

CHLORIDE REMOVAL FROM LANDFILL LEACHATE BY THE ULTRA-HIGH LIME WITH ALUMINUM PROCESS

Gang Chen^{1*}, Peter Grasel², Gary Millington², John Hallas³, Hafiz Ahmad⁴ and
Kamal Tawfiq¹

¹Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering, Tallahassee, FL,

²Florida Department of Environmental Protection, Tallahassee, FL, ³Talquin Electric Company,
Tallahassee, FL, ⁴Department of Civil and Environmental Engineering, Florida State University Panama City
Campus, Panama City, FL, United States

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Abstract:

Besides organic contaminants, nutrients and heavy metals, high concentrations of chloride have also been observed in landfills accepting ash deposition from waste-to-energy applications, which is difficult to be removed in wastewater treatment processes. Chloride may percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil. In plants, chloride tends to accumulate in the tissues, especially the leaves. Conventional removal techniques are not feasible from the cost perspective. In this research, the ultra-high lime with aluminum process was evaluated for chloride removal from landfill leachate by precipitation as calcium chloroaluminate ($\text{Ca}_4\text{Al}_2\text{C}_{12}(\text{OH})_{12}$) in the presence of calcium and aluminum at high pH. Chloride removal was found to be a function of both aluminum concentration and pH. Chloride removal increased with the increase of alum addition until 20 mg/L, after which the chloride removal became moderate. With the increase of pH, obviously more chloride was removed. At pH of 10, the removal reached 90%. To save the chemical costs, alum sludge from a drinking water treatment plant was tested for the removal of chloride from the landfill leachate. The results showed that the supernatant of the alum sludge was more efficient than that of alum sludge suspension in chloride removal. The usage of alum sludge can dramatically save the chemical costs.

Keywords:

Landfill Leachate; Chloride; Aluminum; Calcium; Ultra-High Lime with Aluminum process

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*Correspondence to: Gang Chen, Tel.: +1 850 4106030; Fax: +1 850 4106142
E-mail: gchen@eng.fsu.edu

INTRODUCTION

Landfilling is widely adopted as one of the most economical processes for solid waste disposal. At the same time, landfill leachate is also a great environmental concern because of its complex composition and high contaminant concentrations (Poulsen *et al.*, 2002). Landfill leachate is the liquid generated from the moisture associated with the solid waste deposited in the landfill cell, which mainly is created when infiltrating rainwater dissolves contaminants within the landfill waste and seeps out of the bottom of the landfill cell into the leachate collection system. Landfill leachate characteristics present a high variation due to several factors such as the composition of the solid waste, waste age, site hydrology, landfill design and operation, sampling procedure, and interactions of leachate with the environment, etc. (Kulikowska & Klimiuk, 2008; Ziyang *et al.*, 2009; Lou *et al.*, 2011; Tsarpali *et al.*, 2012).

Besides organic contaminants, nutrients and heavy metals, high concentrations of chloride have also been observed in several landfills, especially with ash deposition from waste-to-energy applications (Qian *et al.*, 2008). The average chloride concentration in landfill leachate accepting waste-to-energy ashes is approximately 600 mg/L and the secondary drinking water standard for chloride is 250 mg/L. Small counties that have waste-to-energy plants therefore are often unable to use local wastewater treatment plants to dispose the leachate due to high concentrations of chloride in the leachate. Chloride has been demonstrated to be the major contribution of total dissolved solids in the landfill leachate and the elevated concentrations of chloride pose significant challenges to the beneficial waste-to-energy process. If this issue cannot be resolved, the environmental impact of waste-to-energy technology may outweigh the benefits. Chloride may percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil (Komarek *et al.*, 2007). In plants, chlorides tend to accumulate in the tissues, especially the leaves.

