

FLUORIDE REMOVAL FROM ZINC SULFATE SOLUTION

by

Yang Liu

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Abstract

During zinc electrowinning, fluoride is the primary cause of aluminum cathode corrosion and the onset of difficulty in stripping zinc from the aluminum blank. It is therefore of great interest to determine how to remove fluoride from zinc plant solutions to prevent cathode corrosion and difficult stripping.

There has been recent work on the removal of fluoride from drinking water and ground water. Research on zinc sulfate electrolyte purification has focused on metallic impurity removal, for example Cu, Co, Ni, Cd, Ti while halide impurities have been briefly investigated. Therefore, the purpose of this work is to investigate a reliable and economical process for fluoride removal from zinc sulfate electrolyte.

In this work, aluminum pre-loaded Lewatit® MonoPlus TP 260 resin was introduced as the absorbent. This absorbent has a high fluoride-loading capacity through the formation of aluminum-fluoride complexes on the resin structure. Also, both aluminum chloride and aluminum sulfate have been found to be effective sources of aluminum for pre-loading of the resin. The loaded aluminum along with co-loaded fluoride may be removed by sulfuric acid stripping. The resin can then be conditioned with sodium hydroxide prior to be re-loaded with aluminum.

As for the results, when 10 ppm fluoride existed in the initial solution, the fluoride capacity of the aluminum pre-loaded resin was calculated as 7.4 g F/L resin. Additionally, the breakthrough point could achieve 1000 bed volumes. Therefore, the cycle of aluminum sulfate pre-loading, fluoride-loading, sulfuric acid stripping, sodium hydroxide regeneration was recommended for effective fluoride removal in the zinc sulfate system.

Preface

This thesis is original, unpublished, independent work by the author, Yang Liu.

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List of Symbols and Abbreviations

AAS – Atomic Absorption Spectroscopy

AMPA-group – Amino-Methyl-Phosphonic-Acid-group

DI – Deionized water

IE – Ion Exchange

ICP-OES – Inductively Coupled Plasma-Optical Emission Spectroscopy

ICP-MS – Inductively Coupled Plasma-Mass Spectrometry

ISE – Ion Selective Electrode

MAS – Molecular Absorption Spectroscopy

SEM-WDS – Scanning Electron Microscope of Wavelength Dispersive X-Ray Spectroscopy

TBP – Tributylphosphate

THF – Tetrahydrofuran

TISAB – Total Ionic Strength Adjustment Buffer

UV – Ultraviolet

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Chapter 1: Introduction

As the fourth most common metal in use, zinc is reported to have an annual production of more than 13 million tonnes by the U.S. Geological Survey (Tolcin, 2015). The hydrometallurgical process produces more than 90% of the zinc and the conventional process can be divided in three steps: roasting, calcine leaching, and electro-winning (Takala, 1999). The concentrated $ZnSO_4$ solution obtained by calcine leaching contains various impurities including for example copper, nickel, cobalt, cadmium, chloride and fluoride. The metallic impurities influence the electro-winning by precipitating on the cathodes and reducing the current efficiency or causing contamination while the non-metallic impurities such as fluoride are the primary cause of cathode corrosion and appearance of difficulty in stripping zinc from the aluminum blank. This is believed to be due to the removal of the oxide layer on the aluminum by reaction with fluoride and the direct bonding of zinc to aluminum (Takala, 1999; Neil 2012). Many researches focused on the removal of metallic impurities using zinc dust cementation or solvent extraction as well as chelating ion exchangers (Van der Pas et al, 1996; Raghavan et al, 1999; Sandberg, 1978; Simpson, 1999). However, there are few published results that concern the removal of non-metallic impurities such as fluoride.

The Teck Cominco Halogon™ process has been developed for extracting a halide and some sulfate from an aqueous zinc sulfate solution containing the halides. In this process, CYANEX™ 923, ALAMINE™ 336, tributylphosphate (TBP), or their mixtures were introduced as extraction

reagents while EXXSOL™ D80 was used as diluent. The halides can be extracted efficiently and selectively, up to chloride 90% and fluoride 80%, in the conditions of 25~40°C and pH=0.5~1.5.

(Mason, 2006)

However, there are still disadvantages with this process. For example, the extraction reagents and diluent are expensive. The solvent process may introduce solvents into the solution for zinc electro-winning. This may impact the quality or efficiency of zinc electro-winning. The process of necessity also extracts sulfate with halides and therefore may impact the overall circuit solution and chemical balance in the zinc refinery.

