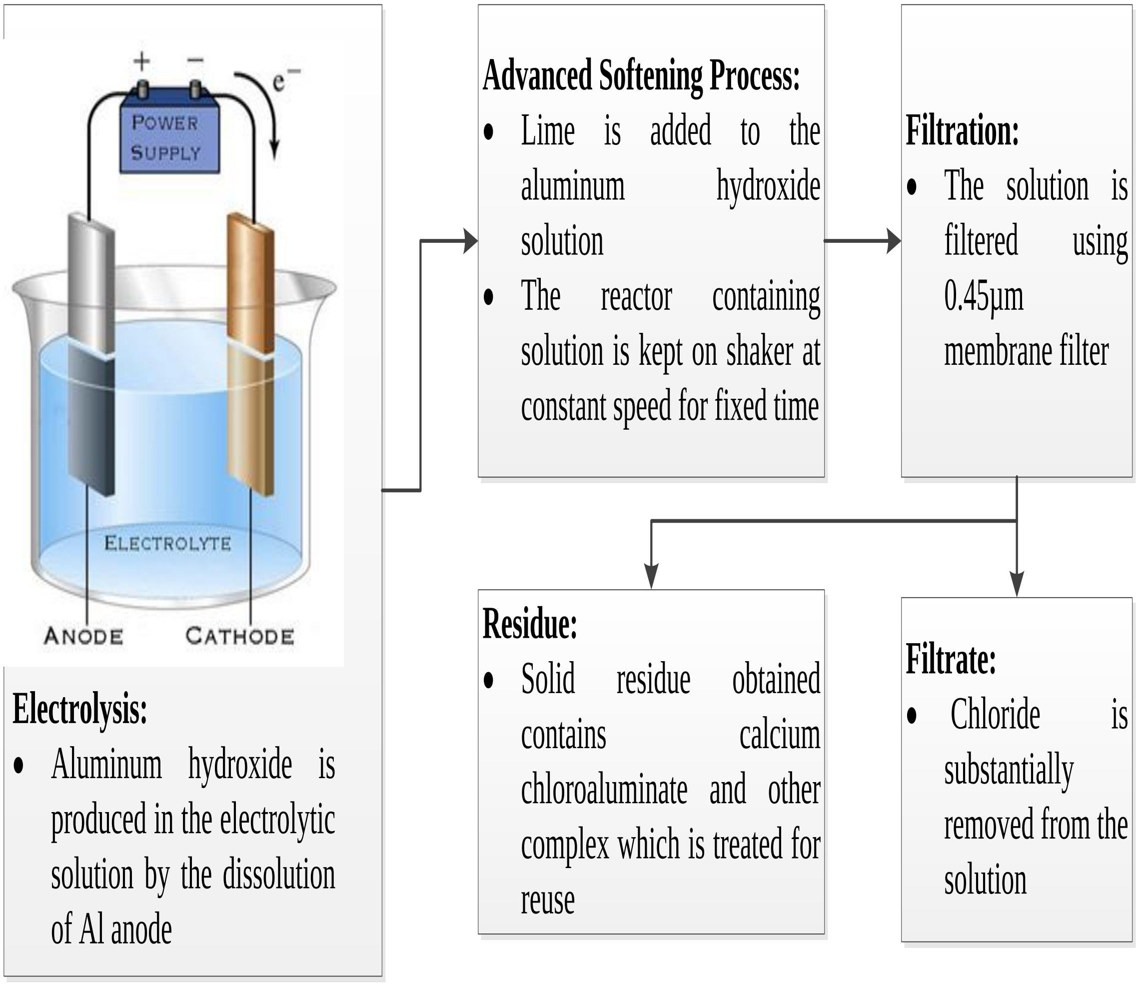
Recently, ultra high lime with aluminum (UHLA) process was developed by using lime and sodium aluminate to remov chloride from water by precipitation of calcium chloroaluminate ($Ca_4Al_2C_{l2}(OH)_{12}$) [12-14]. However, chloride removal efficiency using this process was limited due to the presence of high hydroxide concentration which was formed as a result of addition of lime and sodium aluminate to water. Although high pH is necessary for calcium chloroaluminate precipitation, hydroxide competes with chloride to form other solids complexes such as calcium hydroxyaluminate. Also, sodium aluminate is expensive chemical reagent which makes the overall treatment cost of chloride removal using this process high. Therefore, using freshly precipitated aluminum hydroxide ($Al(OH)_3$) instead of sodium aluminate is expected to result in less hydroxide in the solution and thus increases the potential of calcium chloroaluminate precipitation over calcium hydroxyaluminate and reduce the cost of the treatment process.

The use of electrochemical method for the removal of pollutant from the waste water has gained interest in last two decades due to its ability to remove suspended solids by electrocoagulation and destruction of contaminants by redox reactions. Electrocoagulation is an emerging electrochemical treatment technology where an applied current generates coagulant in situ as a result of dissolution of sacrificial metal anode (Aluminum or Iron).. During the same time hydrogen gas is evolved at the cathode. Several studies have been conducted on removal of impurities from water and wastewater by electrocoagulation. It was found that electrocoagulation process could be employed to remove contaminants such as organic dyes [15], tannic acid [16], MS2 virus [17] with appreciable result. Also, fluoride could be removed from wastewater by addition of aluminum hydroxide and calcium salt to the waste water [18].

This research investigates employing advanced softening process using electrochemically-generated aluminum hydroxide and lime to remove chloride from water. The kinetics and equilibrium characteristics of chloride removal were evaluated.

Other key perspective of this research was to study the effects of aluminum dose, lime doses, and final pH on chloride removal efficiency. The possibility of regenerating precipitated solids and recycling calcium and aluminum into the process was also evaluated.

Work was performed in two steps namely electrolysis for aluminum production in the solution and then addition of lime to the solution. Schematic diagram of the overall treatment process is shown in Figure 1.



Electrolysis:

- Aluminum hydroxide is produced in the electrolytic solution by the dissolution of Al anode

Advanced Softening Process:

- Lime is added to the aluminum hydroxide solution
- The reactor containing solution is kept on shaker at constant speed for fixed time

Filtration:

- The solution is filtered using 0.45µm membrane filter

Residue:

- Solid residue obtained contains calcium chloroaluminate and other complex which is treated for reuse

Filtrate:

- Chloride is substantially removed from the solution

Figure 1 Schematic diagram of the advanced softening process using electrochemically-generated aluminum.

2. BACKGROUND

In many industries, water is used for different purposes. Owing to its low cost and easy availability, it is extensively used in process industry as well as in cooling system. However due to the presence of chloride and scale forming chemicals in the water, corrosion and scale formation is common feature occurring in industrial pipes when dissolved solids are concentrated by water evaporation from cooling towers. Similarly in the process of detoxification of chlorofluorocarbons (CFC), there is addition of $CaCl_2$ which eventually lead to addition of chloride to the wastewater. Additionally, in tertiary treatment process for domestic wastewater, removal of chloride and other dissolved solids is an important step before reuse of treated wastewater. Furthermore, chloride removal from industrial wastewater can facilitate water reuse and recycle.

Reverse osmosis (RO) is widely used for chloride and other dissolved solids removal from water by physical separation. Electrodialysis is also used for removal of dissolved solids from water. However, these processes are sensitive to water quality, require pretreatment step, and produce brine which needs to be managed properly. This makes chemical treatment processes for chloride removal from water and wastewater as an attractive alternative.

Hydrotalcite (HT) and calcined hydrotalcite (CHT) compounds were used for chloride removal by adsorption or ion exchange mechanisms. These compounds are also referred as layered double hydroxides (LDHs).which is a type of anionic clay having high anion exchange capacities. Significant attention has been paid to the potential use of LDHs in treating wastewater. The uptake of Cl^-, F^-, BO_3^{3-}, phosphate, phenols, colored organics and some anionic surfactants from aqueous solution by LDHs were previously studied [19].

2.1 Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs) also called as hydrotalcite (HTs)-like compounds are originally metal-metal-hydoxysalts. It is a group of natural and synthetic materials containing different chemical and structural alternating layers. It is made up of negatively charged interlayers with reversibly exchangeable anions, additional cations and water molecules occur alternating to the positive charged brucite-like mainlayers as shown in Figure 2 [10].

The general formula of LDHs can be described as $M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.mH_2O$ where M^{2+} and M^{3+} are metal cations which occupy octahedral sites in the hydroxide layers. A^{n-} is an exchangeable anion, and x is the ratio $M^{3+}/(M^{2+}+M^{3+})$ with the value ranging from 0.17-0.50 [5].

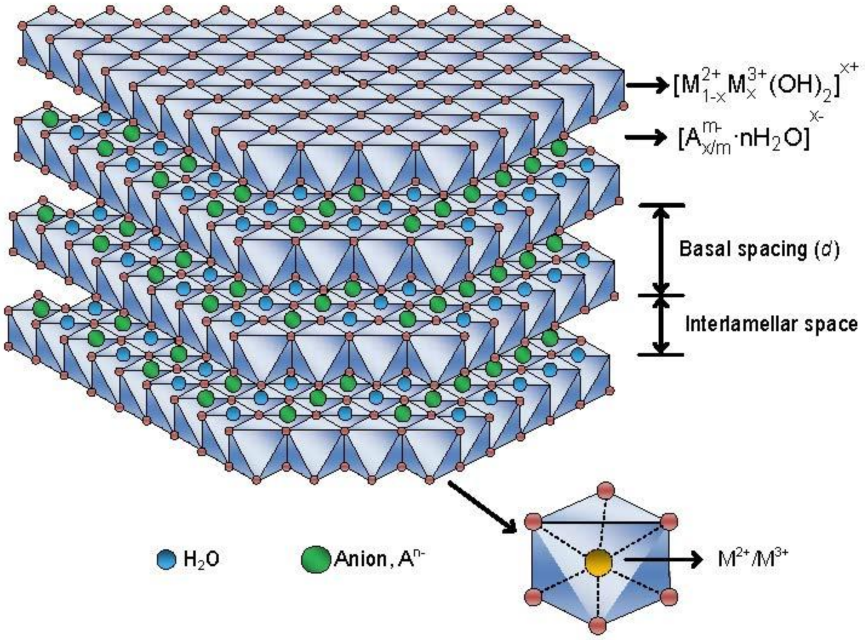


Figure 2 Schematic representation of the LDH structure [20]

Naturally occurring mineral hydrotalcite has carbonate as the interlayer anions. These anionic clays with high anion exchange capacities act as good adsorbents during the removal of anionic pollutants from aqueous solution.

Hydrotalcite having carbonate as the interlayer occurs naturally, however the carbonate interlayer hinder the process of anionic exchange. It is found that the removal of interlayer CO_3^{2-} by anionic exchange is almost impossible as the CO_3^{2-} anion has very high affinity to the LDH. However calcination of the carbonate hydrotalcite can result in driving out CO_3^{2-}. The temperature range for the process of calcination is found to be between 450°C - 800°C [11].

The process of calcination follows the following equation [21]:

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg1-xAlxO1+x/2 + 1\ 2xCO_2 + H_2O \qquad (1)$$

The calcined CO_3^{2-} - hydrotalcite forms magnesium–aluminum oxide (Mg–Al oxide), which can rehydrate and combine with anions to reconstruct the HT structure [21], as expressed in following equation:

$$Mg_{1-x}Al_xO_{1+x/2} +(x/n)\ A^{n-} + (1+x/2)\ H_2O \rightarrow Mg_{1-x}Al_x\ (OH)_{\ 2Ax/n} + xOH^{-} \qquad (2)$$

The above reaction makes the HT suitable for combining with different inorganic and organic anions and after combination, it reconstructs its original layered structure. It is found that the selectivity with which Mg-Al oxide or calcined layered double hydroxide (CLDH) combine with monovalent inorganic anion is in the order of $OH^- > Cl^- > NO_3^-$ [21]. However divalent anions like SO_4^{2-} and CO_3^{2-} possess higher selectivity than monovalent ion to combine with CLDH [21]. Based on the above tendency of the CLDH, it is found that the selectivity of Mg-Al oxide (CLDH) increases with increasing electric charge of anion and decreasing anion size [21].

2.1.1 Use of magnesium aluminum oxide as layered double hydroxide for removal of various anions

Magnesium aluminum oxide was used as a calcined layered double hydroxide (CLDH) in treating various dilute acids [11]. It was found that calcined Mg-Al oxide reacts with different acid according to the following reactions [11]:

$$Mg_{1-x}Al_xO_{1+x/2}\ +\ xHNO_3 + (1-x/2)H2O \rightarrow Mg_{1-x}Al_x(OH_2)(NO_3)_x \qquad (3)$$

$$Mg_{1-x}Al_xO_{1+x/2}\ +\ xHCl + (1-x/2)H2O \rightarrow Mg_{1-x}Al_x(OH_2)(Cl)_x \qquad (4)$$

$$Mg_{1-x}Al_xO_{1+x/2} + x/2H_2SO_4 + (1-x/2)H2O \rightarrow Mg_{1-x}Al_x(OH_2)(SO_4)_{x/2} \quad (5)$$

$$Mg_{1-x}Al_xO_{1+x/2} + x/2H_3PO_4 + (1-x/2)H2O \rightarrow Mg_{1-x}Al_x(OH_2)(HPO_4)_{x/2} \quad (6)$$

The anion removals followed the following order: $H_3PO_4 > H_2SO_4 > HCl > HNO_3$.

During the removal of chloride from hydrochloric acid using magnesium-aluminum oxide LDH, it was reported that the extent of chloride removal from hydrochloric acid was increased with increase in reaction time [19]. It was also found that chloride removal increases with increased amount of LDH. An important observation of this process was that the Cl^- removal was controlled by surface reaction [19].

Mg-Al oxide was also used to precipitate Ca^{2+} and Cl^- from wastewater containing $CaCl_2$ [4]. Comparison of chloride removal from $CaCl_2$ and NaCl solution was also studied. The Mg-Al oxide reactions with $CaCl_2$ and NaCl were assumed by the following equations [4]:

$$Mg_{0.80}Al_{0.20}O_{1.10} + 0.10CaCl_2 + 1.10H_2O \rightarrow Mg_{0.80}Al_{0.20}(OH)_2Cl_{0.20} + 0.10Ca(OH)_2 \quad (7)$$

$$Mg_{0.80}Al_{0.20}O_{1.10} + 0.20NaCl + 1.10H_2O \rightarrow Mg_{0.80}Al_{0.20}(OH)_2Cl_{0.20} + 0.20NaOH. \quad (8)$$

It was reported that for same initial concentration of chloride ion, the degree of chloride removal from NaCl was less than that of chloride removal from $CaCl_2$ [4].

Table 1 summarizes the degree of chloride removal from the above two solutions and the initial and final pH of the solution. It was observed that the above process was efficient in removing chloride ion from $CaCl_2$ but it was not very effective in removing chloride ion from NaCl solution.

Table 1 pH of the $CaCl_2$ and NaCl solutions before and after the removal of Cl^-, and the degree of Cl^- removal from both solutions by $Mg_{0.80}Al_{0.20}O_{1.10}$[4]

$[Cl^-]$ = 0.5M	pH		Degree of Cl- removal (%)
	Initial	Final	
CaCl2	6.1	12.4	68.7
NaCl	5.3	13.4	51.4

Another type of LDH made up of ZnAl-NO_3 was investigated for chloride removal [10] by an anion exchange process. In this process, chloride of the solution take the place of nitrate in the LDH which results in removal of chloride and release of nitrate to the solution. It was also observed that the removal percentage of chloride increases upon increasing the reaction time and reaches the maximum at 4hrs and thereafter it remains almost constant. The maximum amount of chloride adsorbed to the LDHs was found to be 64.1% in 4 hrs with a constant chloride ion concentration of 100 mg/L and LDHs dosage of 1000 mg/L [10].

2.2 Removal of chloride from recycled cooling water using ultra high lime with aluminum process

Ultra-high lime with aluminum (UHLA) process was used for chloride removal in previous research [22]. In that process, dry lime ($Ca(OH_2)$) and dry sodium aluminate ($NaAlO_{2)}$ were used as chemical reagents to precipitate chloride as calcium chloroaluminate solid ($Ca_4Al_2Cl_2(OH)_{12}$) according to the following reaction.

$$4Ca^{2+} + 2A1^{3+} + 2C1^{-} + 12OH^{-} \rightleftharpoons Ca_4Al_2Cl_2(OH)_{12} \qquad (9)$$

Considerable amount of chloride was removed with reasonable combination of lime and aluminum dose [22-26]. However, deviation from theoretical stoichiometry of calcium chloroaluminate precipitation occurred in the equilibrium experiments. It was assumed that this deviation could be due to the fact that as a result of high OH^- concentration, solids like calcium hydroxyaluminate $Ca_4Al_2(OH)_{14}$ were also formed along with calcium chloroaluminate. Table 2 shows the various methods and processes employed in the removal of chloride from different medium.