A variety of techniques have been investigated for the removal of chloride, which include ion exchange, reverse osmosis, and norecure, etc (Hamidi *et al.*, 2013; Ding *et al.*, 2015). However, these techniques, though effective, are not feasible from the cost perspective. Therefore, it is the need of time to come up with novel and low cost treatment methods to remove chloride from landfill leachate. As an innovative technology, the ultra-high lime with aluminum process can remove chloride efficiently (Abdel-Wahab and Batchelor, 2006). The essential of the ultra-high lime process is the addition of high doses of lime to maintain a high pH and

calcium concentration. With aluminum addition, the ultra-high lime with aluminum process has been practiced to promote removal of sulfate as calcium sulfoaluminate ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$), which has demonstrated the ability to achieve high sulfate removal efficiency (Zhou *et al.*, 2006; Qian *et al.*, 2008). The ultra-high lime with aluminum process has been further expanded to remove chloride by precipitation as calcium chloroaluminate ($\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$). Calcium chloroaluminate is a layered double hydroxide, also known as the Friedel's salt (Abdel-Wahab & Batchelor, 2006, 2007). The interlayer anions of layered double hydroxides can be exchanged with various organic and inorganic charged compounds including chloride. The ultra-high lime with aluminum process is attractive economically because of the less expensive chemicals in addition to the easy operation.

The objective of this study was to evaluate chloride removal from landfill leachate by the ultra-high lime with aluminum process as calcium chloroaluminate precipitate in the presence of aluminum at high pH. The impact of pH and aluminum concentration on chloride removal was examined. In order to save the chemical costs, alum sludge from a drinking water treatment plant was tested for the replacement of alum addition. During conditioning and dewatering, lime was added to the alum sludge, making it possible to be used for chloride removal.

MATERIALS AND METHOD

Landfill leachate was collected from the Leon County Landfill, located in Tallahassee, FL and Springhill Landfill, located in Campbellton, FL. Leon County Landfill accepts class III commercial and residential waste, including yard trash, C&D debris, processed tires, asbestos, carpet, cardboard, paper, glass, plastic, furniture other than appliances, and other material approved by Florida Department of Environmental Protection. Besides domestic waste, Springhill Landfill also accepts asbestos-friable, asbestos-non-friable, auto shredder fluff, biosolids, construction and demolition debris, drum management-liquids, drum management-solids, industrial and special waste, liquifix (solidification services), municipal solid waste, tires, yard waste and CERCLA waste. The leachate was collected in temperature-controlled containers at 4°C and transported to the laboratory immediately. The leachate was stored under refrigeration at 4°C until the reaction. BOD₅ and COD were quantified following the standard methods and ammonium and chloride were characterized using the ion chromatography system (Dionex ICS-900). Aluminum was analyzed by a flame atomic absorption spectroscopy (Agilent Technologies 4100 MP-AES).

The laboratory scale ultra-high lime with aluminum process consisted of two reactors in series, i.e., a reaction tank followed by a sedimentation tank. The reaction tank was continuously stirred by a single mechanical blade. Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ or alum) at a concentration up to 100 mg/L was added and the pH was adjusted with lime. Both alum and lime were added under flash-mixing conditions. With aluminum and calcium addition at high pH, calcium chloroaluminate was formed and precipitated in the sedimentation tank. Calcium chloroaluminate precipitation was reported to be fast and calcium chloroaluminate was able to be formed immediately upon the addition of aluminum and calcium at high pH. For this research, chloride removal was first tested as a function of reaction time. It was discovered that after 5 minutes' of reaction and 20 minutes' sedimentation, chloride removal became stable. Landfill leachate was introduced to the reaction tank. After chemical addition and 5 minutes' mixing and reaction, the leachate was transformed to the sedimentation tank for precipitation. After sedimentation for 20 minutes, supernatant was measured for chloride concentration by the Dionex ICS-900 system.

Considering reducing the chemical costs for the treatment, chloride removal was also tested using the alum sludge, a waste from surface water treatment. For drinking water treatment, alum was utilized to remove color, turbidity, and other impurities. The alum sludge contained about 5 percent solids and most states prohibited disposal of any liquid waste containing less than 20 percent solids in landfills. The subsequent alum sludge was conditioned and dewatered with lime addition. The lime addition resulted $\text{pH} > 12.5$, which made the sludge classified as corrosive and can only be deposited in hazardous landfills. Sustainable management of the alum sludge has become an increasing concern in drinking water treatment. The beneficial reuse of alum sludge is therefore highly desirable and has attracted considerable research efforts. The alum sludge used for this research was collected from Atlanta-Fulton Water Treatment Plant and contained approximately 39% aluminum by weight. The collected sludge was added to de-ionized water and the supernatant of alum sludge suspension was characterized. Specifically, 100 mL distilled water was added to a 250-mL Erlenmeyer flask containing 100 g dry sludge. The suspension was stirred using a multiple position magnetic stirring plate. The effect of pH and reaction time on aluminum extraction was investigated. The pH was adjusted either using 1 M H_2SO_4 to solubilize Al as Al^{3+} or 1 M NaOH to extract Al as $\text{Al}(\text{OH})_4^-$. Reaction time up to 25 minutes was studied. Based on the stoichiometry of calcium, aluminum and chloride on calcium chloroaluminate precipitation, both

the alum sludge suspension and supernatant were tested for their roles in chloride removal through calcium chloroaluminate precipitation with proper pH adjustment.