In order to solve this problem, an alternative process for fluoride removal from zinc sulfate solutions has been sought.

There are many research results on the removal of fluoride from ground water and industrial wastewater, for example electrodialysis, sorption, precipitation, ion exchange, reverse osmosis and Donnan dialysis (Guo et al, 2012). Previous works in this field were investigated to reduce fluoride concentration in water. The Lanxess Process involves the removal of fluoride in industrial effluent to meet the legal limitation of disposal, which is typically 1 ppm. The resin used has the functional group of an amino-methyl-phosphonic-acid-group, or AMPA-group. Before the removal of fluoride ions, the resin should be activated or pre-loaded by aluminum chloride. The favorable loading of aluminum on the phosphonic acid group limits loss of the aluminum ions. When the aluminum pre-loaded resin is contacted with fluoride containing

wastewater, the chloride ions remaining in the resin bound with the aluminum ions will be replaced by the fluoride ions. After the resin is exhausted, AlCl_3 solution can be used to regenerate the resin. The higher concentration of Al in the AlCl_3 solution will form several complexes with fluoride and affect removal. Finally, adding lime milk can precipitate the aluminum and fluoride in the eluent solution. (Kedar, 2012)

The Lanxess process for fluoride removal may form the basis for control of fluoride in hydrometallurgical circuits. A fundamental study on fluoride removal from zinc sulfate solution by ion exchange was performed. The objectives of this project are:

- (1) To determine the aluminum loading behavior of Lanxess resin (Monoplus TP 260 resin).
- (2) To investigate the loading behavior of fluoride on the pre-loaded Lanxess resin (Monoplus TP260 resin) in low concentration fluoride solution and concentrated zinc sulfate solution.
- (3) To study the stripping behavior of different strip reagents (NaOH , Na_2CO_3 , NaHCO_3 and H_2SO_4).

In this thesis, previous studies on zinc electrolyte purification, fluoride removal from aqueous solutions and other background information are reviewed in Chapter 2. Chapter 3 describes the results of the fundamental characterization of Lanxess resin. The experimental study results of fluoride removal by Monoplus TP 260 resin in concentrated zinc sulfate solution are shown in Chapter 4. The commercial aluminum pre-loading and stripping process for fluoride removal

from zinc sulfate system and the influence of impurities was studied in Chapter 5. Finally, conclusions and recommendations of this research are discussed Chapter 6.

Chapter 2: Literature Review

2.1 Zinc background

2.1.1 Zinc production

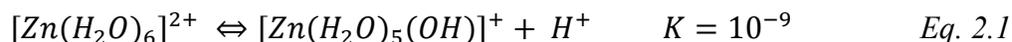
Zinc is the fourth most common metal in use, trailing only iron, aluminum, and copper with an annual production of about 13 million tonnes. The world's largest zinc producer is Nyrstar, a merger of the Australian company OZ Minerals and the Belgian company Umicore. About 70% of the world's zinc originates from mining, while the remaining 30% comes from recycling secondary zinc. Commercially pure zinc is known as Special High Grade, normally abbreviated as SHG, which is 99.995% pure. (Tolcin, 2011; Madelene, 2006; Nyrstar, 2008)

Worldwide, 95% of the zinc is mined from sulfidic ore deposits, in which sphalerite ZnS is nearly always mixed with the sulfides of copper, lead and iron. There are zinc mines throughout the world, with the main mining areas being China, Australia and Peru. China produced 29% of the global zinc output in 2010. (Porter, 1991; Tolcin, 2011)

2.1.2 Zinc chemical properties

2.1.2.1 Zinc halides properties

This section will discuss the chemistry of aqueous zinc solutions and Eh-pH diagrams are drawn by HSC 6.0 (Outokumpu, 2009). Zinc forms numerous water soluble salts, for examples, the nitrates, sulfates, sulfites, perchlorates, and acetates, that contain the aqua ions, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ (Lindgern, 1992). The $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ions are slightly hydrolyzed in water:



In more concentrated solutions, polynuclear species, beginning with $\text{Zn}_2(\text{OH})^{3+}$ are formed.

Figure 2.1 shows the predominant stable region of zinc species in water. The increasing concentration of hydroxides causes precipitation of ZnO, for which the solubility product is as low as $\text{p}K_{\text{sp}}=16.5$. (Lange's Handbook of Chemistry) However, $\text{Zn}(\text{OH})_2$ dissolves as much to the extent of 10^{-6} molar. It also dissolves completely in excess aqueous base to give principally $[\text{ZnO}_2]^{2-}$.