Table 2 Various chloride removal processes

Chloride removal process	**Limitation and constraints**	**Author**
Use of magnesium-aluminum oxide LDH in removing chloride from hydrochloric acid	Research is limited to removal of chloride from hydrochloric acid.	Kameda; 2006
Use of magnesium-aluminum oxide LDH in removing chloride and calcium ions from calcium chloride solution	Chloride removal was substantial from calcium chloride solution, but be similar result couldn’t achieved for sodium chloride	Kameda; 2003
Use of magnesium-aluminum oxide LDH in chloride removal from aqueous solution with different cations	High degree of chloride removal was restricted to the solution of $AlCl_3$ and NH_4Cl	Kameda; 2005
Use of ZnAl-NO3 LDH in removal of chloride ion from aqueous solution by anion exchange	Chloride is removed at the cost of addition of nitrates to the solution.	Liang Lva; 2009

Table 2 Continued

Chloride removal process	**Limitation and constraints**	**Author**
Use of Amberlite in chloride removal from aqueous solution by adsorption	Resin has limited useful capacities. Could be applied at small scale only.	Carmona; 2008
Removal of chloride ion from zinc sulfate aqueous solution by electrochemical method	Limited to the chloride removal from zinc sulfate solution.	Wu, X;2013
Removal of chloride from concrete by electrochemical chloride extraction	Application is limited to chloride removal from concrete.	Orellan; 2004
Removal of sodium chloride from seawater sample by electrochemical process with nafion membrane	Expensive	Eva Grygolowicz-Pawlak;2012
Removal of chloride salts from seawater by desalination technologies	Expensive and operational problems like membrane fouling and disposal.	Khawajia; 2008
Multi stage flash distillation(MSF)	Expensive, high installation cost.	Khawajia; 2008

Table 2 Continued

Chloride removal process	**Limitation and constraints**	**Author**
Multi Effect Distillation (MED):	Expensive, high installation cost	Michels; 1993
Use of reverse osmosis (RO) in removal of salts including chloride from waste water	Energy intensive.	Mielke; 1991
Removal of chloride from recycled cooling water using ultra high lime with aluminum process	Research was performed on recycled cooling water	Abdel-Wahab; 2002

2.3 Removal of chloride by advanced softening process using electrochemically-generated $Al(OH)_3$

Application of electrochemistry in recent years has been successful for removal of various contaminants from wastewater with desired results.

2.3.1 Electrochemistry

It is a branch of chemistry that deals with the relationship between electrical and chemical phenomena. Electrochemistry involves chemical reaction taking place in the electrolyte at the interface of electrode. It involves electron transfer between the electrode and the electrolyte. Electrochemistry can be linked with coagulation and flotation to remove suspended solids and other contaminants from water and wastewater by electrocoagulation and electrofloatation as shown in Figure 3 [27].

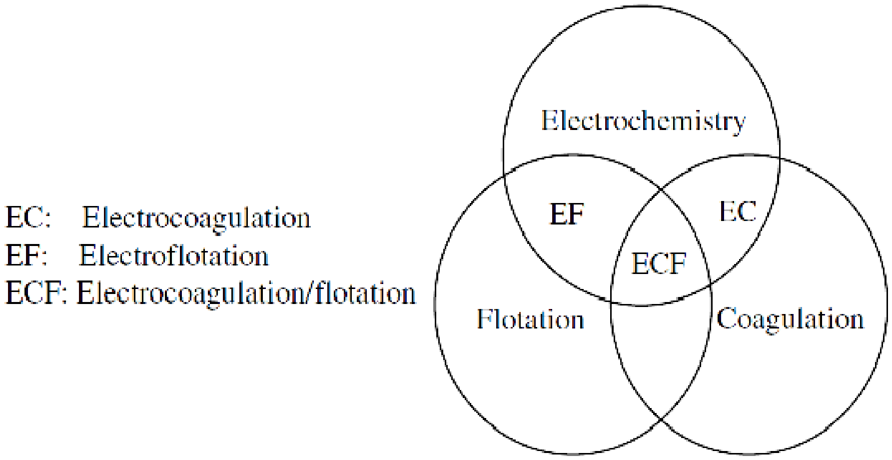


Figure 3 Interactions occurring within an ECF process [27]

2.3.2 Electrocoagulation

In recent years electrocoagulation have received considerable attention because of its versatile character, safe handling, selective in nature and environmental compatibility. It is an electrochemical method where coagulants are produced by passing D.C. current through aqueous media. Anode is dissolved in order to produce the coagulants. In addition, hydrogen gas is evolved at cathode and oxygen or chlorine gas may evolve at anode. There are different electrodes available which could be used for electrolysis however aluminum and iron electrodes are commonly used as anode due to its sacrificial character and easy availability. In brief, electrocoagulation is a hybridization of coagulation, floatation and electrochemistry. In its simplest form, an electrocoagulation reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material electrochemically corrodes due to oxidation. Figure 4 shows an electrolysis system consisting of an electrolytic cell which contains an anode and cathode connected to current supply.

Electrocoagulation, which is known for its reliability and cost-effective wastewater treatment process [28] is characterized by simple and easy operated equipment, short operation time, less amount of chemicals than conventional coagulation and thus low sludge production.

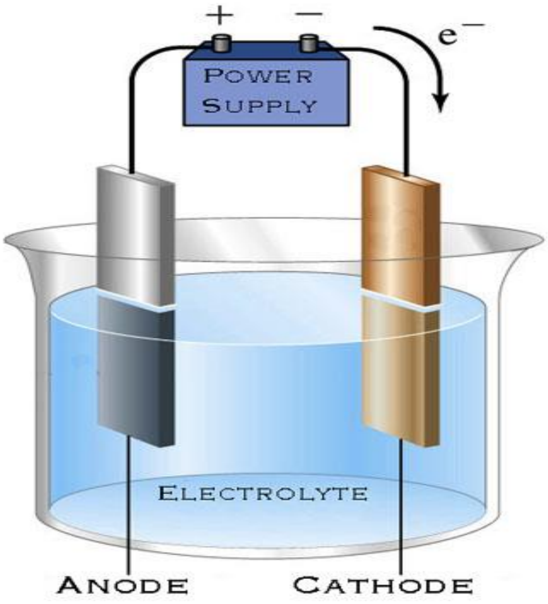


Figure 4 The electrolytic process [29]

2.3.3 *Advanced softening process*

In UHLA process, chloride is removed by precipitation of calcium chloroaluminate ($Ca_4Cl_2Al_2(OH)_{12}$). However due to high concentration of hydroxide ions in that process produced as a result of addition of water to lime and sodium aluminate, Cl^- ion of calcium chloroaluminate is replaced by OH^- from the aqueous phase to form hydroxyaluminate ($Ca_4Al_2(OH)_{14}$). Therefore a solid solution is formed containing a mixture of chloroaluminate ($Ca_4Al_2Cl_2(OH)_{12}$) and hydroxyaluminate ($Ca_4Al_2(OH)_{14}$) [30-33]. This results in less removal of chloride. Additionally, sodium aluminate is an expensive chemical reagent which results in high operating cost for chloride removal using UHLA.

The drawback of the above process could be overcome by performing electrolysis to produce aluminum hydroxide instead of adding sodium aluminate.

2.4 Calcium chloroaluminate

Calcium chloroaluminate also known as Friedal's salt [34] is mainly composed of calcium, aluminum and chloride with hydrogen and oxygen constituting hydroxide part. The chemical formula of this compound is $Ca_4Al_2Cl_2(OH)_{12}$ and it is a layered double hydroxide. Layered double hydroxides (LDHs) which is commonly termed as metal–metal-hydroxysalts and anionic clay minerals, are a group of natural and synthetic materials containing different chemical and structural alternating layers [35, 36]. The general formula of calcium aluminum LDH could be written as $[Ca_2Al(OH)_6]^+x^-$, where brackets indicate the composition of the positively charged layer unit. The excess positive charges are balanced by anions (x) in interlayer spaces (e.g. OH^-, Cl^-, $S04^{2-}$, CO_3^{2-}) [37, 38].

3. MATERIALS AND METHODS

3.1 Experimental plan

Experimental plan was divided into three main parts. First, different sets of electrolysis experiments were conducted to obtain the relationship between operating conditions (i.e. applied current, electrode area, and electrolysis time) and the amount of generated $Al(OH)_3$. Second, kinetic and equilibrium experiments were conducted to evaluate chloride precipitation using lime and aluminum hydroxide that was generated electrochemically. Effects of different lime dose and aluminum dose on chloride precipitation were also studied. Finally, experiments were performed to regenerate the precipitated solids so as to recover calcium and aluminum and reuse them in the chloride removal process.

3.2 Chemicals and reagents

The chemicals used in this research were: sodium chloride (ACS 99.7%, Fisher), calcium hydroxide (ACS reagent, $\geq$ 95.0%, Sigma Aldrich), calcium chloride (USP, Sigma Aldrich), nitric acid (60%, GPR Rectapur), hydrochloric acid (35%, GPR Rectapur), aluminum sheet (99% purity), steel sheet. Table 3 shows the specifications of chemicals that were used in this research.

Table 3 Chemicals used and their specifications

Chemical name	Chemical formula	Vendor	Specifications
Sodium Chloride	$NaCl$	Fisher Scientific	Analytical reagent grade, conforms to EP & ACS
Calcium Hydroxide	$Ca(OH)_2$	Sigma Aldrich	ACS reagent, $\geq 95.0\%$
Calcium Chloride	$CaCl_2$	Sigma Aldrich	Conform USP testing specification
Nitric Acid	HNO_3	GPR Rectapur	60%
Hydrochloric Acid	HCl	GPR Rectapur	35%

All solutions used in the experiments were prepared using decarbonated deionized water (DI water, hereafter) which was purified with a Barnstead Nanopure system to greater than 18 MΩ and was degassed by purging it with nitrogen gas. All lab ware was cleaned and washed according to the following procedure:

- Soak 24 hours in 2 % laboratory detergent (VWR)
- Soak 24 hours in 10% nitric acid
- Wash and rinse the items with deionized water.
- Dry before use

The stock solutions of sodium chloride and calcium chloride were prepared daily by dissolving appropriate amounts of the chemical reagents in the DI water. All primary standard solutions (aluminum, calcium, chloride,) were reagent grade chemicals (Fisher).

Secondary standard solutions which was used in samples calibration curves were prepared daily from the primary stock solutions by diluting it with DI water.

3.3 Experimental procedures

Three types of major experiments were conducted as shown in Figure 5

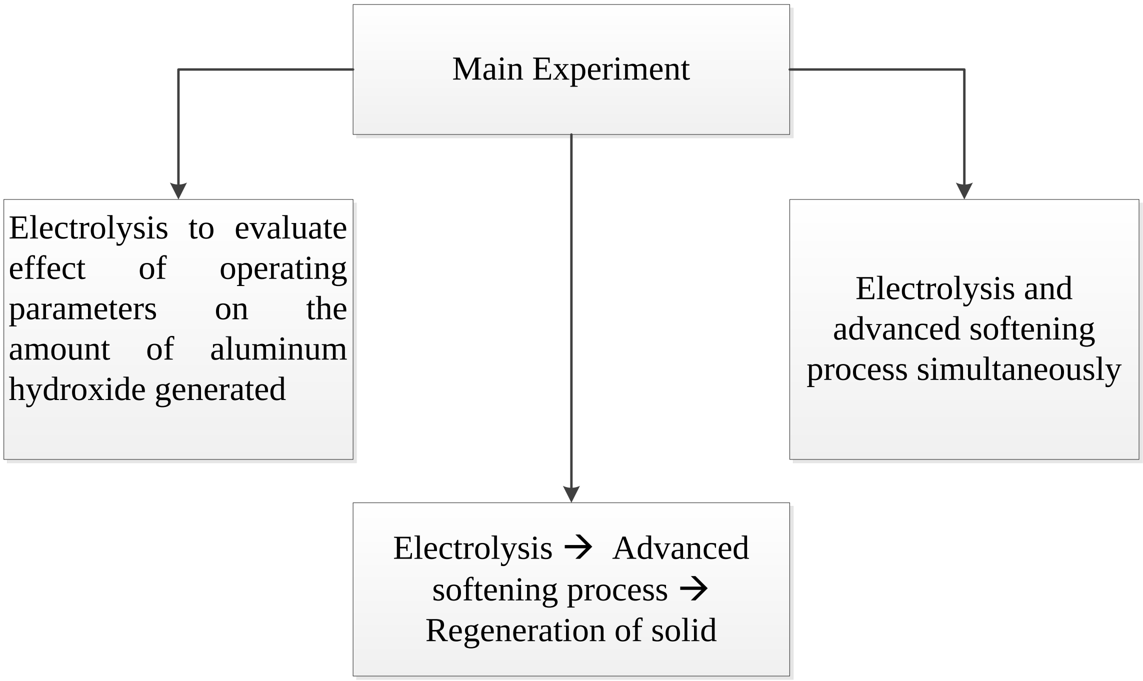


Figure 5 Schematic representation of three sets of experiments performed.

3.3.1 Electrolysis to evaluate effect of operating parameters on the amount of aluminum hydroxide generated

Electrolysis was performed to study the relationship between the experimental mass of aluminum hydroxide generated to the theoretical mass as given by Faraday’s law. Experiments were performed to obtain the optimum conditions where the generated mass of aluminum hydroxide follows Faraday’s law.

Glass beaker of 500 mL (pyrex) was used as electrolytic cell with magnetic stirrer present inside it to keep the concentration of electrolyte constant during the course of electrolysis. Aluminum sheet (99% purity) was used as sacrificial anode and steel sheet was used as cathode. The anode was mechanically scrubbed with a waterproof silicon paper sanding sheet (100 Grit, McMaster-Carr) before each experiment in order to maintain the aluminum generation efficiency. Electrode area was kept constant at 60 cm^2 and the distance between electrodes was fixed at 3 cm. Digital DC power supply (Monacor PS-430) operating under galvanostatic options was the source of fixed current required during electrolysis. 30 mM of NaCl in 500 mL of DI water was used as electrolyte. NaCl solution was prepared daily by dissolving required amount of dry NaCl in 500 mL of DI water.

Electrolysis experiments were performed at different current values (50 mA, 100 mA, 200 mA, 500 mA, 1000 mA) so as to generate aluminum and thereby obtain the relation between mass of anode dissolved (aluminum hydroxide generated) to that as predicted by Faraday’s Law. An appropriate aliquot (0.5 mL) was taken from the electrolyte at various times by auto-pipette into different plastic tubes. Samples taken were immediately acidified using hydrochloric acid (30%) and were diluted using DI water. Diluted samples were analyzed for aluminum concentration. Another aliquot (8-10 mL) was taken simultaneously with the above samples into different plastic tubes for the pH measurement. The pH was measured instantly and the same sample was dropped back into the electrolyte after pH measurement.

3.3.2 Advanced softening experiments

Experiments were performed to evaluate chloride removal from 30 mM initial chloride solution using electrolysis as a source of aluminum. Dry lime was added to the solution containing chloride and aluminum.

A kinetic experiment was performed to study the kinetics of chloride removal.. 30 mM NaCl solution used above as an electrolyte in the electrolysis also serves as a source of chloride in the lime softening experiment. The operating conditions of electrolysis were adjusted to obtain dose of 30 mM aluminum in the solution. The solution then was transferred from glass beaker to plastic reactor to which 60 mM of lime was added. The experiment was conducted in a high-density polyethylene (HDPE) sealed plastic bottles (500 mL) as a complete mixed batch reactors. After the addition of lime, the reactor was immediately closed and tightly sealed.

The reactor was mixed by placing it on the shaker at constant speed of 250 rpm at room temperature (23-25ºC). Samples (8-10 mL) were taken at different times from the reactor using a plastic syringe. The pH was measured and then samples were filtered with 0.45 μm Whatman® membrane filters (VWR) and analyzed for chloride, calcium, and aluminum.

Equilibrium experiments were conducted using the same aforementioned procedure but with constant reaction time at which the system approached equilibrium according to the kinetic experiment. Multiple equilibrium experiments were conducted at room temperature 23 - 25 °C to evaluate the effects of lime dose (30 mM, 60 mM, 90 mM) and aluminum dose (15 mM, 30 mM, 45 mM) on chloride removal and to study the characteristics of calcium chloroaluminate precipitation. To generate 15 mM, 30 mM and 45 mM aluminum solution, current value of 500 mA, 1000 mA, and 1500 mA, respectively, were used during electrolysis for 73 minutes. Initial chloride concentration was kept fixed at 30 mM for all the sets of experiment.