RESULTS AND DISCUSSION

The landfill leachate collected from Leon County Landfill had a BOD_5 of 221 mg/L, COD of 961 mg/L, $\text{NH}_4^+\text{-N}$ of 314 mg/L and chloride of 384 mg/L. The Springhill Landfill leachate had a BOD_5 of 421 mg/L, COD of 1,532 mg/L, $\text{NH}_4^+\text{-N}$ of 526 mg/L and chloride of 527 mg/L. The precipitate of the Leon County Landfill leachate had 78% C, 12% O, 7% Si, and 3% Fe. For comparison, Springhill Landfill Leachate precipitate had 74% C, 16% O, 9% Si and 1% Fe.

Chloride removal from landfill leachate by the ultra-high lime with aluminum process as calcium chloroaluminate precipitate was a function of both aluminum concentration and pH. Chloride removal increased with the increase of alum addition until 20 mg/L, after which the chloride removal became moderate (Fig. 1). It is therefore recommended that alum of 20 mg/L be used for chloride removal during leachate treatment.

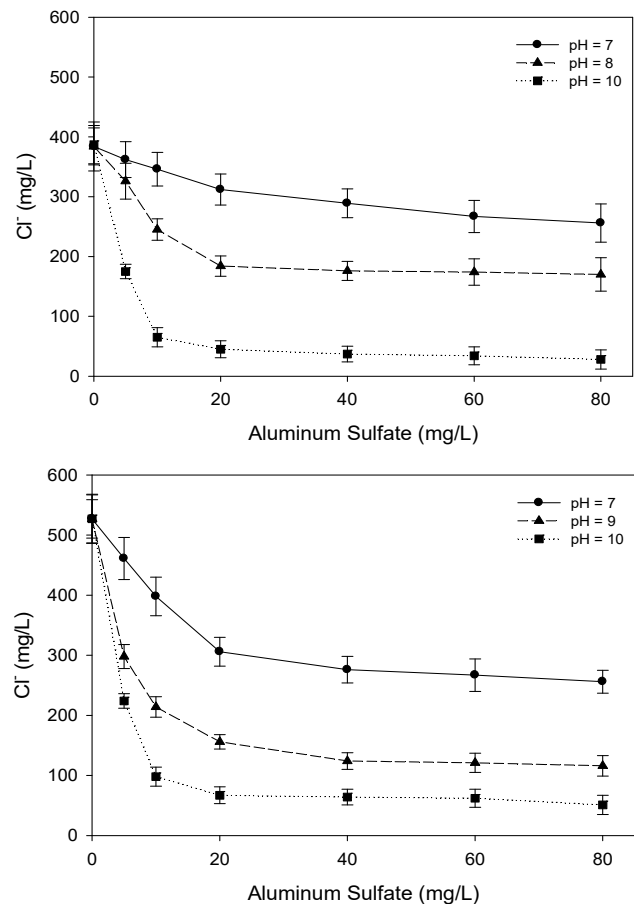


Fig. 1 Chloride Removal as a Function of Alum Concentration for Leon County Landfill (Top Image) and Springhill Landfill Leachate (Bottom Image).

With the increase of pH, obviously more chloride was removed. Chloride removal as a function of pH when aluminum was applied at 20 mg/L is illustrated in **Fig. 2**. For both Leon County Landfill leachate and Springhill Landfill leachate, chloride removal increased linearly with the increase of pH. At pH of 7, around 20% to 40% chloride was removed. However, at pH of 8, the removal rate increased to 50% to 55% (**Fig. 2**). At pH of 10, the removal reached to around 90% for both Leon County Landfill leachate and Springhill Landfill leachate. The increase of chloride removal with the increase of pH was more pronounced for the Leon County Landfill leachate as compared with that of Springhill Landfill leachate. This was mainly because Leon County Landfill had lower chloride concentration than that of Springhill Landfill (384 mg/L as compared to 527 mg/L). Chloride removal through the ultra-high lime with aluminum process was impacted by pH because the solubility of calcium chloroaluminate, which was a function of pH, the driving force of chloride removal in the form of calcium chloroaluminate precipitate.