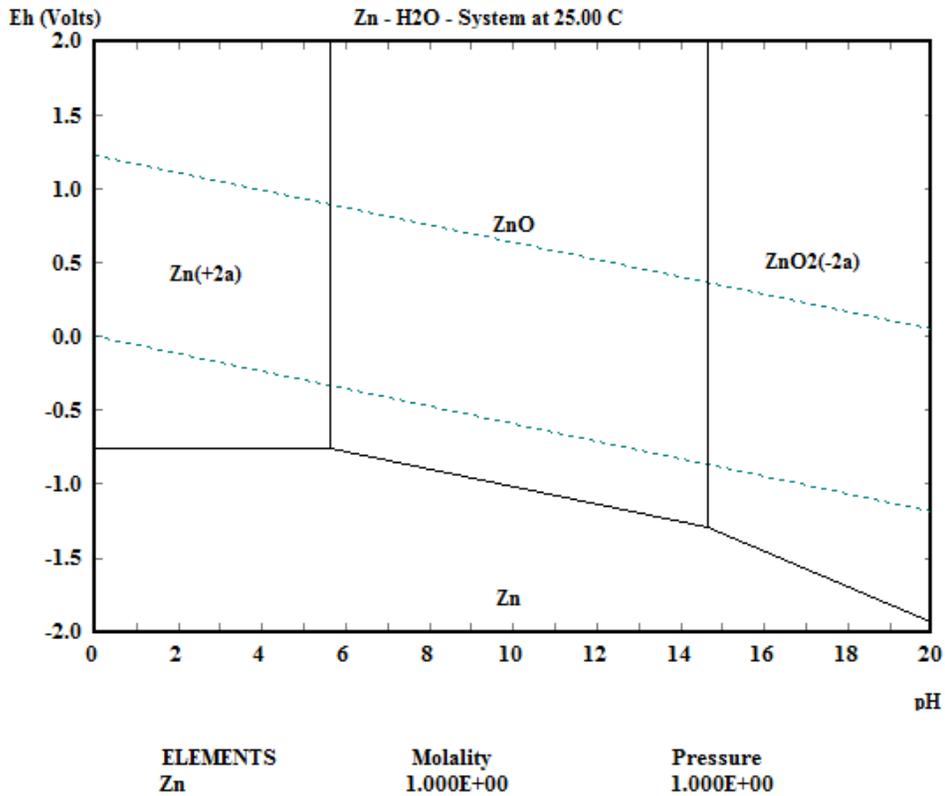


Figure 2.1 Eh-pH diagram for zinc-water system at 25°C, 1 atm and 1 M zinc by HSC 6.0

The Zn(OH)₂ species can also dissolve in ammonium hydroxide which forms amine complexes (for example, [Zn(NH₃)₄]²⁺). According to the Lange's Handbook of Chemistry, the logK₁ to logK₄ of zinc ammine complexes are 2.37, 2.44, 3.50 and 2.15, which means [Zn(NH₃)₄]²⁺ is the most stable species in solution. The predominant region of [Zn(NH₃)₄]²⁺ is illustrated in Figure 2.2.