3.3.3 Regeneration experiments

Experiments were performed to regenerate the precipitated solids in order to recover calcium and aluminum and reuse them in the chloride removal process. After the completion of first set of chloride removal experiment on 30 mM chloride solution using 60 mM lime dose and 30 mM aluminum dose, solution was centrifuged to collect the solids. The above combination of lime and aluminum doses were chosen based on the results of equilibrium experiments which showed maximum chloride removal under these conditions. An appropriate amount of solid was dried in the furnace and the dried solid was weighed and later acidified using 1mL of nitric acid (60%) and was further diluted by 25 mL of DI water. The diluted solution was heated to dissolve the entire solid in it. The digested solution was later analyzed for chloride, calcium and aluminum. The rest of collected solid was converted into slurry by adding measured amount of DI water (5 mL) to it. Carbon dioxide was purged into the obtained slurry. Magnetic stirrer was placed in the slurry which kept the slurry uniform in concentration. The purging was continued till the pH of the slurry reached the desired value. Then the slurry was filtered using 0.45µm Whatman® membrane filter. The filtered solid was dried and the dried solid was weighed and later acidified using nitric acid (60%). The acidified solution was further diluted by 25mL of DI water and was heated to digest the entire solid in it. The digested solution was later analyzed for chloride, aluminum and calcium.

Three set of experiments were conducted to reuse the regenerated solid for chloride removal from a 30 mM NaCl solution. Figure 6 shows a schematic diagram of solids regeneration procedure.

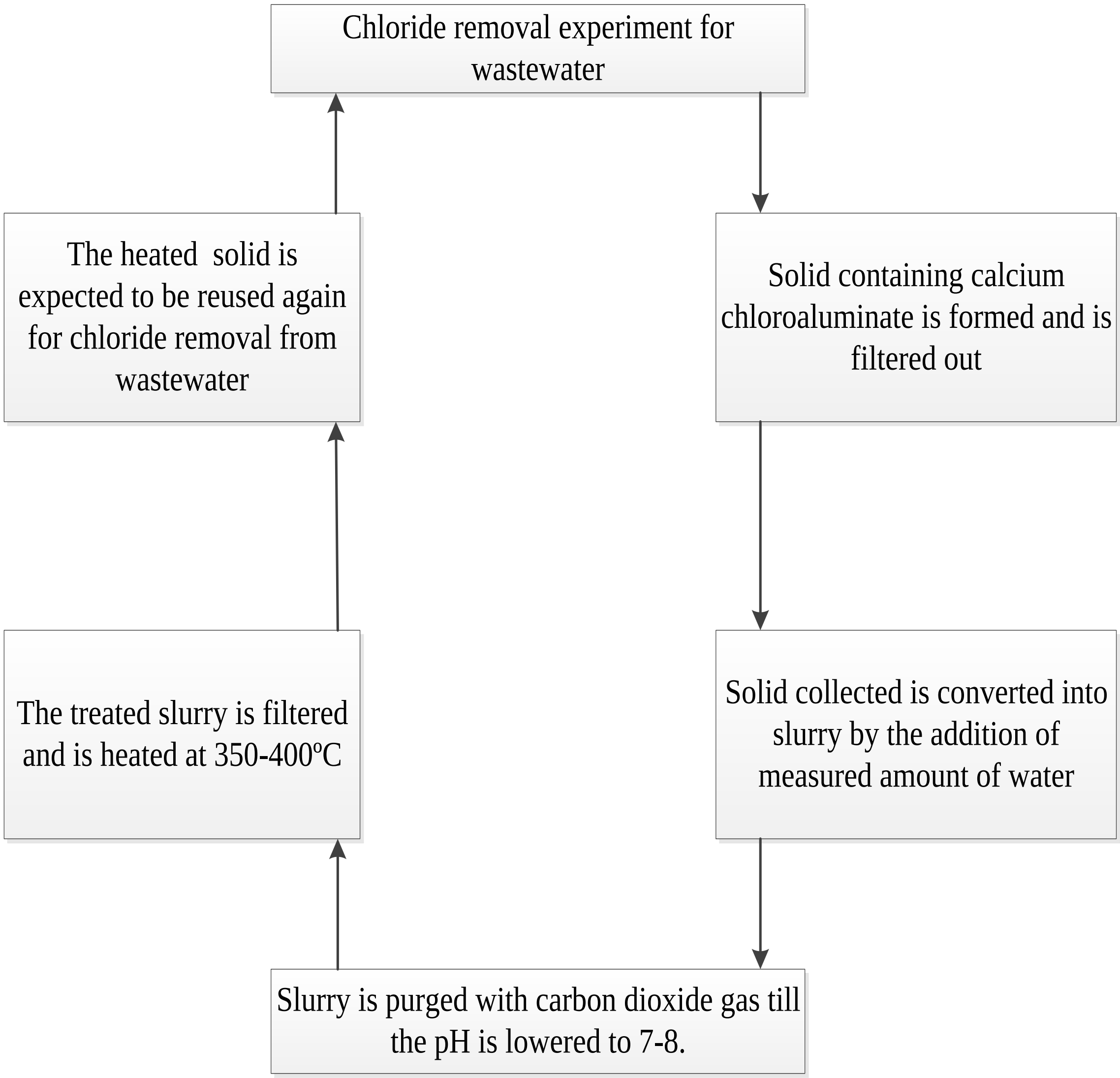


Figure 6 Schematic diagram of regeneration experiments

3.3.4 Effect of addition of lime at the beginning of electrolysis

Two sets of experiments were conducted where 90 mM lime dose was added at the beginning of electrolysis with employed currents of 1500 mA and 2000 mA. All the electrolytic conditions were similar to the previous electrolysis experiments. The initial NaCl concentration was fixed at 30 mM in 500 mL DI water. After addition of lime, two samples (0.5 mL, 5 mL) were collected using auto pipette at various times. One sample (0.5 mL) was directly acidified using hydrochloric acid (30%), diluted using DI water, and analyzed for aluminum. The other sample was filtered using filter paper similar to the previous experiments. The filtered samples were diluted and analyzed for chloride and calcium.

3.4 Analytical procedures

All the analytical procedures were performed using the Standard Methods for The Examination of Water and Wastewater [39] and according to the instructions mentioned on the instrument manuals.

3.4.1 Chloride and calcium

1000 mg/L of stock solution of chloride was prepared using NaCl and DI water. From the stock solution, different standards were prepared with the following concentration 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 50 mg/L which were used for calibration of chloride measurements. Similarly 1000 mg/L of stock solution was prepared using calcium chloride and DI water. From the stock solution, different standards were prepared with the following concentrations: 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L which were used for calibration of calcium measurements.

To analyze the concentration of chloride and calcium in the filtrate taken from the reactor, ion chromatogram (IC) was used. The IC system was equipped with dual gradient pump, AS auto sampler, and eluent generation module with the following conditions:

- Eluent: 4.5 mM Na_2CO_3 / 0.8 mM $NaHCO_3$
- Flow rate: 0.25 mL/min
- Temperature: 30˚C
- Detection: Suppressed conductivity
- Suppressor: Anion self-regenerating suppressor (ASRS 300, 2 mm)
- Applied current: 7 mA
- Injection volume: 1200 µL

3.4.2 Aluminum

0.1 mg/L, 1 mg/L, 10 mg/L, 20 mg/L, 50 mg/L of standard aluminum solutions was prepared from a stock solution of 1000 mg/L Fisher aluminum standard solution.

To analyze the concentration of aluminum, ICP-OES spectrometer was used. This spectrometer was of iCap 6000 series from Thermo Scientific. Aluminum was measured using Al 396.1(85) method. Standards and samples were prepared after dilution with DI water and were analyzed as per the procedures described for the method [39].

3.4.3 pH

pH was measured using a pH meter (Orion 420A) with an Orion Ross Sure-Flow combination electrode which was calibrated with pH 4 , pH 7 (VWR) and pH 13.0 buffers. pH 13 buffer was prepared in our lab by mixing 25% of 0.2 M KCl with 66% of 0.2 M NaOH and 9% of DI water [40, 41].

4. RESULTS AND DISCUSSION

4.1 Effect of current on mass of aluminum dissolved in solution

Multiple experiments were performed to evaluate the mass of aluminum produced during electrolysis as compared to theoretical amounts as predicted by Faraday's law. Table 4 shows the experimental conditions for the five sets of electrolysis performed using different currents.

Table 4 Electrolysis at different currents and fixed electrolytic concentration

Experiment	Electrolyte	Employed current (mA)	Volume of solution (mL)	pH
1	30 mM NaCl	50	500	7.9
2	30 mM NaCl	100	500	8.2
3	30 mM NaCl	200	500	8.3
4	30 mM NaCl	500	500	8.4
5	30 mM NaCl	1000	500	8.5

It was observed that initial experimental results matches closely with the Faraday's law for 3-electron transfer (z=3) according to the below equation:

$$M= (26.98*I*t)/ZF \qquad (10)$$

where M is the mass in grams of Al generated at a specific current (I, ampere) over a time interval (t, s), Z is the number of electrons transferred per Al atom, 26.98 g mol−1 is the atomic weight of Al, and F is Faraday's constant (96 486 C eq−1).

However as the electrolysis progresses, the mass of aluminum dissolved slightly deviates from what was predicted by Faraday's law as shown in Figure 7. This could be attributed to the fact that at later stage of electrolysis, current seems to increase from its initial value, though the increase is not substantial but that leads to higher production of aluminum than expected. Another reason could be the high concentration of chloride ions which can promote pitting corrosion on the anodic surface leading to dissolution of aluminum in the electrolyte. Despite chloride concentration remaining constant throughout electrolysis, its pitting character is effective as time passes [42-45].

Figure 7 shows that at low current, the experimental results followed Faraday's law more closely than at high current.

The major chemical reactions that occur during hydrolysis were report by several previous researchers [46, 47]. These reactions are:

Anode: $Al^0(s) \rightarrow Al^{3+} + 3e^-$ (11)

Hydrolysis: $Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$ (12)

Cathode: $3H_2O + 3e^- \rightarrow 3OH^- + 1.5H_2$ (13)

$3H^+ + 3\,OH^- \rightarrow 3\,H_2O$ (14)

The complete Reaction during Electrolysis is [46]:

$Al^0(s) + 3H_2O \rightarrow Al(OH)_3(s) + 1.5H_2$ (15)

Aluminum ions (Al^{3+}) produced during electrolysis quickly undergoes spontaneous hydrolysis reactions resulting in the generation of various monomeric species according to the following [47]:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \tag{16}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^+ \tag{17}$$

$$Al(OH)_2^{+} + H2O \rightarrow Al(OH)_3 + H^+ \tag{18}$$

In addition to the above reaction products, dimeric, trimeric and polynuclear hydrolysis products of Al such as $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$,$Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ can also form [46]. The cationic hydrolysis products of aluminum may further react with OH^- ions to convert into amorphous $Al(OH)_3$(s).

Due to the above hydrolysis reactions, the anodic region becomes acidic. Conversely the hydrogen liberation at cathode makes the cathodic region alkaline. It was observed that the pH of the solution gradually increased with time from its initial value of 5.5±0.15 to reach equilibrium value of 8.1±0.15 after which there was no substantial change in pH as shown in Figure 8. The increase in pH could be explained by the formation of OH^- ions from the reduction of H^+ or H_2O on the surface of the cathode [48, 49]. In these circumstances, it appears that hydroxide ions formed at the cathode were not completely involved in the formation of hydroxo-aluminum species. Rather, the excess of OH^- ions increased the pH of the solution.

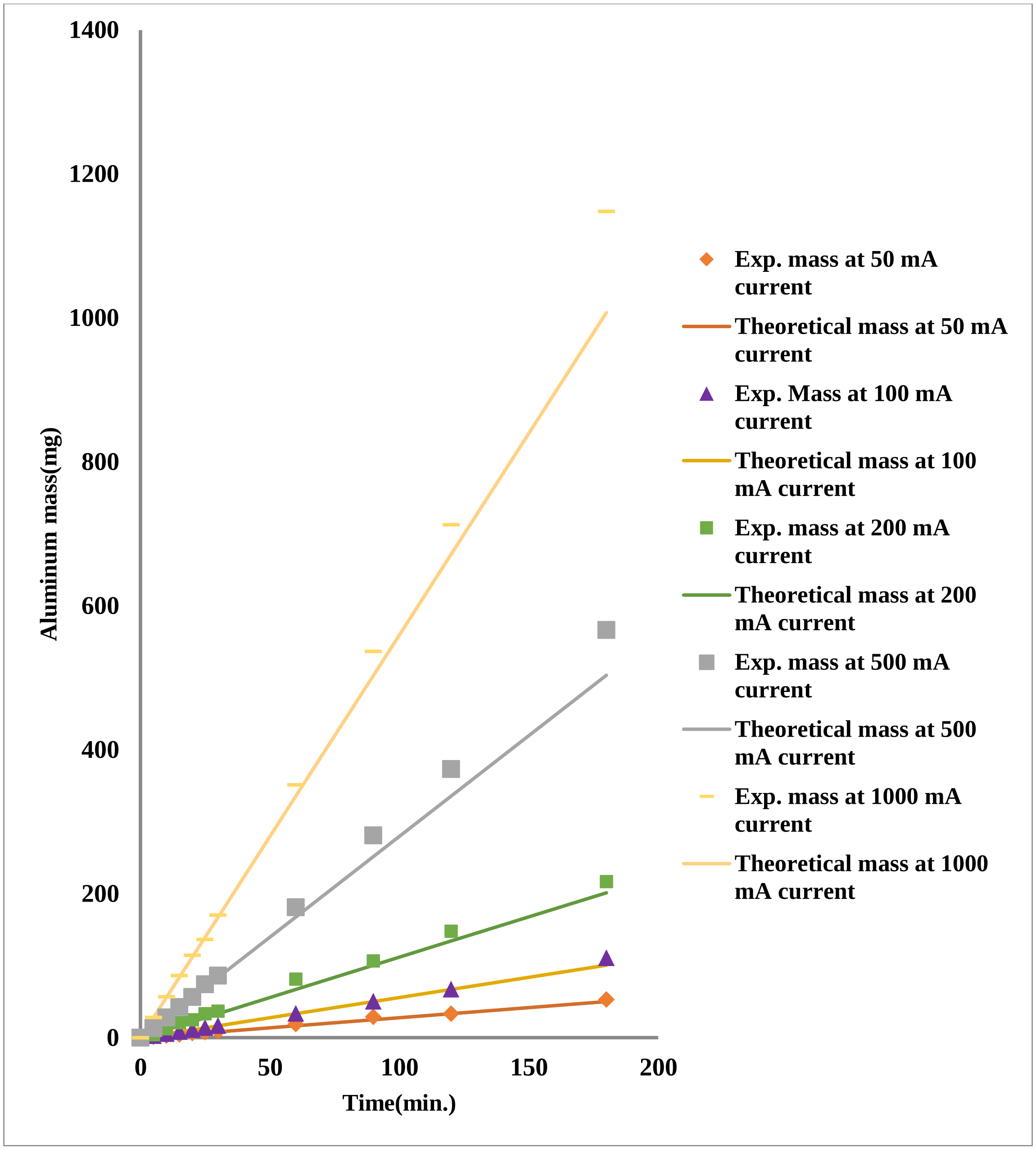


Figure 7 Relationship between produced mass of aluminum and theoretical mass as predicted by Faraday's law vs time during electrolysis of 30 mM NaCl electrolyte solution.