The high pH and calcium contents of alum sludge as a result of dewatering and conditioning with lime addition made alum sludge possibly be used for chloride removal by calcium chloroaluminate precipitation. Besides aluminum, the alum sludge used for this research also contained Si, O and Ca as analyzed by scanning electron microscopy (**Fig. 3**). However, the mechanisms for alum sludge suspension and supernatant in chloride removal by means of calcium chloroaluminate precipitation are different. Within the alum sludge, octahedral sheets of $\text{Ca}(\text{OH})_2$ are substituted with Al^{3+} and the charge is neutralized by interlayer anions such as CO_3^{2-} , SO_4^{2-} , OH^- , and SiO_4^{4-} , Cl^- , Br^- , I^- , etc. When alum sludge suspension was added to the landfill leachate, the bulk Cl^- ions present in the solution diffused into the interlayers of the principal layers, $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2\text{H}_2\text{O}]^+$ by anion-exchange. The thus formed calcium chloroaluminate contained two metallic cations in the main layers with interlayer domains containing anionic species and water molecules (Abdel-Wahab and Batchelor, 2006). The exchange of chloride with the interlayer anions of the layered double hydroxides removed chloride from the solution. Once chloride was exchanged into the interlayers, calcium chloroaluminate was composed of positively charged main layers of composition $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and negatively charged interlayers of composition $[\text{Cl}^- \text{ and } 2\text{H}_2\text{O}]$ (Rapin *et al.*, 1999). The chloride anions were surrounded by 10 hydrogen atoms, of which six belonged to hydroxyl groups and four belonged to water molecules (Glasser *et al.*, 1999; Rapin *et al.*, 2002). Chloride removal through inter-ionic exchange was possible because the interlayer

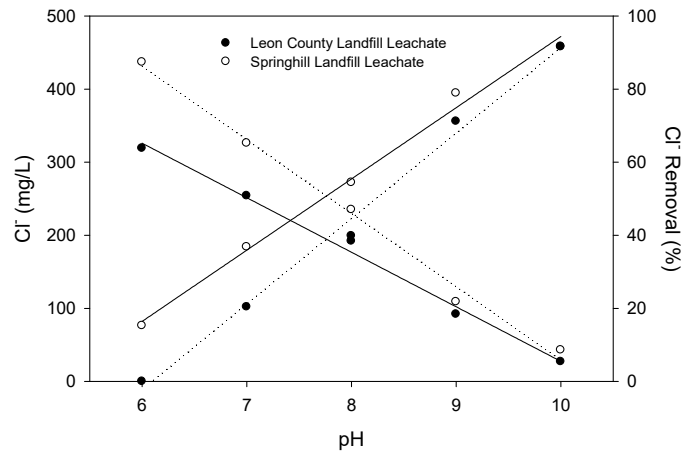


Fig. 2 Chloride Removal as a Function of pH.

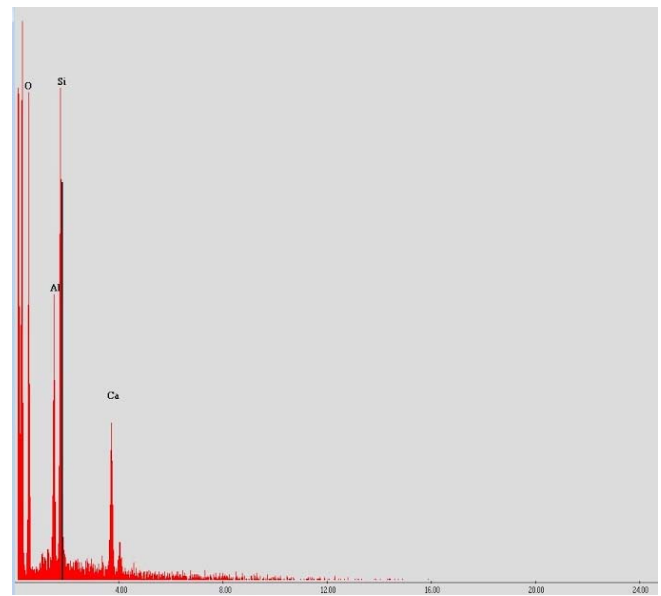


Fig. 3 Composition Analysis of Alum Sludge by Scanning Electron Microscopy.