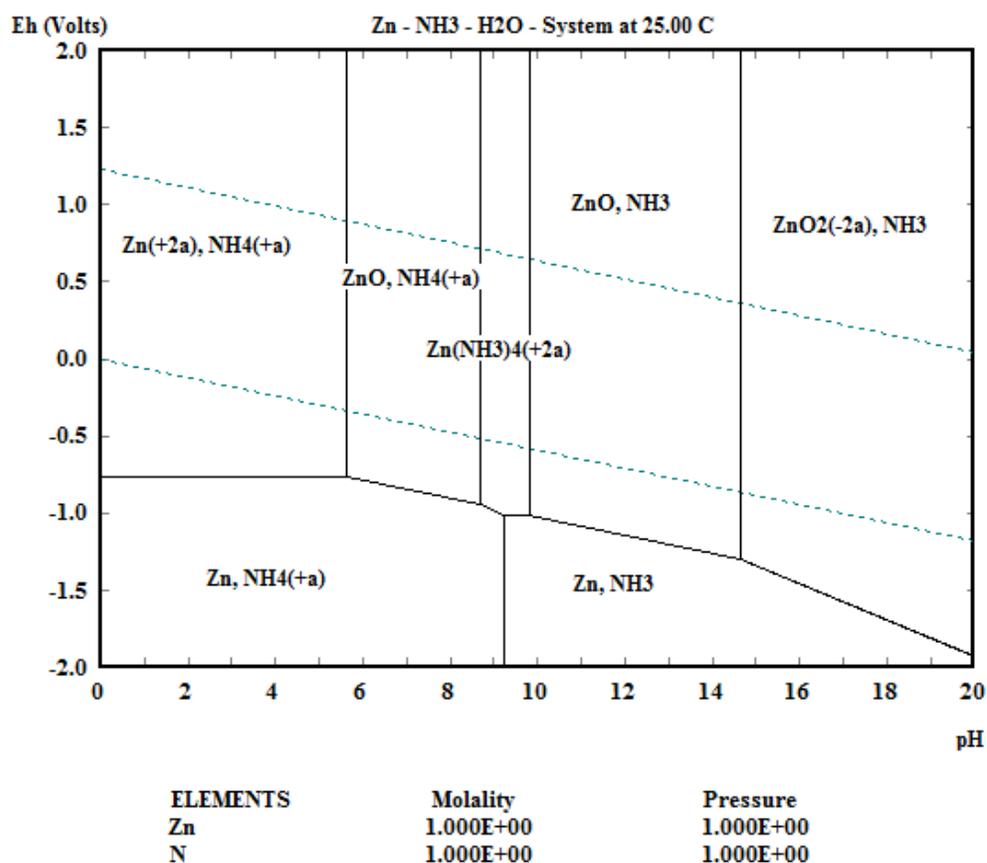


Figure 2.2 Eh-pH diagram for zinc-ammonia-water system at 25°C, 1 atm and 1 M zinc by HSC 6.0

Zinc forms salts with all four halide ions, and all the halides are fairly or even highly soluble in water, as well as other donor solvents such as ethanol, acetone, and THF. The solubility of $ZnCl_2$ in water is extraordinarily great and the highly concentrated solutions correspond to liquid hydrates, i.e., $ZnCl_2 \cdot nH_2O$, $n = 1\sim 4$, with all Cl^- ions bridging to the Zn^{2+} ions. In less concentrated solutions of $ZnCl_2$ discrete complexes such as $[ZnCl_4]^{2-}$, $[ZnCl_4(H_2O)_2]^{2-}$, $[ZnCl_2(H_2O)_4]$, and eventually $[Zn(H_2O)_6]^{2+}$ are present. Roughly the same behavior is displayed by the other halides of zinc except for the fluorides. The Zn^{2+} complexing by F^- is very weak and

no species beyond ZnF^+ has any importance (Hefter, 1992) and its predominant region is between $pH=2$ and $pH=6$ and higher Eh than -0.75 which is illustrated in Figure 2.3.