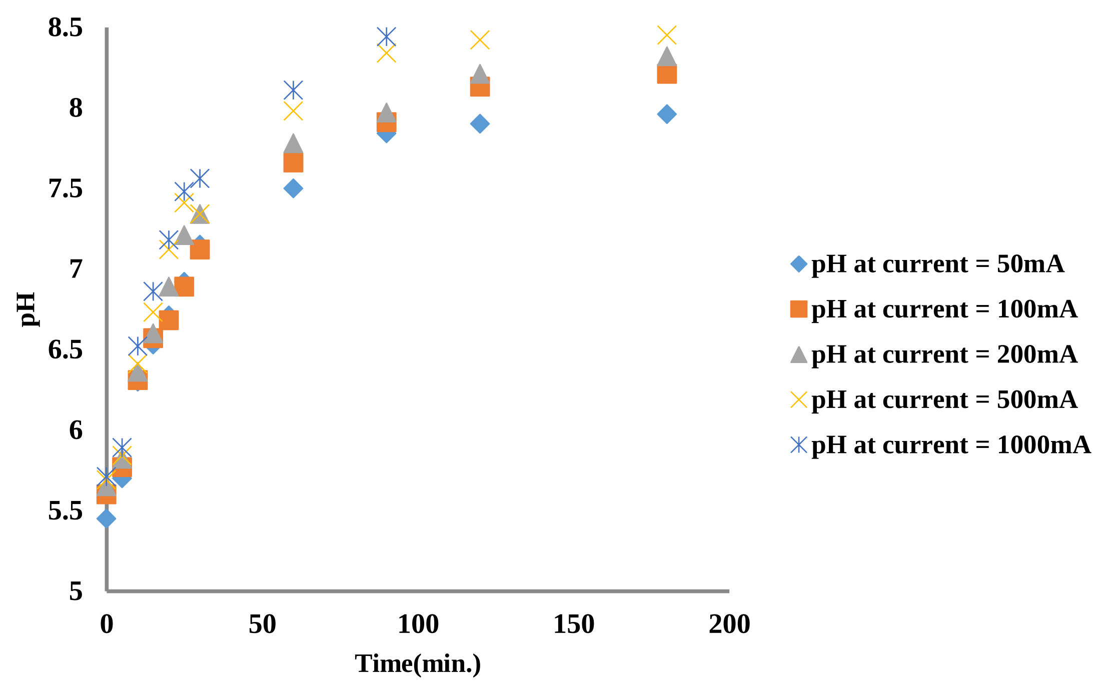


Figure 8 Change of pH versus time during electrolysis performed at different current values of 30mM NaCl electrolyte solution.

4.2 Advanced softening process

Advanced softening experiments were performed by adding different lime dose to the obtained aluminum solutions after hydrolysis. Samples were taken at different time intervals and were analyzed for chloride, calcium, aluminum, and pH.

4.2.1 Effect of lime and aluminum doses on chloride removal

Nine advanced softening experiments were conducted using combinations of three current values (500 mA, 1000 mA and 1500 mA) and three lime doses (30 mM, 60 mM and 90 mM). Initial chloride concentration was kept constant at 30 mM. The results of these experiments are summarized in Table 5. It was observed that, increasing the aluminum and lime dose results in decreasing final chloride concentrations. The precipitation of chloride with calcium and aluminum forming Ca-Cl-Al-OH precipitate is the inferred mechanism. It is hypothesized that formation of calcium chloroaluminate precipitate primarily controls the chloride removal process according to the following equation:

$$4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4(OH)^- = Ca_4Al_2Cl_2(OH)_{12}(s) \qquad (19)$$

Minimum chloride concentration was obtained at lime dose of 90 mM and aluminum dose of around 33 mM which was generated at current value of 1000 mA. However, the difference between chloride removals at 60 mM and 90 mM lime doses was negligible indicating that 60 mM is adequate for optimum chloride removal. Maximum efficiency of chloride removal was achieved when the molar ratio of initial chloride concentration to aluminum dose is around 1.0. Effects of different operating conditions are described in more details in the subsequent sections.

Table 5 Minimum chloride concentrations and final pH obtained for different combinations of lime dose and current.

Experiment no.	Initial chloride conc. (mM)	Current (mA)	Al conc. (mM obtained after electrolysis)	Lime dose (mM)	Minimum chloride conc. (mM) obtained	Percentage chloride removal (%)	Final pH
1	30	500	16.2	30	18.7	37.5	11.9
2	30	500	17.1	60	20.1	37.2	12.2
3	30	500	14.5	90	17.3	42.7	12.3
4	30	1000	33.0	30	18.7	37.4	11.9
5	30	1000	33.9	60	9.5	68.9	12.1
6	30	1000	33.3	90	9.3	69.3	12.3
7	30	1500	49.0	30	18.8	36.5	12.2
8	30	1500	47.6	60	18.7	39.6	12.3
9	30	1500	47.7	90	11.7	62.0	12.5

4.2.2 *Effect of lime dose on chloride removal at fixed current of 500 mA*

First, electrolysis was performed at 500 mA current for 73 minutes in a 30 mM chloride solution to obtain the desired concentration of 15 mM of aluminum. Then the solution was transferred to the reactor and then lime was added. Samples were taken at various times and analyzed for chloride, calcium, pH and aluminum concentration. Figure 9Figure 9 shows final chloride concentration at different lime doses and indicate that chloride removal was very fast and the major removal was obtained at the first sampling time of 5 min. Chloride removal was found to be maximum at 90 mM of lime dose achieving minimum chloride concentration of 17.3 mM (42.7 % removal) after 4 hours reaction time.

Minimum chloride concentrations obtained at 30 mM and 60 mM lime dose were 18.7 mM and 20.1 mM after 4 hours reaction time which are corresponding to 37.5 % and 37.2 % removal respectively.

Final calcium concentration was depended on lime dose as shown in Figure 10. Calcium concentration increased with increasing lime dose. This is because at high lime doses, there was not enough aluminum to react with calcium and precipitate it. Figure 10 shows that calcium concentration increased with time. This could be because the unreacted lime stayed insoluble in the reactor and then it dissolved gradually with time.

The pH was measured for these experiments and the results are shown in Figure 11. It was found that as soon as lime was added to the aluminum solution obtained after electrolysis, pH increased from 8.7±0.05 to 12.2±0.10 and then remained unchanged until the end of the experiment. Figure 12 presents final aluminum concentration which shows negligible aluminum present in the solution indicateing that almost all aluminum is present in the solid phase.

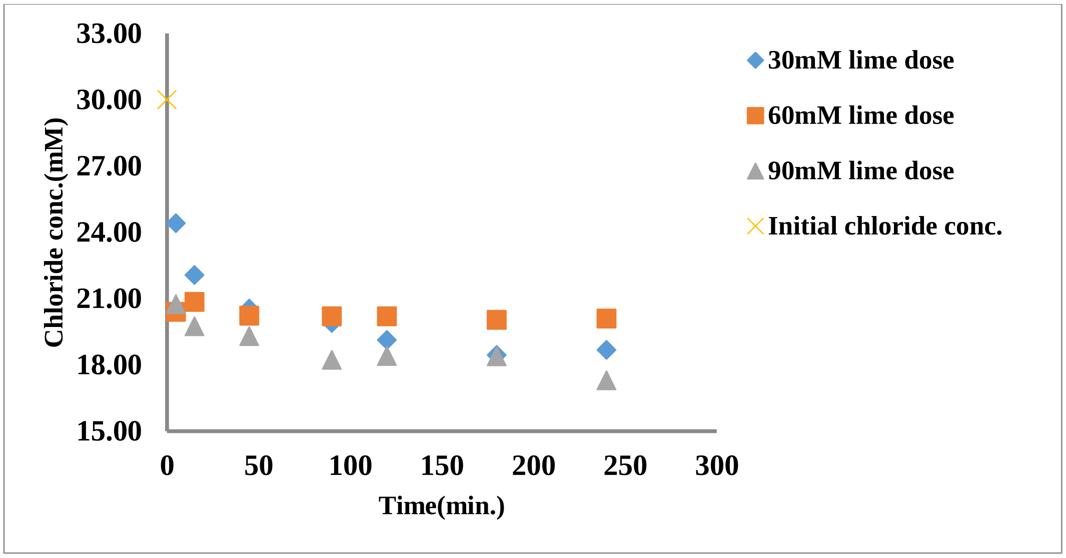


Figure 9 Removal of chloride during advanced softening experiment performed after electrolysis at 500 mA current in a 500 mL of 30 mM NaCl electrolyte.

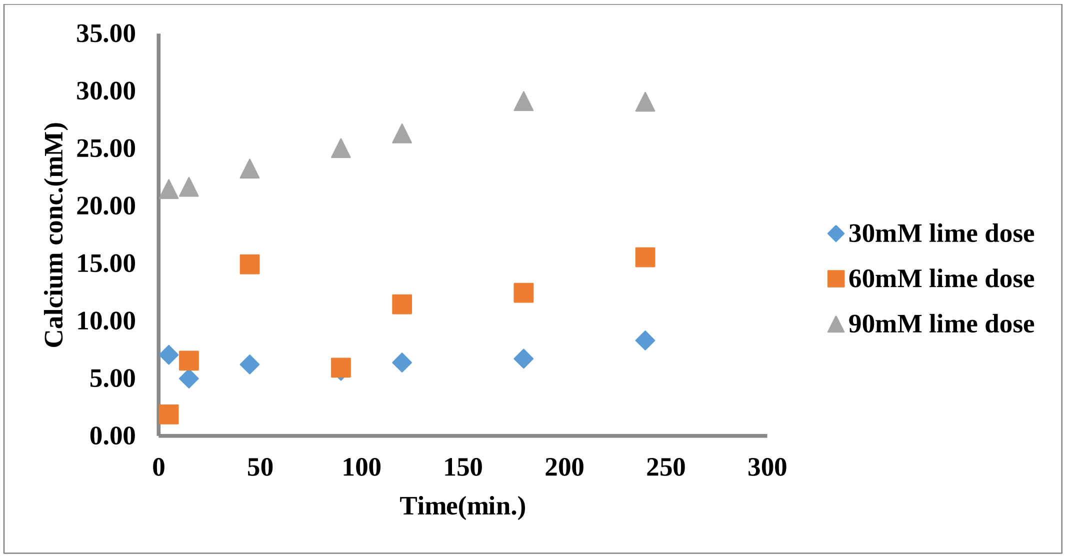


Figure 10 Calcium concentration during advanced softening experiment performed after electrolysis at 500 mA current in a 500 mL of 30 mM NaCl electrolyte.

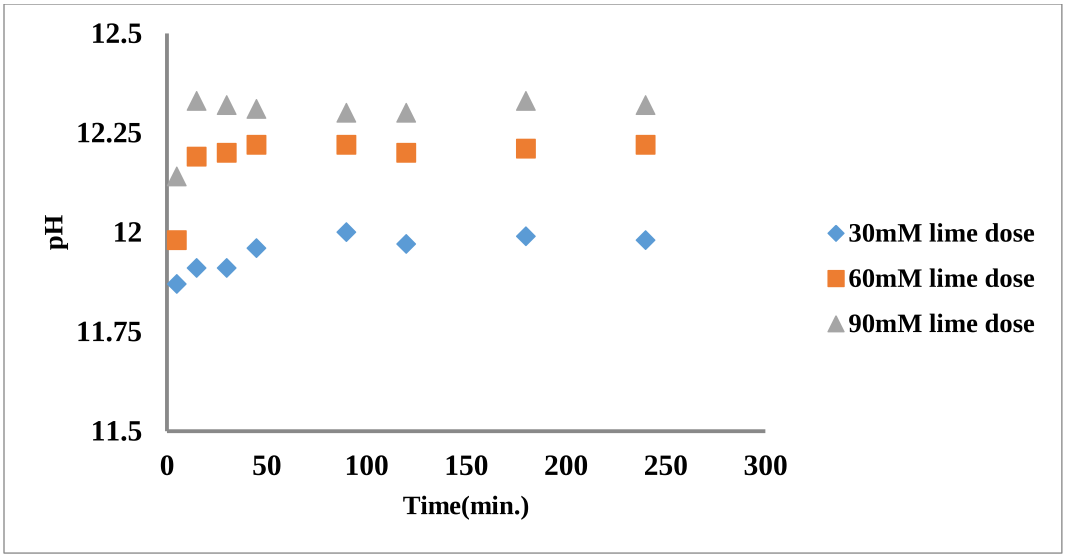


Figure 11 pH during advanced softening experiment performed after electrolysis at 500 mA current in a 500 mL of 30 mM NaCl electrolyte. Initial pH after electrolysis was observed to be 8.8.

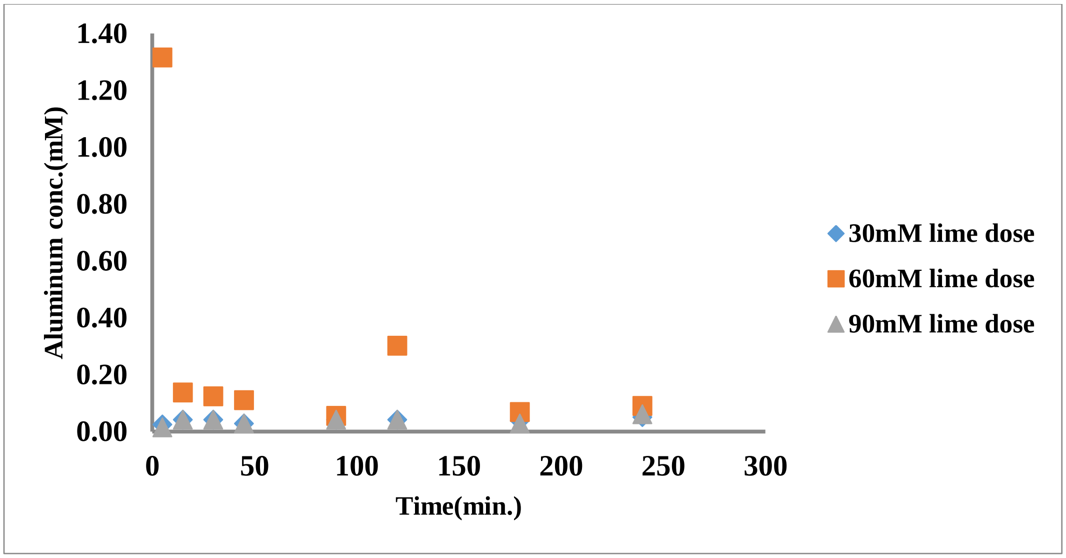


Figure 12 Aluminum concentration during lime softening experiment performed after electrolysis at 500 mA current in a 500 mL of 30 mM NaCl electrolyte. Initial Al. concentration after electrolysis was measured to be16.2 mM

4.2.3 Effect of lime dose at fixed current of 1000 mA

Like the previous experiment with 500 mA, similar experiments involving electrolysis and lime softening was performed but with current of 1000 mA to get the desired aluminum concentration of 30 mM Different lime doses (30 mM, 60 mM, 90 mM) were added to the solution. Figure 13 shows that final chloride concentrations at 30 mM lime dose were similar to the obtained concentrations at 500 mA current indicating that chloride removal was limited by the inadequate concentration of calcium. However more than 50% chloride removal was observed at 60 mM and 90 mM lime doses. This indicates that chloride concentration depends on both lime and aluminum dose which confirms that chloride is removed by precipitation of calcium chloroaluminate solid. Minimum chloride concentrations achieved at 60 mM and 90 mM lime doses were 9.5 mM (68.9% removal) and 9.3 mM (69.4% removal), respectively, after reaction time of 4 hrs. It was observed that chloride removal increased with increasing lime dose and its removal efficiency was almost twice at 60 mM lime dose of that obtained at 30 mM lime dose. However, with further increase of lime dose from 60 mM to 90 mM, chloride removal efficiency was not increased appreciably. Therefore for 30mM chloride concentration, 1000 mA current and 60 mM lime dose was the preferred dose.

Similar trend was observed for final calcium concentration to that obtained at 500 mA. However, final calcium concentrations at 1000 mA current (30 mM aluminum) (Figure 14) were much lower than the corresponding concentrations at 500 mA current (15 mM aluminum). This is because at high aluminum dose, there was enough aluminum in the reactor to react with calcium and form solids.

The behavior of pH (Figure 15) was similar to that at 500 mA current pH increases from 8.7±0.05 to 12.2±0.10 very quickly and then remained almost constant until the end of the experiment. Soluble aluminum is negligible in this case as well (Figure 16).

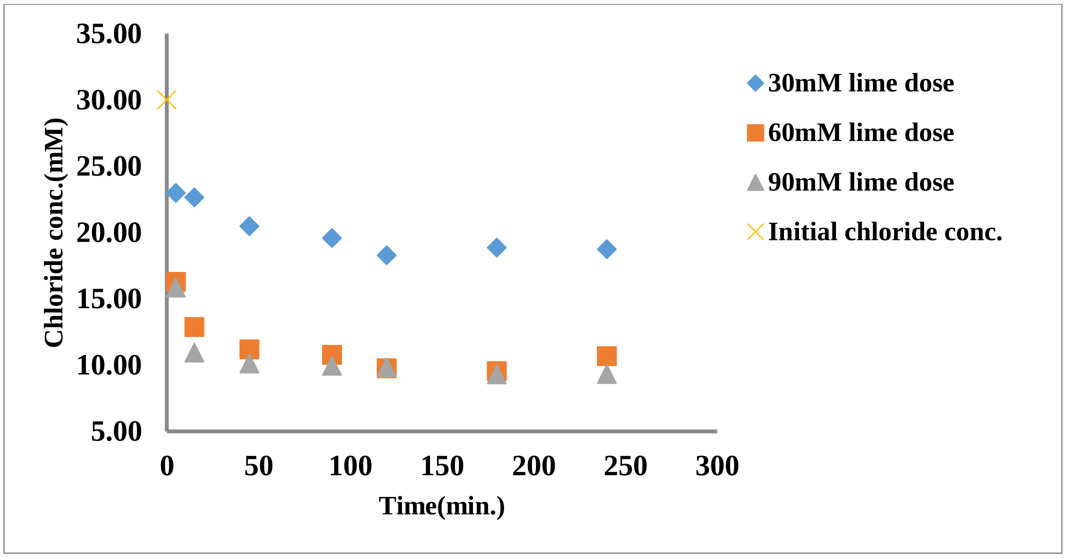


Figure 13 Removal of chloride during lime softening experiment performed after electrolysis at 1000 mA current in a 500 mL of 30 mM NaCl electrolyte.