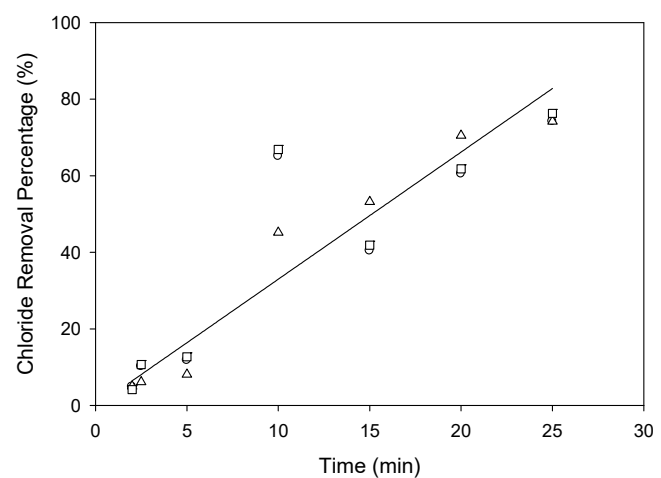
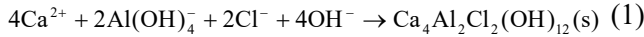


Fig. 4 Chloride Removal by Alum Sludge Suspension as a Function of Reaction Time.

anions were loosely held by electrostatic forces. It should be noted that chloride removal by inter-ionic exchange was a function of reaction time. The effect of the reaction time on chloride removal by alum sludge suspension is illustrated in Fig. 4. Chloride removal increased with the reaction time. At a reaction time of 25 minutes, a removal efficiency of 75% was achieved.

For alum sludge supernatant, chloride was removed by calcium chloroaluminate precipitation according to the followed reaction,



By analyzing the supernatant of the alum sludge suspension, it was discovered that 57% of aluminum was in the form of aluminate (AlO_4^-). To investigate the impact of pH on the speciation, the solution pH was adjusted with sulfuric acid and sodium hydroxide. Aluminate content was found to exhibit an exponential function of pH. Higher aluminate content was obtained if pH was further increased (Fig. 5). According to Equation 1, high pH, calcium and aluminate contents favored chloride removal by calcium chloroaluminate precipitation. Chloride removal results showed that the supernatant of the alum sludge was more efficient than that of alum sludge suspension in chloride removal (Fig. 6). It is therefore recommended that the supernatant of the alum sludge be used for chloride removal from landfill leachate to save the operation chemical costs.

For chloride removal in terms of $Ca_4Al_2Cl_2(OH)_{12}$, chloride, aluminum, calcium and hydroxide concentrations played the key roles based on Equation 1. Chloride removal was thus modeled as a function of the concentrations of Ca^{2+} , Cl^- , $Al(OH)_4^-$ and OH^- :

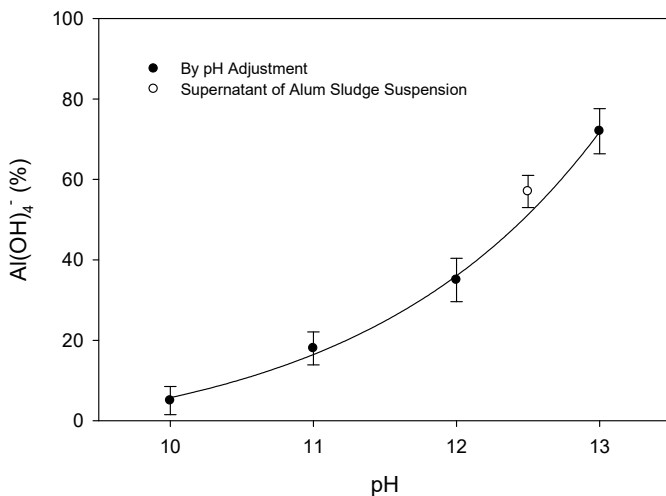


Fig. 5 Aluminate as a Function of pH.