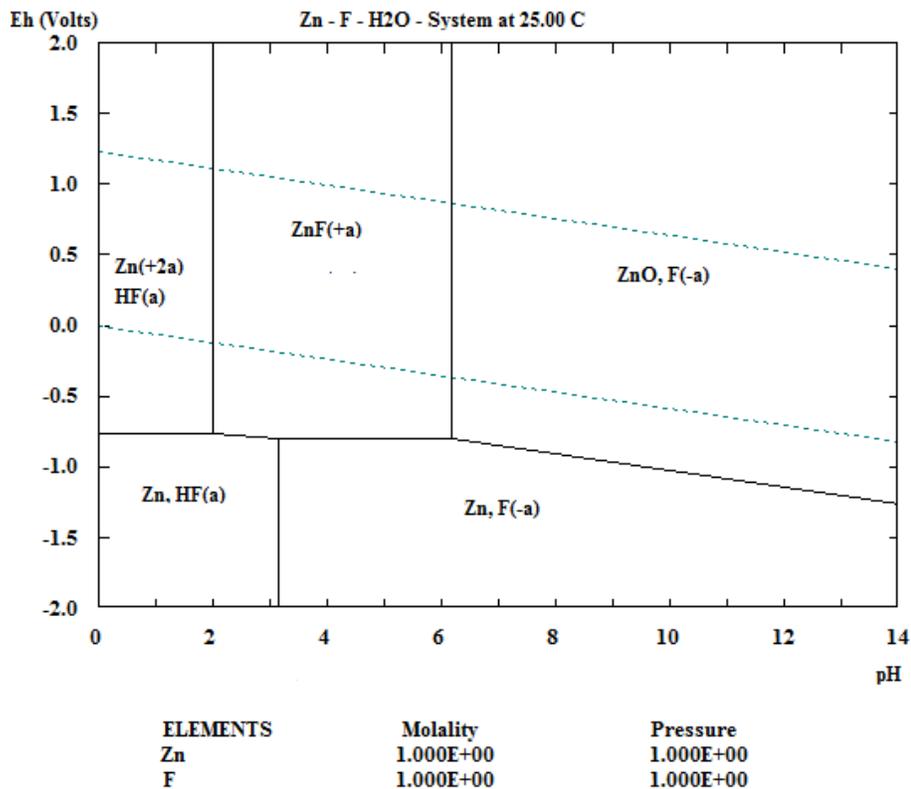


Figure 2.3 Eh-pH diagram for zinc-fluoride-water system at 25°C, 1 atm and 1 M zinc by HSC 6.0

2.1.3 Chemistry of zinc sulfate electrolyte system

The conventional process of zinc production includes three steps: zinc concentrate roasting, roaster calcine leaching and electrowinning. During the roasting part of this process, the zinc sulfides are roasted to oxides and sulfates. Figure 2.4 shows the predominant area of zinc sulfate,

which excludes other sulfur species such as thiosulfate and some metastable species. It illustrates the zinc sulfate dominant in acidic and oxidation environment.

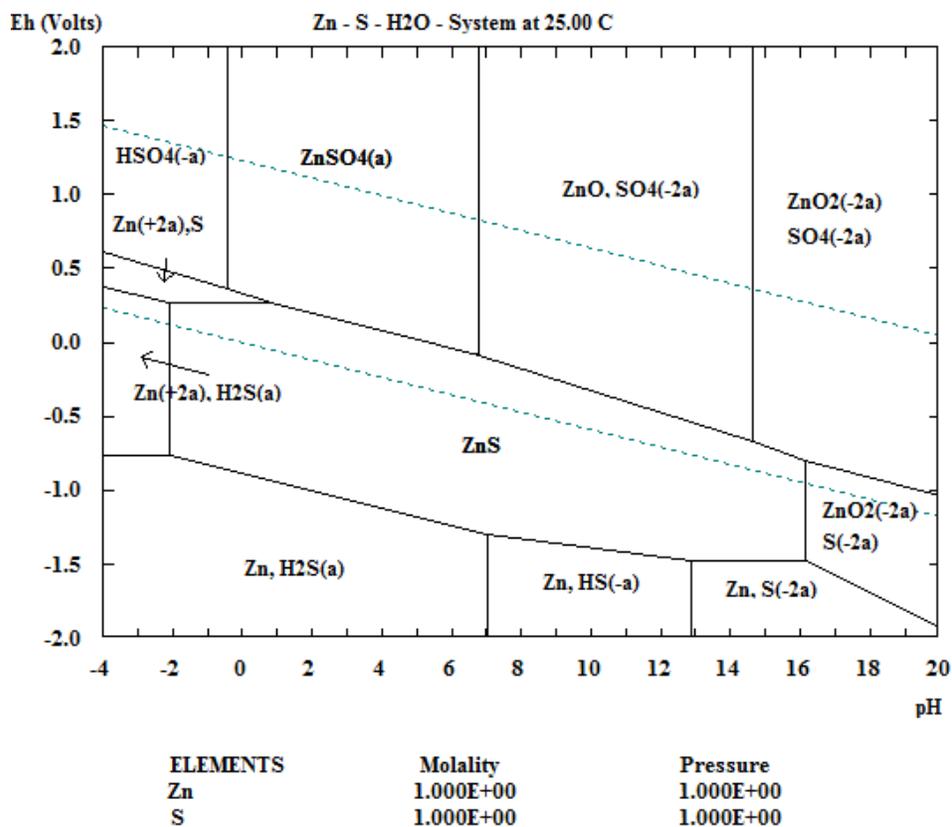
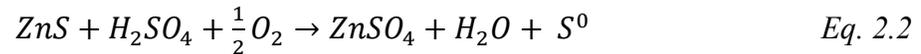


Figure 2.4 Eh-pH diagram for zinc-sulfate-water system at 25°C, 1 atm and 1 M zinc by HSC 6.0

However, during the conventional process most of the sulfide sulfur is oxidized to sulfur dioxide which increases the capture cost and also storage cost. Therefore alternative processes are developed such as medium temperature pressure leaching process and atmospheric leaching process. The reaction of pressure leaching process is listed as Eq. 2.2 and the Eq. 2.3 is the

reaction involved in the atmospheric leaching process. (Dreisinger et al, 1989; Dutrizac, 1974; Dutrizac et al, 2013)



2.2 Previous results on zinc electrolyte purification

After the calcine leaching, the concentrated zinc sulfate solution normally contains a variety of deleterious impurities, such as copper, nickel, cobalt, cadmium, fluoride, chloride. The concentrations of these impurities may range from 10ppm to 1000ppm depending on ore composition (Laatikainen et al, 2010).