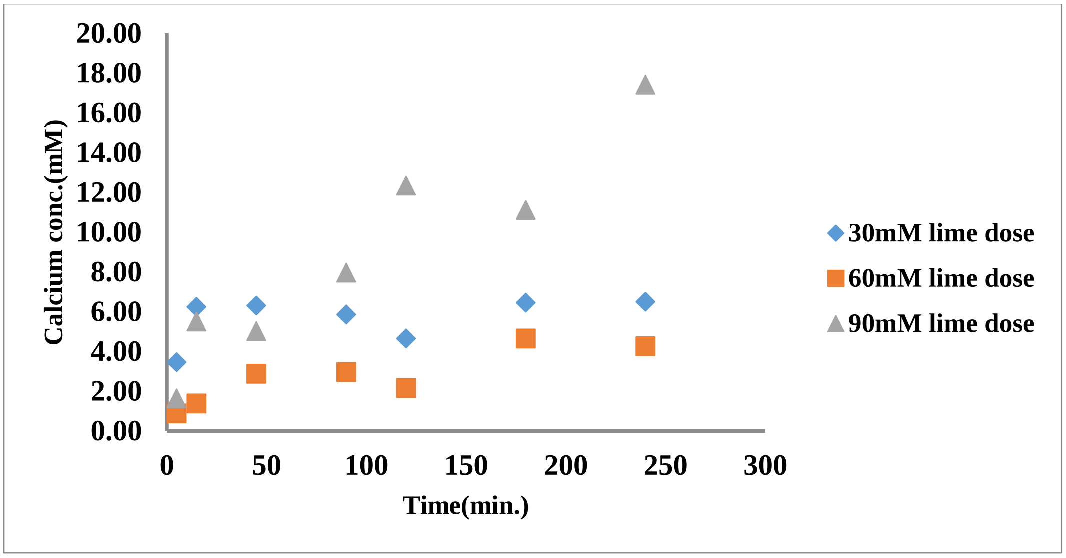


Figure 14 Calcium concentration during lime softening experiment performed after electrolysis at 1000 mA current in a 500 mL of 30 mM NaCl electrolyte

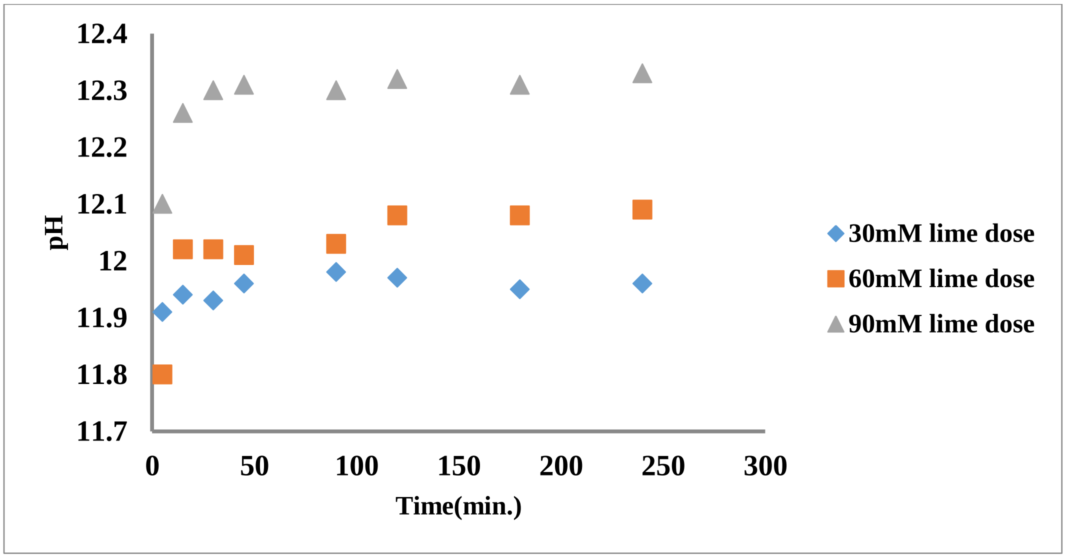


Figure 15 pH during lime softening experiment performed after electrolysis at 1000 mA current in a 500 mL of 30 mM NaCl electrolyte. . Initial pH after electrolysis was observed to be 8.7.

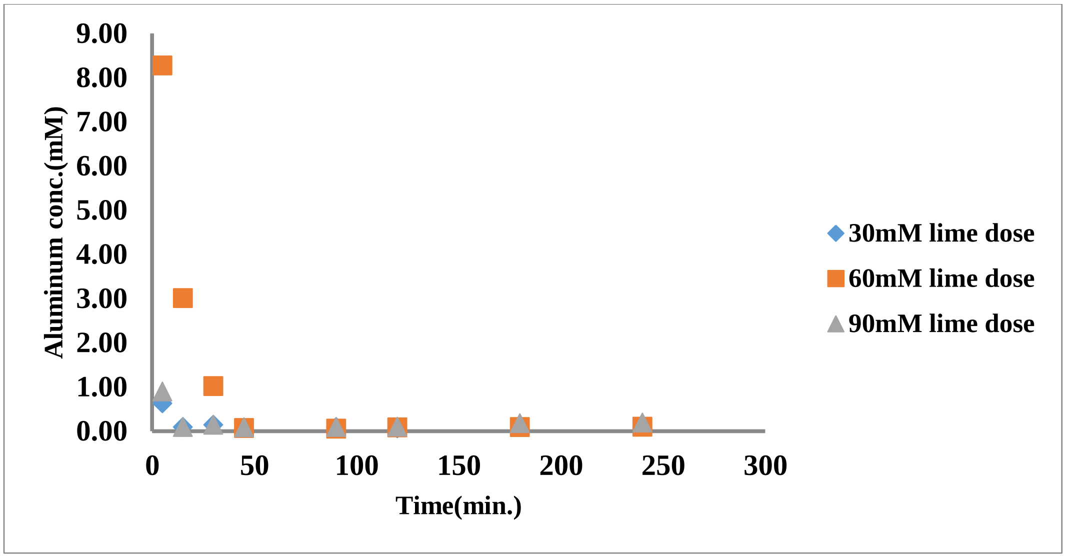


Figure 16 Aluminum concentration during lime softening experiment performed after electrolysis at 1000 mA current in a 500 mL of 30 mM NaCl electrolyte. Initial Al. concentration after electrolysis was measured to be32.9 mM

4.2.4 *Effect of lime dose at fixed current of 1500 mA*

Similar to the previous experiments with 500 mA and 1000 mA, experiments involving electrolysis and lime softening were performed with current of 1500 mA to get the desired aluminum concentration of 45 mM Figure 17 shows that chloride removal at 30 mM and 60 mM lime doses were not substantial with minimum chloride concentration obtained was 18.8 mM and 18.7 mM, respectively after 4 hrs reaction time resulting in 36.5 % and 39.6 % chloride removal, respectively. However at 90 mM lime dose, minimum chloride concentration was 11.7 mM with percentage chloride removal of 62.0 %. Less removal of chloride at 30 mM and 60 mM lime doses indicates that chloride removal was controlled by lime dose. Comparing results obtained at 45 mM aluminum with corresponding results at 30 mM aluminum shows that less chloride is removed at 45 mM aluminum than at 30 mM. This could be due to a formation of other Ca-Al-OH solid phases that are promoted by high aluminum to calcium ratio.

Behavior of calcium, pH and aluminum (Figure 18, Figure 19 and Figure 20, respectively) was similar to that obtained at other investigated currents.

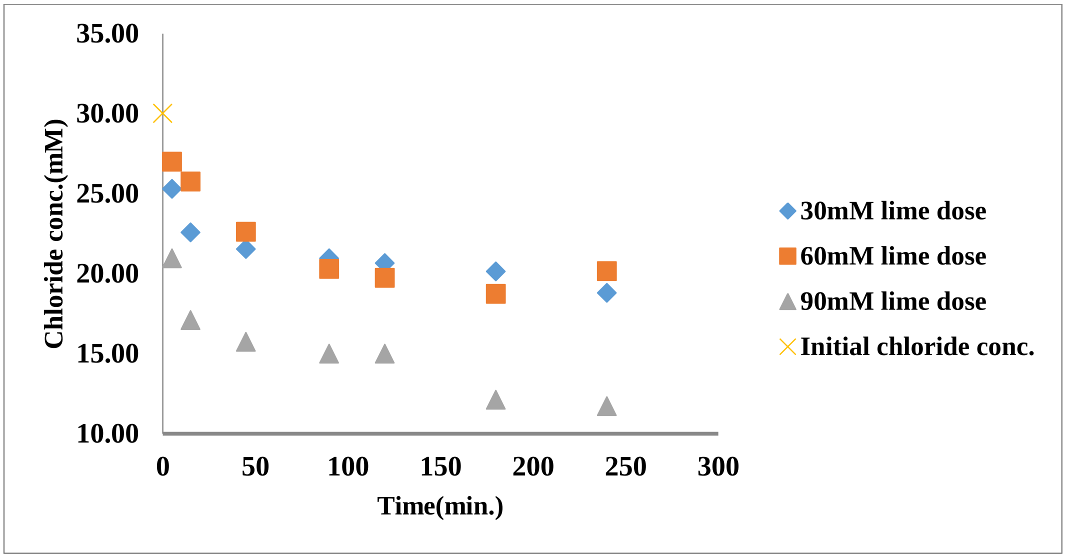


Figure 17 Removal of chloride during lime softening experiment performed after electrolysis at 1500 mA current in a 500 mL of 30 mM NaCl electrolyte.

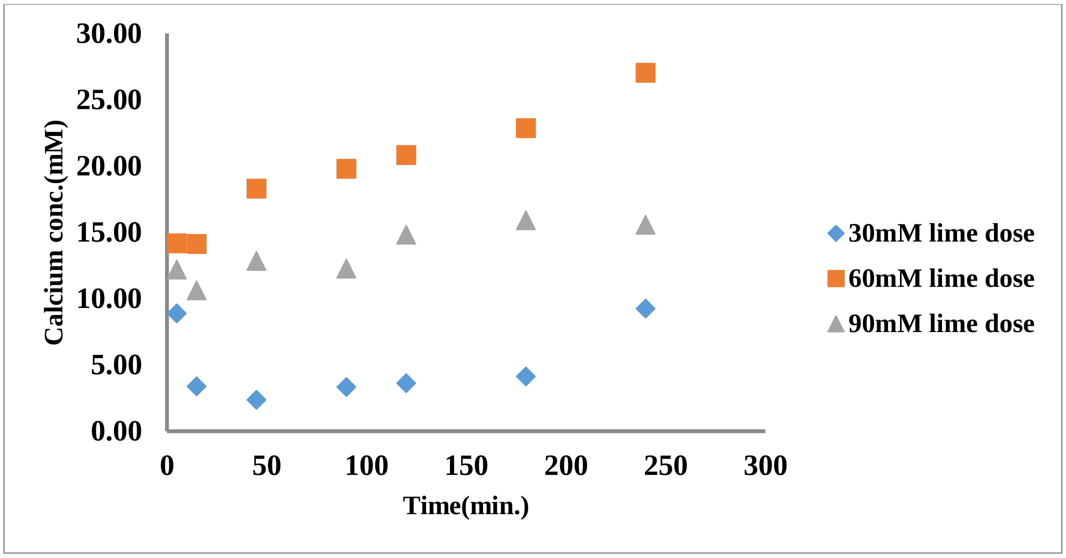


Figure 18 Calcium concentration during lime softening experiment performed after electrolysis at 1500 mA current in a 500 mL of 30 mM NaCl electrolyte.

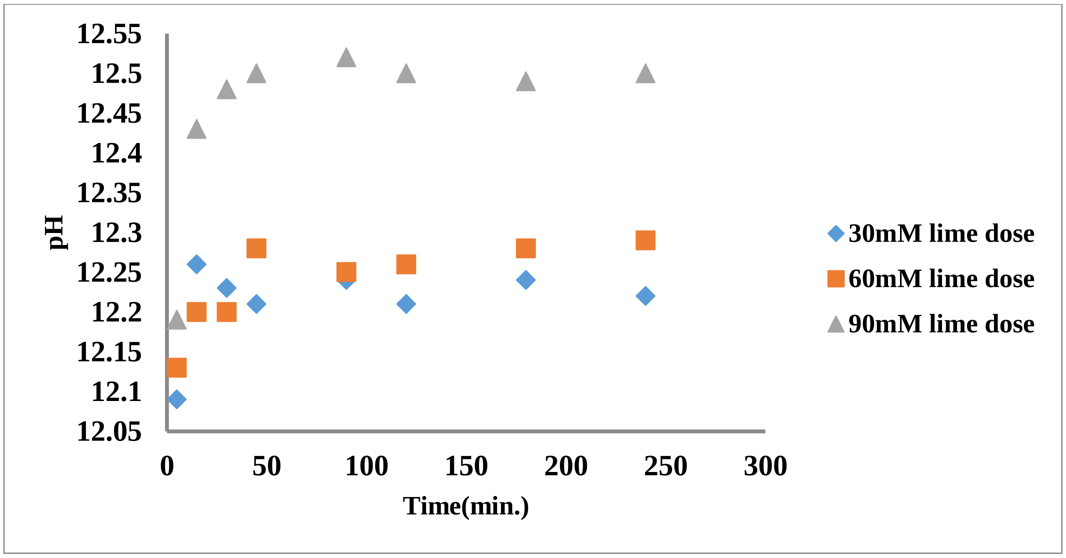


Figure 19 pH during lime softening experiment performed after electrolysis at 1500 mA current in a 500 mL of 30 mM NaCl electrolyte. Initial pH after electrolysis was observed to be 8.8.

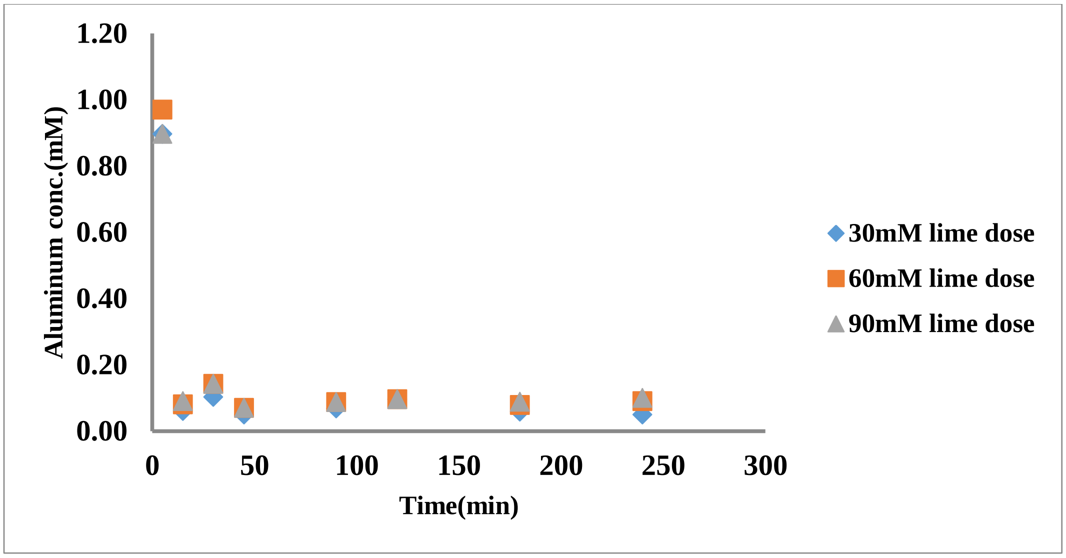


Figure 20 Aluminum concentration during lime softening experiment performed after electrolysis at 1500 mA current in a 500 mL of 30 mM NaCl electrolyte. . Initial Al. concentration after electrolysis was measured to be 47.6 mM

4.3 Equilibrium characteristics of chloride removal

Figure 21 and Figure 22 summarize final chloride concentration and removal efficiency, respectively, at different lime and aluminum doses. Chloride removal efficiency at 500 mA current (15 mM aluminum dose) remains almost constant for all lime doses signifying that aluminum concentration in the solution is less than the minimum required concentration for maximum chloride removal. However, it was evident that for 1000 mA current, chloride removal efficiency increases with lime dose suggesting that at lower lime dose, calcium was not sufficient enough to precipitate the solid. For 60 mM lime dose, it shows the optimum removal with 1000 mA current. The efficiency further increases with increase in lime dose from 60 mM to 90 mM but not on proportion of the additional lime. Therefore 1000 mA current with 60 mM lime dose is the optimum combination to remove chloride from initial 30 mM chloride solution.