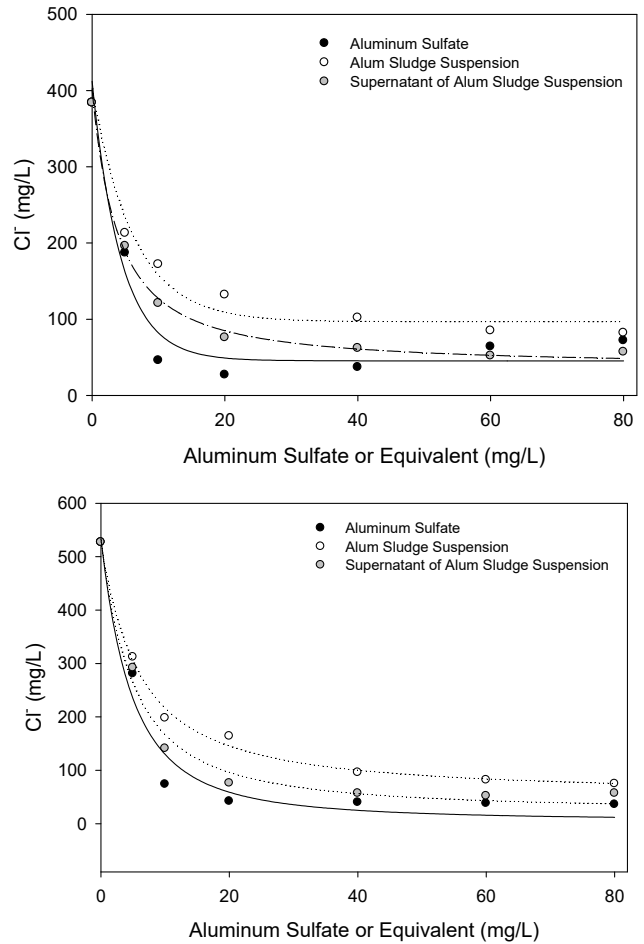


Fig. 6 Chloride Removal by Supernatant and Suspension of Alum Sludge for Leon County Landfill Leachate (Top Image) and Springhill Landfill Leachate (Bottom Image).

$$\frac{d[Cl^-]}{dt} = k[Ca^{2+}]^a [Cl^-]^b [Al(OH)_4^-]^c [OH^-]^d \quad (2)$$

where k is the chloride removal reaction rate coefficient and a , b , c and d are the parameters to be determined. Based on the evaluation of these impact factors, chloride removal was described as:

$$\frac{d[Cl^-]}{dt} = 0.338 \cdot [Ca^{2+}] [Cl^-]^{0.5} [Al(OH)_4^-]^{0.25} \log[OH^-] \quad (3)$$

The simulation fitting against the observed data is illustrated in Fig. 7.

CONCLUSIONS

Chloride removal from landfill leachate by the ultra-high lime with aluminum process was investigated and was found to be a function of both aluminum concentration and pH. From this research, it is recommended that alum of 20 mg/L be used for chloride

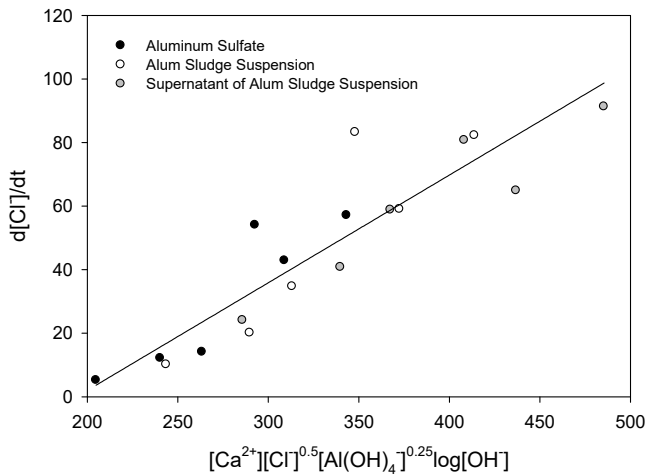


Fig. 7 Chloride Removal Rate Simulated Against Eq. (2).

removal during leachate treatment. The high pH and calcium content of alum sludge as a result of dewatering and conditioning with lime addition also made alum sludge possibly be used for chloride removal by calcium chloroaluminate precipitation. However, the mechanisms for alum sludge suspension and supernatant in chloride removal by means of calcium chloroaluminate precipitation were different. For alum sludge suspension, inter-ionic exchange was the mechanism and for the supernatant of alum sludge, chloride was removed by calcium chloroaluminate precipitation with aluminum in the form of aluminate. Chloride removal results showed that the supernatant of the alum sludge was more efficient than that of alum sludge suspension. It is therefore recommended that alum sludge supernatant be used for chloride removal from landfill leachate to save the operation chemical costs.