2.2.1 Metallic impurities removal

Decades ago, in order to obtain high quality zinc metal; researchers have noticed the detrimental influence of even low-level metallic impurities. For example, those metallic impurities which are nobler than zinc may affect the purity of zinc deposits by co-deposition and some of them (Co and Ni) cause the re-dissolution of deposited zinc; iron may increase the over-potential and prevent the deposition of zinc and the parallel discharge of copper ions takes place and hydrogen is produced. Additionally, cadmium favors zinc deposition by diminishing the nucleation over potential and it is co-deposited with zinc on an aluminum cathode. The grain size of the deposit

is larger than in the absence of cadmium (Mureşan et al, 1996). Generally, these metallic elements reduce the purity of the zinc deposit and impact the morphology of products as well the current efficiency of zinc plating.

2.2.1.1 Zinc dust cementation

The most original process of metallic impurities purification is zinc dust cementation. Depending on the ingredients of the ore, typically, the concentrations of metallic impurities may be copper 500 ppm to 1000 ppm, nickel 10 ppm to 30 ppm, cobalt 10 ppm to 30 ppm and cadmium 200 ppm to 600 ppm. Conventionally, the purification process is divided into 3 steps. The practice varies from plant to plant. The purpose of the first step is to remove 80% to 90% of the copper by adding zinc dust and then alpha-nitroso-beta-naphthol at about 50 °C. During this step, most of the copper precipitates along with the cobalt and nickel. The remaining copper is used to affect the cementation of cobalt and cadmium because the cobalt cannot be deposited in a pure form, but is deposited as a cobalt-zinc alloy, which consists primarily of underpotential, deposited zinc. The addition of soluble copper and arsenic or antimony as ‘activators’ to the electrolyte improves the rate and extent of cobalt cementation (Raghavan, 1999). Adding charcoal after this step can remove any deleterious organic compounds remaining in the solution. By the second step, the remaining copper, nickel and other impurities are precipitated by antimony chemicals or arsenic trioxide as well as zinc dust at 90 °C and pH 4. Also, an additional zinc dust cementation following this step may further reduce the concentration of residual nickel and cadmium. After that, the residual cadmium is precipitated with zinc dust at

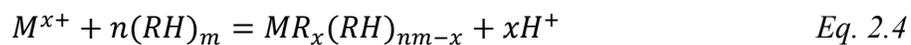
lower temperature (40 °C) in the final stage. Previous works also announced that the final stage could be replaced by a modified purification step. This step involves of zinc dust and potassium antimony tartrate addition in a relative high temperature (85 °C) (Raghavan, 1999).

The zinc dust cementation process requires a significant zinc dust addition. Typically 1-7% of the zinc metal production is recycled as zinc dust to purification. Also, the hydrogen evolution reaction may occur, which increases zinc dust consumption. In order to reduce the zinc consumption, many researchers have focused on minimizing zinc dust addition by optimizing the operation conditions. In these researches, depending on the operation condition and the purification process, the usage of zinc dust could be reduced to 40kg/Mt (Sandberg, 1978; Singh, 1996). Additionally, researchers are also developing alternative processes for impurity removal including, for example, extraction.

2.2.1.2 Solvent extraction

Solvent extraction is one of the alternative processes, which could reduce the usage of zinc dust significantly. Owusu investigated the extraction behavior of LIX 622 (a derivative of 5-dodecyl salicylaloxime) with Tri-butyl phosphate as phase modifier and SX-1 as diluent. Within these conditions, they successfully selectively extracted up to 98% of copper and trace iron from the acidic zinc sulfate solution by 2 stages of solvent extraction. During the two stages of countercurrent stripping, 98% of the copper could be stripped off from organic phase by 150 g/L sulfuric acid (Owusu, 1999).

Xingbin Li from State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization announced the process of D2EHPA and Acorga M5640 to selectively collect indium and copper from zinc reductive leaching solution. The cation extraction reaction could be written as Eq. 2.4 (Li, 2015).



As the recommended process illustrated in Figure 2.5, indium could be selectively extracted by 15% D2EHPA with counter-current procedure. The A/O ratio of organic loading stage was 6/1 and operation pH was 1.5 in this process. By adding 4 M HCl solution, indium was stripped during the stripping stage while the O/A ratio was 5/1.