The mechanism of chloride removal was assumed to be by precipitation of calcium chloroaluminate ($Ca_4Al_2Cl_2(OH)_{12}$ solid. This means that for 1 mM of calcium removed, 0.5 mM of aluminum and 0.5 mM of chloride should be removed. According to the stoichiometry, the ratio of aluminum removed to chloride removed must be one and the ratio of calcium removed to chloride removed must be two. However, experimental results showed deviation from the stoichiometry of calcium chloroaluminate precipitation. Figure 23 and Figure 24 show that the ratios of aluminum removed and calcium removed to chloride removed, respectively, are above the stoichiometric ratios. The deviation from the theoretical stoichiometry could be attributed to the fact that other Ca-Al solids which does not contain chloride are formed along with calcium chloroaluminate solid. Previous researchers [22] reported that these solids are tetracalcium hydroxyaluminate ($Ca_4Al_2(OH)_{14}$) and tricalcium hydroxyaluminate ($Ca_3Al_2(OH)_{12}$). Ratio of aluminum dose to lime dose above 0.5 would favor the formation of tricalcium hydroxyaluminate over tetracalcium hydroxyaluminate and calcium chloroaluminate. This explains low chloride removal at aluminum dose of 45 mM compared to that at 30 mM at the same lime dose as shown in Figure 25. As per the theoretical stoichiometry, the ratio of calcium removed to aluminum removed should be two. However it was found from Figure 25 that when there was sufficient aluminum dose present to react with all the calcium in the solution, the above hypothesis is followed. When the ratio of aluminum dose to lime dose = 0.5, the experimental data falls near the predicted theoretical line. Figure 26 shows the relationship between final calcium concentration and the final aluminum concentrations.

Figure 27 shows that maximum removal of chloride was achieved when the lime dose to aluminum dose was 2 which is consistent with the stoichiometric ratios in the calcium chloroaluminate solid.

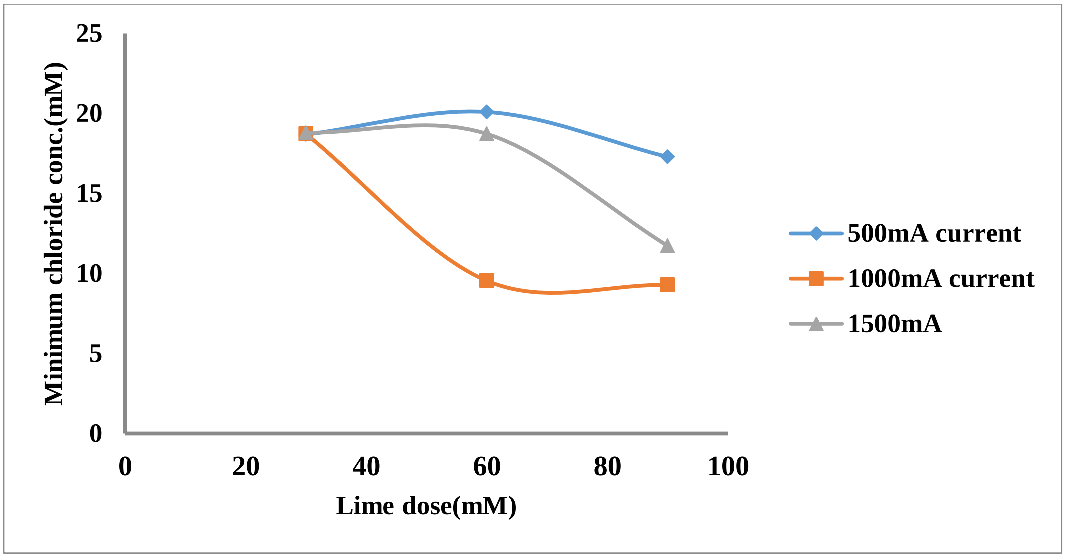


Figure 21 Minimum chloride concentration (mM) obtained vs lime dose (mM) at different current for initial chloride concentration of 30 mM.

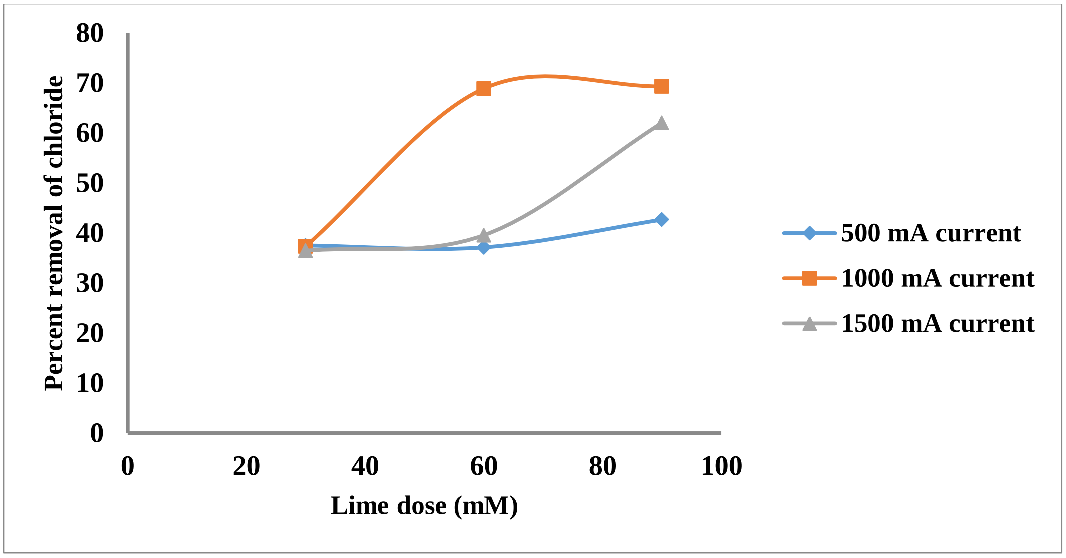


Figure 22 Percentage removal of chloride vs lime dose (mM) after advanced softening experiment for 500 mA, 1000 mA, and 1500 mA current for initial chloride concentration of 30 mM.

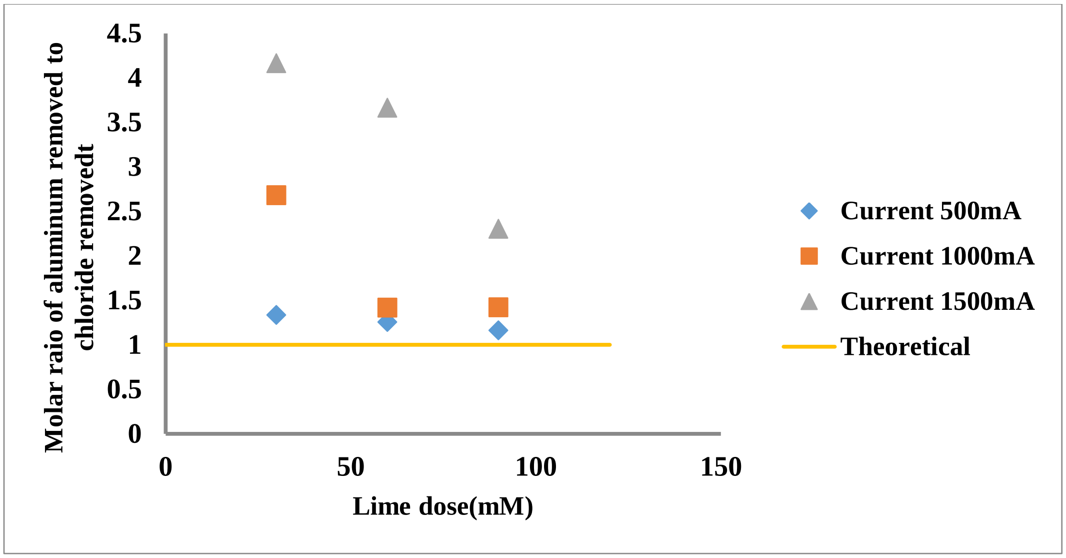


Figure 23 Effect of current and lime dose on molar ratio of aluminum removed to chloride removed.

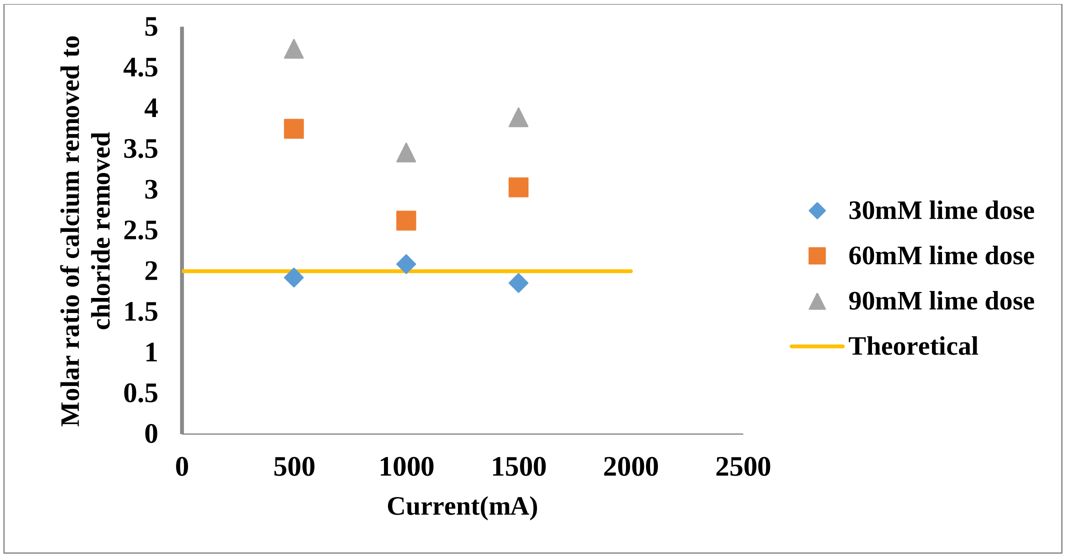


Figure 24 Effect of current and lime dose on molar ratio of calcium removed to chloride removed.

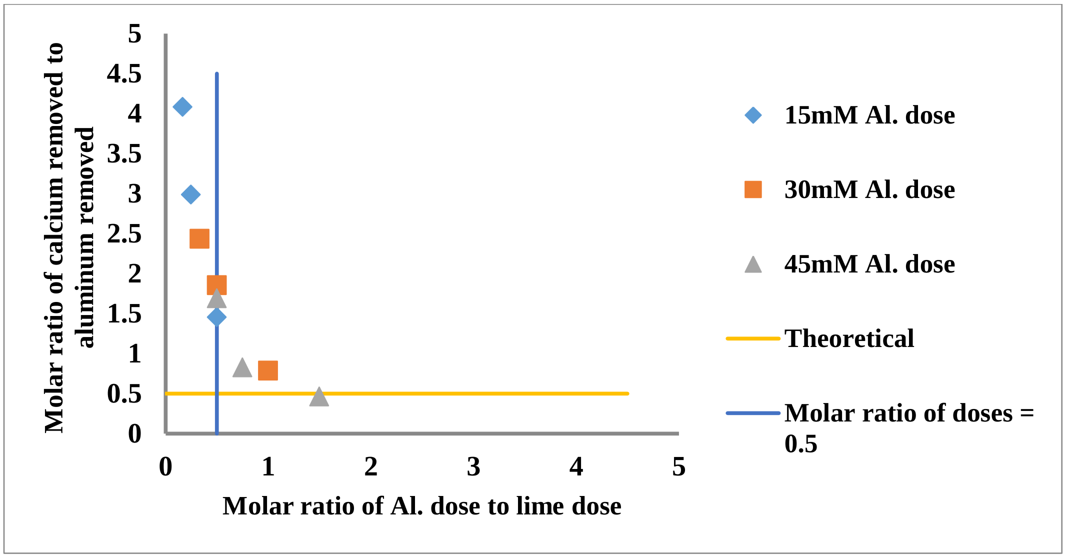


Figure 25 Effect of ratio of Al. dose to lime dose on molar ratio of calcium removed to Al. removed.

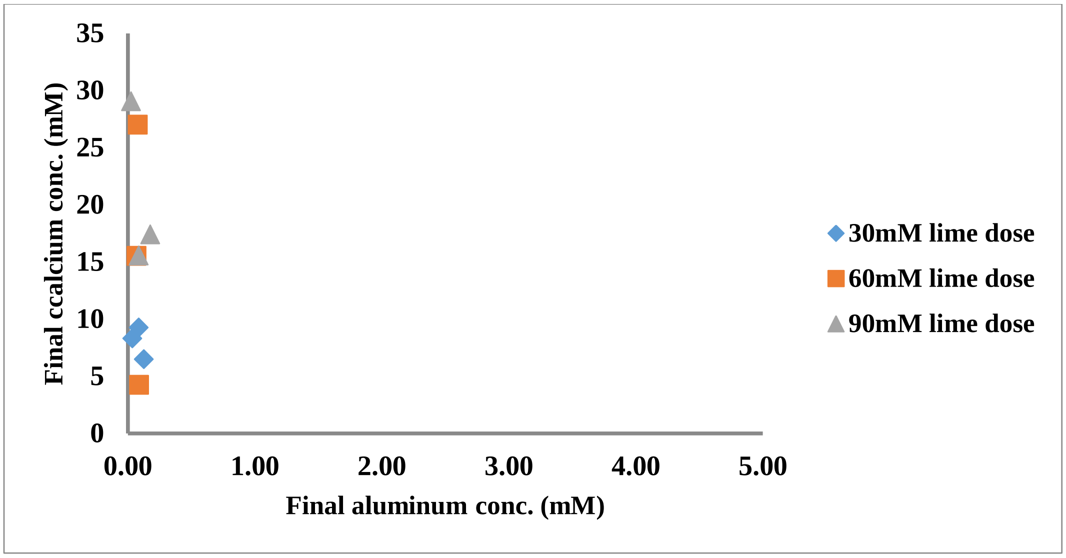


Figure 26 Relationship between final calcium concentration and final aluminum concentration.

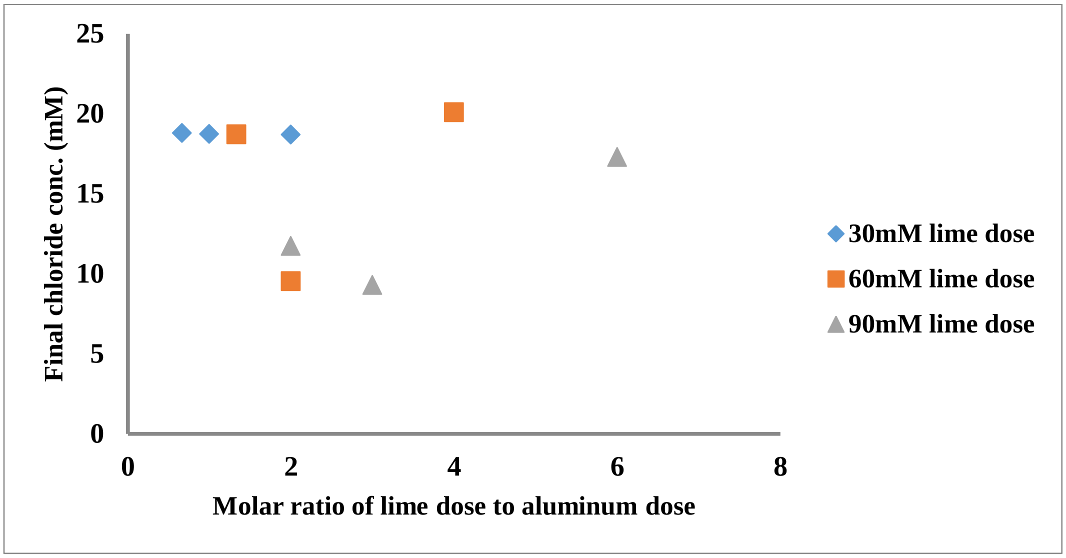


Figure 27 Minimum chloride concentration obtained vs molar ratio of lime dose to Al. dose in a 500 mL of 30 mM initial NaCl concentration.