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REFERENCES

- Abdel-Wahab, A. & Batchelor, B. (2006) Effects of pH, temperature, and water quality on chloride removal with ultra-high lime with aluminum process. *Water Environ. Res.* **78**, 930–937. Doi: 10.2175/106143005X72821
- Abdel-Wahab, A. & Batchelor, B. (2007) Interactions between chloride and sulfate or silica removals from wastewater using an advanced lime-aluminum softening process: Equilibrium modeling. *Water Environ. Res.* **79**, 528–535. Doi: 10.2175/106143006X123058
- Ding, J., Zhao, Q.L., Zhang, J., Jiang, J.Q., Li, W., Yu, H., Huang, L.K. and Zhang, Y.S. (2015) Hybrid electrooxidation and adsorption process for the removal of ammonia in low concentration chloride wastewater. *Environ Sci Pollut Res Int.* **24**(6), 5098–5105. Doi: 10.1007/s11356-015-5793-8
- Glasser, F.P., Kindness, A., Stronach, S.A. (1999) Stability and solubility relationships in AFm phases: Part I. Chloride, sulfate and hydroxide. *Cement Concrete Res.* **29**, 861–866. Doi: 10.1016/S0008-8846(99)00055-1
- Hamidi, R., Kahforoushan, D., Fatehifar, E. (2013) The simultaneous removal of calcium, magnesium and chloride ions from industrial wastewater using magnesium-aluminum oxide. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **48**, 1225–1230. Doi: 10.1080/10934529.2013.776855
- Komarek, M., Tlustos, P., Szakova, J., Chrastny, V. (2007) The role of chloride salts in chemically enhanced phytoextraction of heavy metals from a contaminated agricultural soil. *Bull. Environ. Contam. Toxicol.* **78**, 176–180. Doi: 10.1007/s00128-007-9029-6
- Kulikowska, D. & Klimiuk, E. (2008) The effect of landfill age on municipal leachate composition. *Bioresour. Technol.* **99**, 5981–5985. Doi: 10.1016/j.biortech.2007.10.015
- Lou, Z., Feng, J., Zhong, S., Yuan, H., Zhu, N. (2011) Effect of layers composition on leachate property from functional layer embedded landfill. *Bioresour. Technol.* **102**, 7057–7063. Doi: 10.1016/j.biortech.2011.04.084
- Poulsen, T.G., Moldrup, P., Sorensen, K., Hansen, J.A. (2002) Linking landfill hydrology and leachate chemical composition at a controlled municipal landfill (Kastrup, Denmark) using state-space analysis. *Waste Manage. Res.* **20**, 445–456. Doi: 10.1177/0734242X0202000508
- Qian, G.R., Shi, J., Cao, Y.L., Xu, Y.F., Chui, P.C. (2008) Properties of MSW fly ash-calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals. *J. Hazard. Mater.* **152**, 196–203. doi: 10.1016/j.jhazmat.2007.06.118
- Rapin, J.P., Renaudin, G., Elkaim, E., Francois, M. (2002) Structural transition of Friedel's salt $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ studied by synchrotron powder diffraction. *Cement Concrete Res.* **32**, 513–519. doi: 10.1016/S0008-8846(01)00716-5
- Rapin, J.P., Walcarius, A., Lefevre, G., Francois, M. (1999) A double-layered hydroxide, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaI}_2\cdot 10\text{H}_2\text{O}$. *Acta Crystallogr.* **55**(12), 1957–1959. Doi: 10.1107/S0108270199008665/br1245sup2.hkl
- Tsarpali, V., Kamilari, M., Dailianis, S. (2012) Seasonal alterations of landfill leachate composition and toxic potency in semi-arid regions. *J. Hazard. Mater.* **233-234**, 163–171. Doi: 10.1016/j.jhazmat.2012.07.007
- Zhou, Q., Milestone, N.B., Hayes, M. (2006) An alternative to Portland Cement for waste encapsulation: the calcium sulfoaluminate cement system. *J. Hazard. Mater.* **136**, 120–129. doi: 10.1016/j.jhazmat.2005.11.038
- Ziyang, L., Youcai, Z., Tao, Y., Yu, S., Huili, C., Nanwen, Z., Renhua, H. (2009) Natural attenuation and characterization of contaminants composition in landfill leachate under different disposing ages. *Sci Total Environ.* **407**(10), 3385–3391. Doi: 10.1016/j.scitotenv.2009.01.028