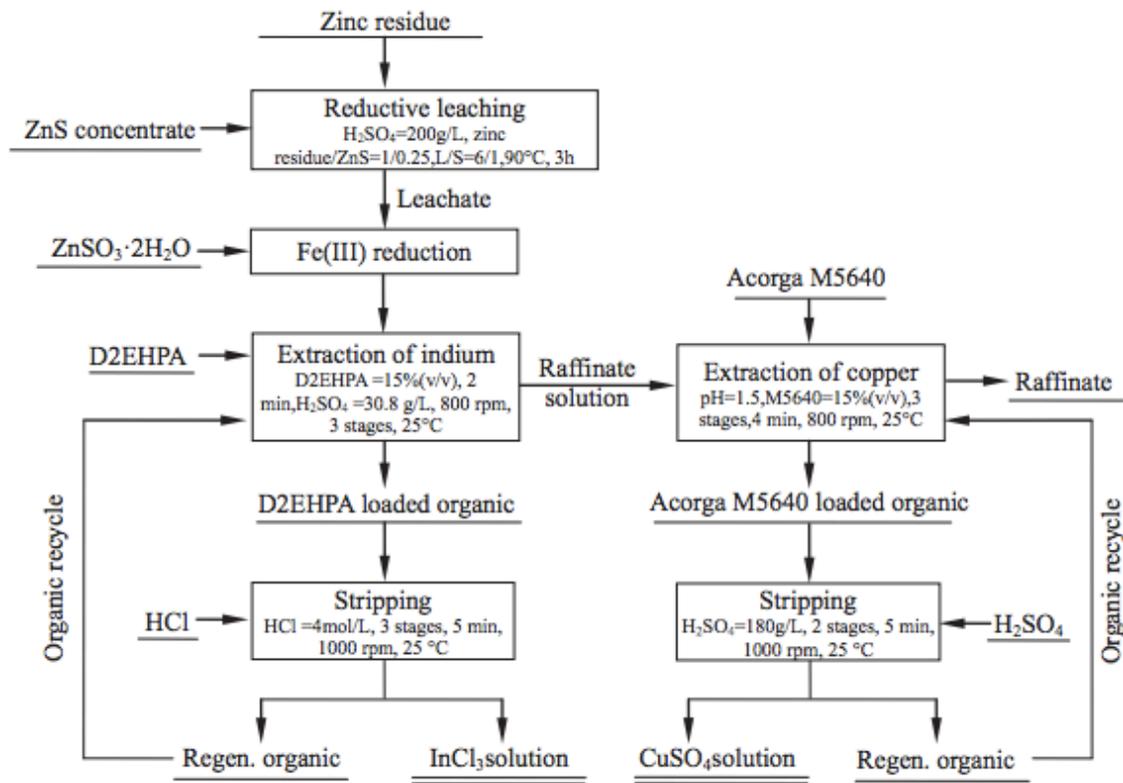


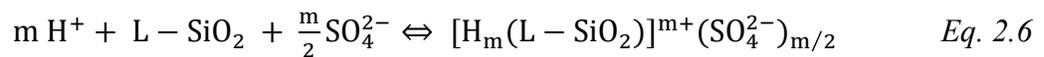
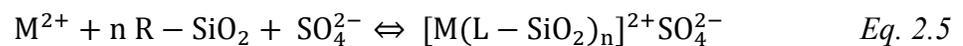
Figure 2.5 Recommended process of D2EHPA solvent extraction

2.2.1.3 Solid separation

Another alternative process that received increasingly concentration recently is solid separation. As early as 1970s, Moore has published and patented a metal impurities removal process. In his research, salicylaldoxime extractant was used to selectively remove nickel, copper and also cobalt in acidic solution. In this century, more attention was paid to chelating ion exchange resins. For example, Simpson reported the chelating ion exchange resin of Purolite S-930 and Lewatit® OC-1026 for the removal of impurities from waste solutions. Zagorodni studied another chelating resin (Amberlite IRC-718) with the functional group of iminodiacetic acid,

picolinic acid and thiourea separately. They used a dual-temperature technique in their process and found the resin with the functional group of picolinic acid had a better capacity of copper removal. (Simpson, 1999; Zagorodni, 1997)

Sirola et al. a from Lappeenranta University of Technology studied the possibility of copper and nickel selective removal from zinc sulfate solution by CuWRAM®, which is chelating resin functionalized with 2-(aminomethyl)pyridine groups. The loading and stripping reaction is shown in Eq. 2.5 and Eq. 2.6 with the functional group written as neutral ligands (Sirola, 2008).