4.4 Effect of addition of lime at the beginning of electrolysis

Two experiments were conducted where 90 mM lime dose was added at the beginning of electrolysis at 1500 mA and 2000 mA current. It was observed that for 1500 mA current and 90 mM lime dose, chloride removal efficiency was almost similar to what was obtained when lime was added after electrolysis for the same combination of lime dose and current. However, unlike in the case of lime after electrolysis where chloride removal was very fast and instantaneous, Figure 28 shows that in case of lime added before electrolysis, removal of chloride is gradual. This is because chloride removal was controlled by the amount of aluminum dissolved in solution which in turn was a function of time of electrolysis. It was also observed that in the presence of lime, current gradually decreased as the electrolysis proceeded (Figure 29). Final current for the electrolysis performed at 1500 mA initial current for 150 minutes was found to be 680 mA. This could be due to the fact that as electrolysis proceeds, lime starts depositing on the anodic surface which results in electrode passivation and reduces the overall conductivity of the electrolyte.

Due to the gradual decrease in current during the electrolytic process, higher initial current (2000 mA) was employed to balance the decrease in current. It was found that the chloride removal efficiency was better at 2000mA current than at1500 mA current. The minimum chloride concentration which was obtained for 2000 mA current was 8.09 mM for 30 mM of initial chloride concentration. However it was observed that chloride concentration increases with time after minimum chloride concentration was reached. This could be due to the fact that when aluminum to calcium ratio increased, tricalcium hydroxyaluminate precipitation was more favorable than calcium chloroaluminate precipitation. pH was found to be 12.2±0.1 right after the start of electrolysis in the presence of lime and slightly decreased 12±0.1 as electrolysis progressed (Figure 30). It was observed that initially the calcium concentration was high, however as electrolysis progressed, the generated aluminum react with calcium to form the solid resulting in decrease in soluble calcium concentration in the solution (Figure 31).

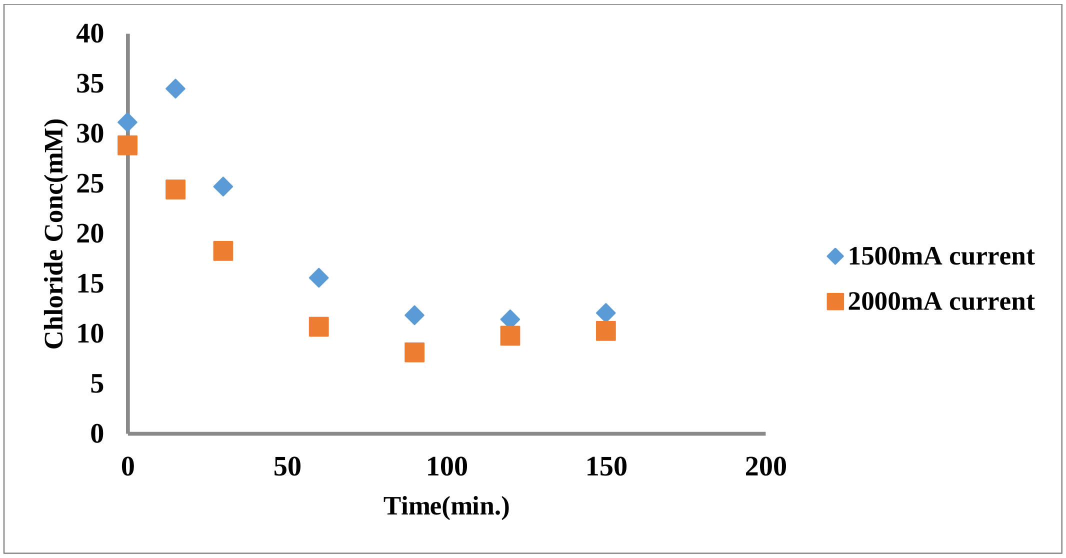


Figure 28 Chloride concentration (mM) vs time (min.) for two current values of 1500 mA and 2000 mA when lime is added at the beginning of electrolysis performed in 500 mL of 30 mM NaCl electrolyte.

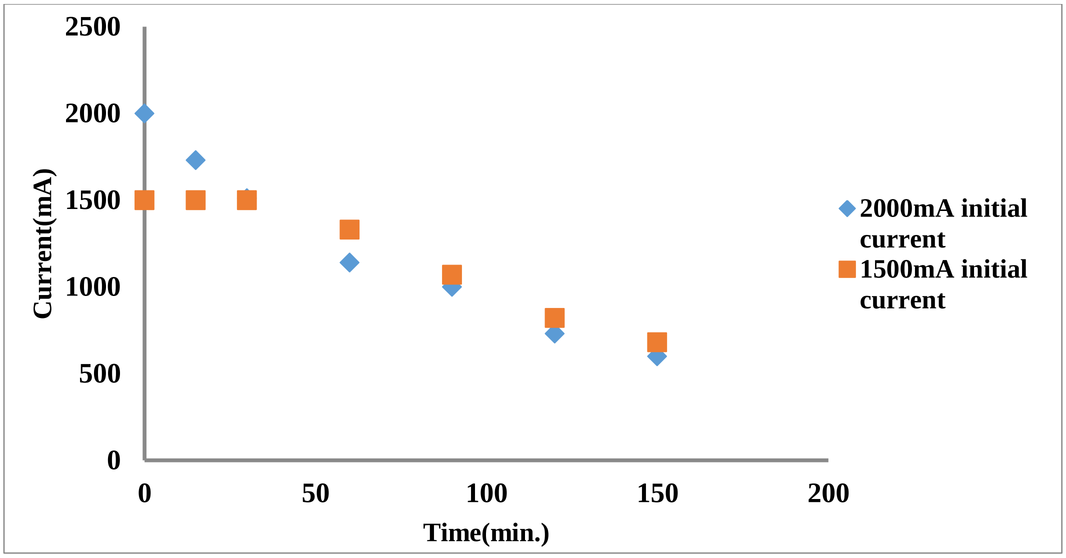


Figure 29 Current (mA) vs time (min.) for two current values of 1500 mA and 2000 mA during electrolysis when lime is added at the beginning of electrolysis performed in 500 mL of 30 mM NaCl electrolyte.

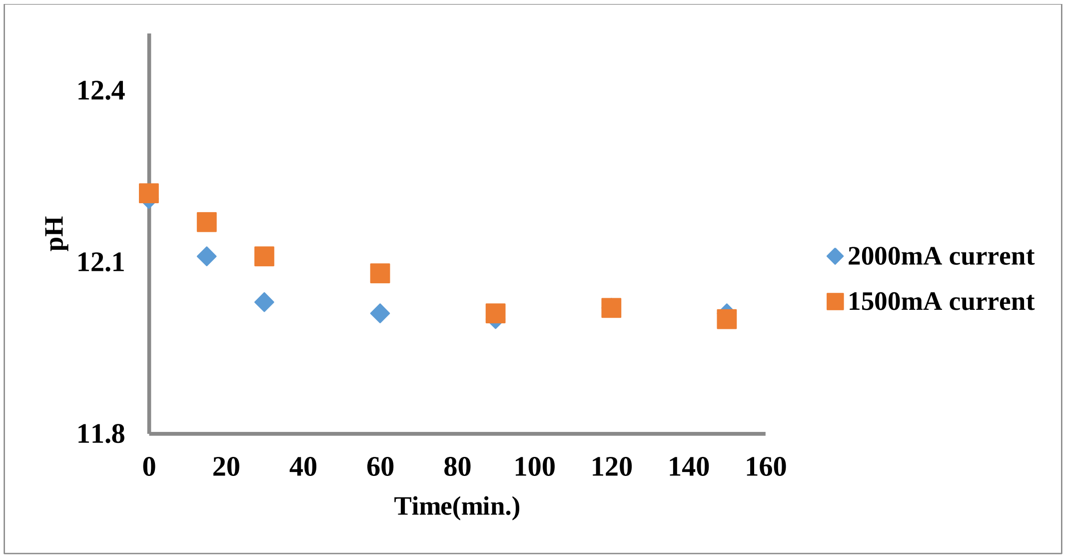


Figure 30 pH vs time (min.) for two current value of 1500 mA and 2000 mA during electrolysis when lime is added at the beginning of electrolysis performed in 500 mL of 30 mM NaCl electrolyte.

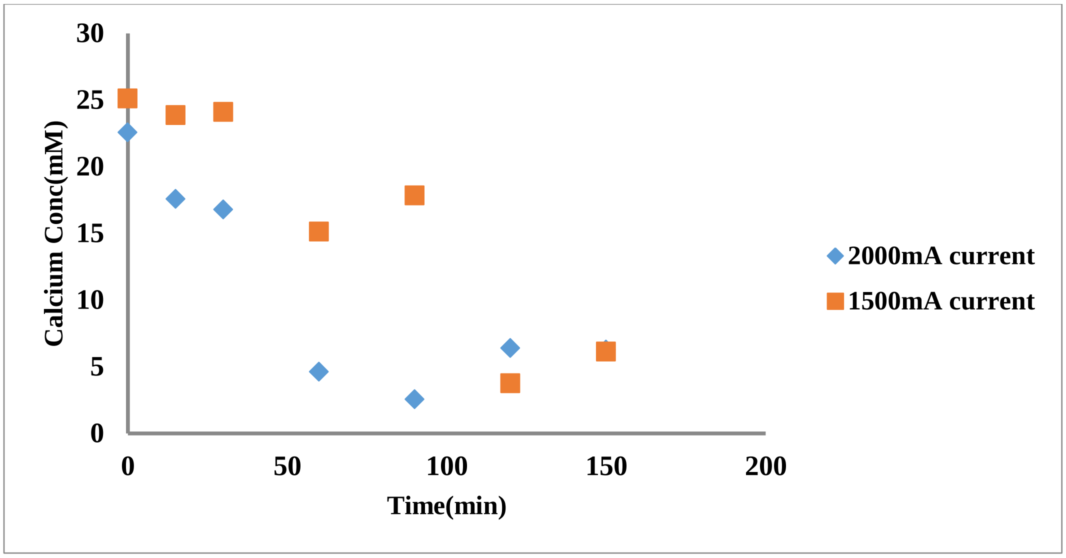


Figure 31 Calcium concentration (mM) vs time (min.) for two current values of 1500 mA and 2000 mA when lime is added at the beginning of electrolysis performed in 500 mL of 30 mM NaCl electrolyte.

4.5 Regeneration of precipitated solids

Multiple experiments were performed to investigate the feasibility of regenerating calcium and aluminum from the precipitated solids and recycling them to partially substitute lime and aluminum reagents. Precipitated solids are layered double hydroxides mainly made of calcium chloroaluminate and calcium hydroxyaluminate[22] . The structure of the solids includes $[Ca_2Al(OH)_6]^+$ as the cationic part and Cl^- or OH^- as the anionic part. Earlier studies have shown that carbonate has higher tendency than chloride ions to take the anionic part [21]. Therefore, if the solids reacted with carbonate source, it is expected that carbonate replaces chloride. Also, lowering pH to a range of pH 9.0-10.5 in the presence of carbonate can result in the formation of calcium carbonate solid. Then the calcium carbonate can go through calcination process to form calcium oxide and release carbonate in the form of carbon dioxide. However, reducing the pH to around pH10.0 did not result in the formation of calcium carbonate and most of the precipitated solids remained insoluble without significant release of chloride from the solids. Additional reduction of pH to around pH 7 can result in precipitation of aluminum in the form of aluminum hydroxide.

Carbon dioxide gas was used as the carbonate source to replace the chloride in the solid by purging the solid slurry with carbon dioxide gas while monitoring pH. Precipitated solids from experiments with initial conditions of 30 mM chloride concentration, 60 mM lime dose, and 1000 mA current were collected and used in the regeneration experiments. After CO_2 purging, the pH of the solid was brought down to 6.5, 7.5, 8.5 in three different experiments, respectively. The obtained solids after CO2 purging was dried and analyzed for chloride, aluminum and calcium concentration. Figure 32 shows that chloride was reasonably removed from the solids. There was also decrease in aluminum and calcium amounts in the solid compared to initial amounts but it was much less reduction compared to chloride (Figure 33 and Figure 34, respectively).

The regenerated solid was re-used in the advanced softening experiments for chloride removal from a solution containing 30 mM chloride concentration. Results of these experiments showed that no removal of chloride was obtained (Figure 35). Additional research is warranted to further modify solids regeneration experiments and investigate chloride removal with regenerated solids.

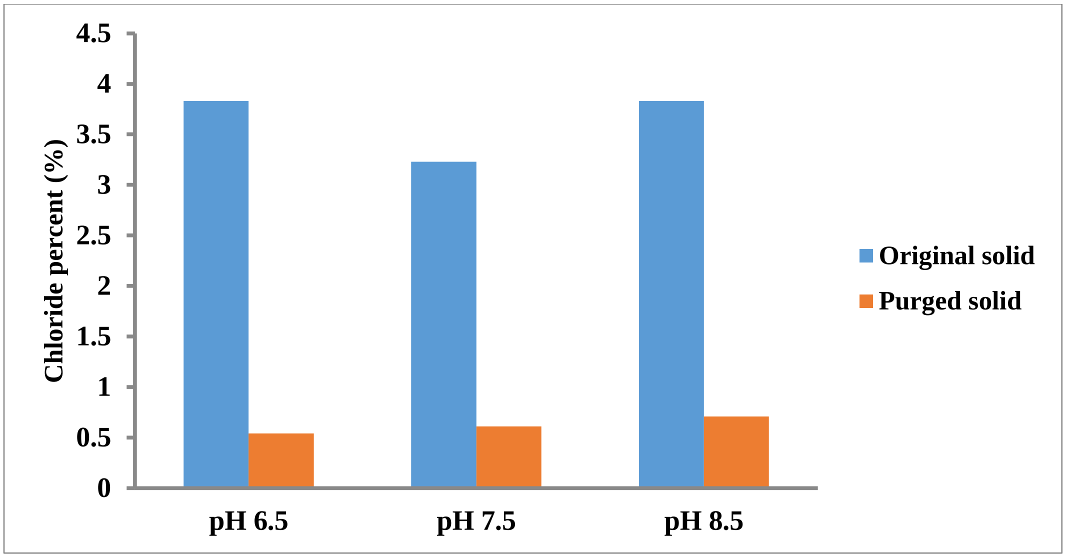


Figure 32 Chloride percent by mass in the purged and unpurged solids at three different pH

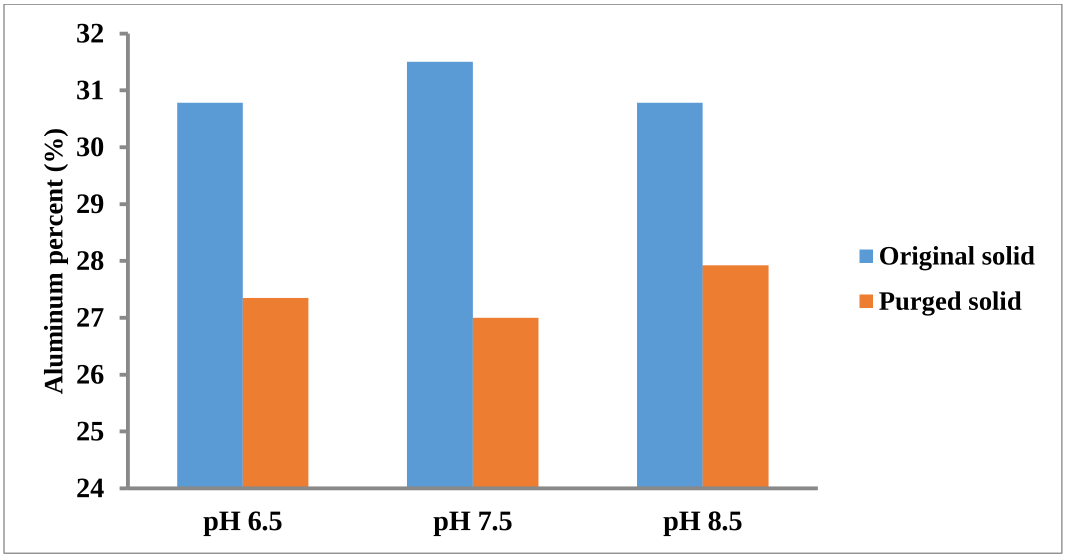


Figure 33 Aluminum percent by mass in the purged and unpurged solids at three different pH.

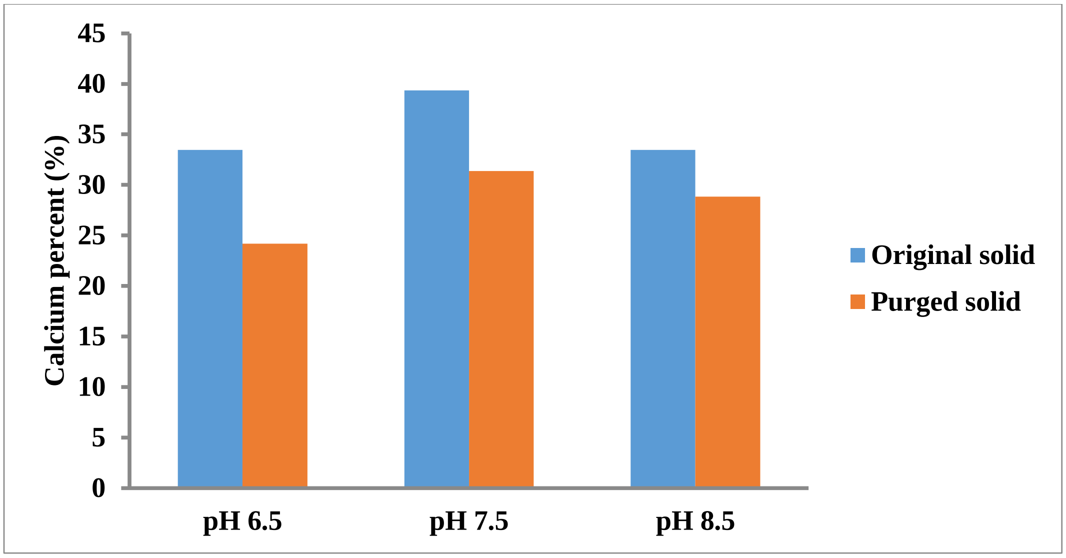


Figure 34 Calcium percent by mass in the purged and unpurged solids at three different pH

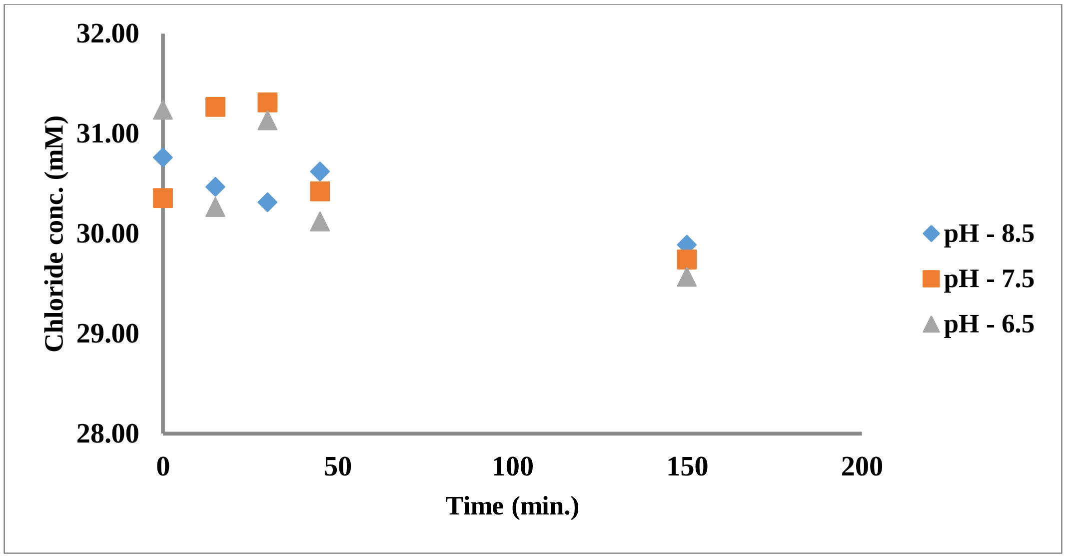


Figure 35 Chloride removal with time using the regenerated solid.

5. CONCLUSIONS AND RECOMMENDATIONS

Advanced softening process using electrochemically generated aluminum was investigated for chloride removal from water. Experimental program was conducted to study the equilibrium conditions and kinetics of chloride removal by precipitation of calcium chloroaluminate. Effect of current on the mass of aluminum produced during electrolysis was evaluated to ascertain the electrolysis conditions for generating the desired amount of aluminum hydroxide. Result of electrolysis showed that for low current and smaller time of electrolysis, the experimental results follow Faraday's law closely, however for higher current and larger time of electrolysis, the experimental results showed positive deviations from the Faraday's law. There was increase in pH as electrolysis progressed approaching final pH in the range of 8-8.4 for different current values. Electrolysis at currents of 500 mA, 1000 mA, and 1500 mA for 73 min were required to generate aluminum concentrations of 15, 30, and 45 mM, respectively.

Multiple experiments were conducted to study the effect of lime dose and aluminum dose on chloride removal. These experiments were performed using fixed initial concentration of 30 mM NaCl. Different combination of lime doses of 30 mM, 60 mM and 90 mM and aluminum doses of 15 mM, 30 mM, 45 mM were investigated to obtain optimum dose for maximum chloride removal and characterize equilibrium conditions.. Optimum chloride removal was observed at lime dose of 60 mM and aluminum dose of 30 mM which are corresponding to molar ratios of 2:1 and 1:1 of initial chloride concentration to aluminum dose respectively. The removal efficiency of chloride at this optimum dose reaches 69 %. The equilibrium pH for the maximum chloride removal was observed at pH 12.1-12.2.

Precipitation of calcium chloroaluminate was hypothesized to control the chloride removal primarily. However, ratios of calcium and aluminum removed to chloride removed from the solution were higher than theoretical ratios of the calcium chloroaluminate precipitation reaction indicating formation of other Ca-Al-OH solids. Formation of tricalcium hydroxyaluminate ($Ca_3Al_2(OH)_{12}$) and tetracalcium hydroxyaluminate ($Ca_4Al_2(OH)_{14}$) among other solids justifies the experimental results.

Experiments were also conducted where lime was added at the beginning of electrolysis to study the chloride removal simultaneously with aluminum generation in one step. It was observed that chloride removal was slow as compared to the previous experiments where lime was added at the end of electrolysis because the removal was controlled by the amount of aluminum released with time. However the final chloride removal efficiency was almost similar to when lime was added after the completion of electrolysis. Also, the current value gradually decreases during the course of experiment when lime was added before hydrolysis. The reason could be the deposition of lime over the surface of the anode which must have increased the electrolytic resistance between the electrodes. It was inferred that this method of chloride removal is not preferable due to operational constraints which includes deposition of solid on electrode surface. The optimum value of current could also be not ascertained in this method because current was found to decrease during the process of electrolysis.

An attempt was made to regenerate the precipitated solids and recycle calcium and aluminum for chloride removal. Results showed that there was appreciable removal of chloride from the solid after regeneration. However, when the regenerated solids were recycled for chloride removal, no chloride removal was observed.

One of the preliminary focuses of future research should be to further study regeneration of precipitated solids to identify optimal regeneration conditions which can result in maximum recovery of calcium and aluminum and reuse them by fully or partially replacing lime and aluminum reagents required for chloride removal. The reuse of solids will make this method of chloride removal using electrochemically generated aluminum capable of maintaining a sustainable environment through resource conservation. It will not only reduce the disposal of sludge as a result of the process, but also will drastically lower down the operational cost of the process. Other methods like treating the solid with measured concentration of sodium carbonate solution should also be studied. Mixing the solid with sodium carbonate solution could replace the chloride ions with carbonate ions which could be further calcined to get calcined double layered hydroxides. The calcined solid could be further studied for its reusability.

The solid formed as a result of the chloride removal experiments are layered double hydroxides (LDHs) which are widely used in anion exchange and adsorption experiments. Therefore future research should focus on using this solid as an anion exchanger or adsorbent for removing varied types of contaminants. Studies should also be performed to check the potential usage of these solids for other applications as well.

Research should also be done to check the use of iron electrodes in place of aluminum electrodes during electrolysis, and comparative study could be done between the chloride removal results using iron electrodes and aluminum electrodes. It could also give the idea on reusability of the solids when iron is used.

REFERENCES

1. Neff, J.M., K. Lee, and E.M. DeBlois, Produced water: overview of composition, fates, and effects, in produced water: environmental risks and advances in mitigation technologies, K.L.a.J. Neff, Editor 2011: Springer Science+Business Media, LLC, 233 Spring Street, New York, USA.

2. Rocha, D.L. and F.R.P. Rocha, An environmentally friendly flow-based procedure with photo-induced oxidation for the spectrophotometric determination of chloride in urine and waters. Microchemical Journal, 2013. **108**: p. 193-197.

3. Abu-Arabi, M.K., S. Emeish, and B.I. Hudaib, Chloride removal from Eshidiya phosphate mining wastewater. Desalination and Water Treatment, 2013. **51**: p. 1634-1640.

4. Kameda, T., et al., The simultaneous removal of calcium and chloride ions from calcium chloride solution using magnesium–aluminum oxide. Water Research 2003. **37**: p. 4045–4050.

5. Lv, L., et al., Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies. WATER RESEARCH, 2006. **40**: p. 735-743.

6. Wu, X., Z. Liu, and X. Liu, Chloride ion removal from zinc sulfate aqueous solution by electrochemical method. Hydrometallurgy, 2013. **134-135**: p. 62-65.

7. Paz-Garcíaa, J.M., et al., Simulation-based analysis of the differences in the removal rate of chlorides,nitrates and sulfates by electrokinetic desalination treatments. Electrochimica Acta, 2013. **89**: p. 436-444.

8. Matson, J.V. and T.G. Harris, Zero discharge of cooling water by sidestream softening. J. water Pollut. Control Fed, 1979. **51**(11),2602.

9. T, W.G., Cooling tower salinity optimization via side stream Desalination. Cooling Tower Institute, 1977.

10. Liang Lva, et al., Removal of chloride ion from aqueous solution by ZnAl-NO3 layered double hydroxides as anion-exchanger. Journal of Hazardous Materials, 2009. **161**: p. 1444–1449.

11. Kameda, T., et al., New method of treating dilute mineral acids using magnesium–aluminum oxide. Water Research 2003. **37**: p. 1545–1550.

12. Batchelor, B., M. McDevitt, and D. Chan, Removal of sulfate from recycled cooling water by the ultra-high lime process, In Proceedings Water Reuse Symposium III1985: AWWA Research Foundation,Denver.

13. Schaezler, D.J., Precipitation of calcium aluminates and sulfoaluminates from water. J. Water Pollut. Control Fed., 1978. **50**(7).

14. Nebgen, J.W., E.P. Shea, and S.T. Chin, The alumina-lime-soda water treatment process, M.R. Institute, Editor 1973: Office of Saline Water Research and Development,Kansas City, Missouri.

15. Martı´nez-Huitle, C.A. and E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. Applied Catalysis B: Environmental, 2009. **87**: p. 105-145.

16. Mansouria, K., et al., Application of electrochemically dissolved iron in the removal of tannic acid from water. Chemical Engineering Journal, 2011. **172**: p. 970-976.

17. Zhua, B., D.A. Clifforda, and S. Chellama, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes. Water Research, 2005. **39**: p. 3098–3108.

18. Parthasarathy, N., J. Buffle, and W. Haerdi, Combined use of calcium salts and polymeric aluminium hydroxide for defluoridation of waste waters. Water Research, 1986. **20**: p. 443-448.

19. Kameda, T., et al., Treatment of hydrochloric acid with magnesium–aluminum oxide at ambient temperatures. Separation and Purification Technology, 2006. **51**: p. 272-276.

20. Tronto, J., et al., Conducting polymers / layered double hydroxides intercalated nanocomposites in Materials Science - Advanced Topics. Yitzhak Mastai (Ed.). 2013. Available from: http://www.intechopen.com/books/materials-science-advanced-topics/conducting-polymers-layered-double-hydroxides-intercalated-nanocomposites

21. Kameda, T., et al., The removal of chloride from solutions with various cations using magnesium–aluminum oxide. Separation and Purification Technology 2005. **42**: p. 25–29.

22. Abdel-Wahab, A. and B. Batchelor, Chloride removal from recycled cooling water using ultra-high lime with aluminum process. Water Environment Research, 2002. **74**: p. 256-263.

23. Batchelor, B., et al., Technical and economical feasibility of ultra-high lime treatment of recycled cooling water. J. Water Pollut. Control Fed., 1991. **63**(7).

24. Batchelor, B. and M. McDevitt, An Innovative process for treating recycled cooling water. J. Water Pollut. Control Fed, 1984. **56**(10).

25. Batchelor, B., M. McDevitt, and D. Chan. Removal of sulfate from recycled cooling water by the ultra-high lime process. In Proceedings of the Water Reuse Symposium III. 1985. AWWA Research Foundation, Denver, Colo.

26. Abdel-Wahab, A.I.A., The ultra-high lime with aluminum process for removing chloride from recirculating cooling water, 2003, Texas A&M University.

27. Mohammad, M.E. and S. Muttucumaru, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes

28. Rajeshwar, K., J. Ibanez, and G.M. Swain, Electrochemistry and the environment,. J. Appl. Electrochem, 1994: p. 1077–1091.

29. Crujera, A. Electro-Etching Made Easy,2013. Available from: http://www.nontoxicprint.com/electroetching.htm.

30. Birnin-Yauri, U.A. and F.P. Glasser, Friedel's salt, Ca2Al(OH)6(Cl,OH)2H2O: its solid solutions and their role in chloride binding. Cem. Concr. Res., 1998. **28,**1713.

31. Stronach, S.A., Thermodynamic modeling and phase relations of cementitious systems, 1996, University of Aberdeen, Aberdeen, UK.

32. Pöllmann, H. Solid solution of complex calcium aluminate hydrates containing Cl-, OH- and CO32- anions. in 8th Intl Symp. 1986. Rio de Janeiro, Brazil,.

33. Turriziani, R., The calcium aluminate hydrates and related compounds, in the chemistry of cements1960: H.F.W. Taylor,Academic Press: London.

34. Rapin, J.P., et al., Structural transition of Friedel’s salt 3Ca).Al2O3.CaCl2.10H2O studied by synchrotron powder diffraction. Cem. Concr. Res., 2002. **32**(513).

35. Cavani, F., F. Trifiro, and A. Vaccari, Hydrotalcite-type anionic clays: preparation,properties and applications. Catal. Today, 1991. **11**: p. 173-301.

36. S., M., Physico-chemical properties of synthesis hydrotalcites in relation to composition. Clays Clay Miner, 1980. **28**: p. 50-56.

37. Glasser, F.P., A. Kindness, and S.A. Stronach, Stability and solubility relationships in AFm phases. Part I: chloride, sulfate, and hydroxide. Cem. Concr. Res., 1999. **29**.

38. A, B.-Y.U. and F.P. Glasser, Friedel's salt, Ca2Al(OH)6Cl,OH)2H20: Its solid solutions and their role in chloride Bindin. Cem. Concr. Res., 1998. **28**.

39. (APHA), A.P.H.A., A.W.W.A. (AWWA), and W.E.F. (WEF), eds. Standard methods for the examination of water and wastewater. 19th Ed ed. 1995, American Public Health Association: Washington, DC.

40. Dean, A.J., Lang's Handbook of Chemistry. 13th Ed. ed1985, NewYork.: McGraw-Hill.

41. Lide, D., CRC Handbook of Chemistry and Physics. 72nd ed1991-1992, Boston, USA: CRC Press, Inc. 8-36.

42. Mansouri, K., et al., Anodic dissolution of pure aluminum during electrocoagulation process: influence of supporting electrolyte, initial pH, and current density. Industrial & Engineering Chemistry Research, 2011. **50**: p. 13362-13372.

43. Trompette, J.L. and H. Vergnes, On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes. J. Hazard. Mater, 2009. **163**: p. 1282–1288.

44. Zaid, B., et al., Effects of pH and chloride concentration on pitting corrosion of AA6061 aluminum alloy. Corros. Sci., 2008. **50**: p. 1841–1847.

45. El Maghraby, A., Corrosion inhibition of aluminum in hydrochloric acid solution using potassium iodate inhibitor. Open Corros. J, 2009. **2**: p. 189–196.

46. Gamagea, N.P. and S. Chellama, Aluminum electrocoagulation pretreatment reduces fouling during surface water microfiltration
in Department of Civil and Environmental Engineering, University of Houston, TX 77204-4003, USADepartment of Chemical and Biomolecular Engineering, University of Houston, TX 77204-4004, USA2011.

47. Mouedhen, G., et al., Behavior of aluminum electrodes in electrocoagulation process. Journal of Hazardous Materials, 2008. **150**: p. 124–135.

48. Mansfeld, F., Tafel slopes and corrosion rates obtained in the pre-Tafel region of polarization curves. Corros. Sci., 2005. **47**: p. 3178–3186.

49. Elsener, B., Corrosion rate of steel in concrete—Measurements beyond the Tafel law. Corros. Sci., 2005. **47**: p. 3019–3033.