2.2.2 Non-metallic impurities removal

There are also other impurities, such as fluoride, which may cause the zinc deposit to stick to the aluminum starter sheet during plating; and chloride, which may cause anode corrosion. There is great interest in control of fluoride ion buildup in zinc electro-winning solutions to minimize operational issues such as ‘sticky’ zinc deposits that are hard to strip. Fluoride ion control would also extend the aluminum cathode lifetime. To date, fluoride removal has been studied using three major technologies viz., adsorption, chemical precipitation and solvent extraction/ion

exchange. Previous works for fluoride and chloride removal are mainly by the means of solvent extraction.

For example, the Teck Cominco Halogon™ process has been developed for extracting a halide and sulfate from an aqueous sulfate solution containing the halide. In this process, CYANEX™ 923, ALAMINE™ 336, tributylphosphate (TBP), or their mixtures were introduced as extractants while the EXXSOL™ D80 was used as diluent. The halides can be extracted efficiently, up to chloride 90% and fluoride 80%, in the conditions of 25~40°C and pH=0.5~1.5. The patent announces the fluoride equilibrium concentration can be as low as 43 ppm fluoride in aqueous and 287 ppm fluoride in extractant when it is of 10% ALAMINE 336 extractant mixed with 25% CYANEX 923 extractant indicated to the system. However, there are still disadvantages about this process. For example, the extractants and diluent are expensive. The solvent process may introduce solvents into the solution for zinc electrowinning. This may impact the quality or efficiency of zinc electro-winning. The process of necessity also extracts sulfate with halides and therefore may impact the overall circuit solution and chemical balance in the zinc refinery. The process scheme is shown in Figure 2.6. (Mason, 2006)

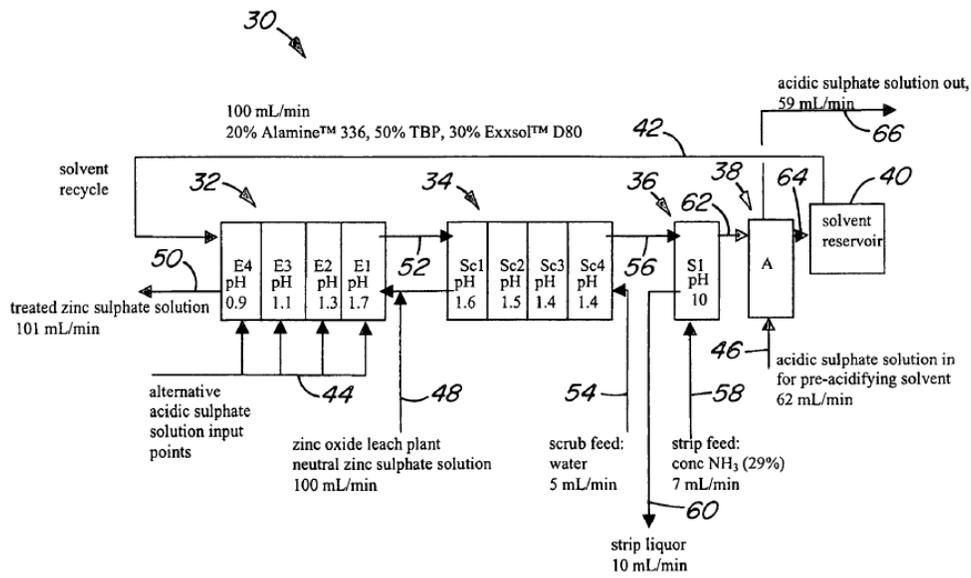


Figure 2.6 Recommended scheme of Teck Cominco Halogon™ process (Mason, 2006)

2.3 Fluoride in aqueous solution

The compound hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is the main mineral ingredients of our teeth enamel and bones. The ingestion of fluoride from drinking water, even at a relatively low concentration may displace the hydroxide ion groups to form fluoroapatite, which is harder, more brittle and has a higher density than hydroxyapatite. Although a small level of fluorapatite enhances teeth and bones, the prolonged exposure to increased salt concentration drinking water causes enamel mottling and embrittlement. This condition is named teeth fluorosis. The World Health Organization (WHO) has set an acceptable concentration in drinking water of 1.5 mg/L. Figure 2.7 illustrates the possible form of fluoride in water.

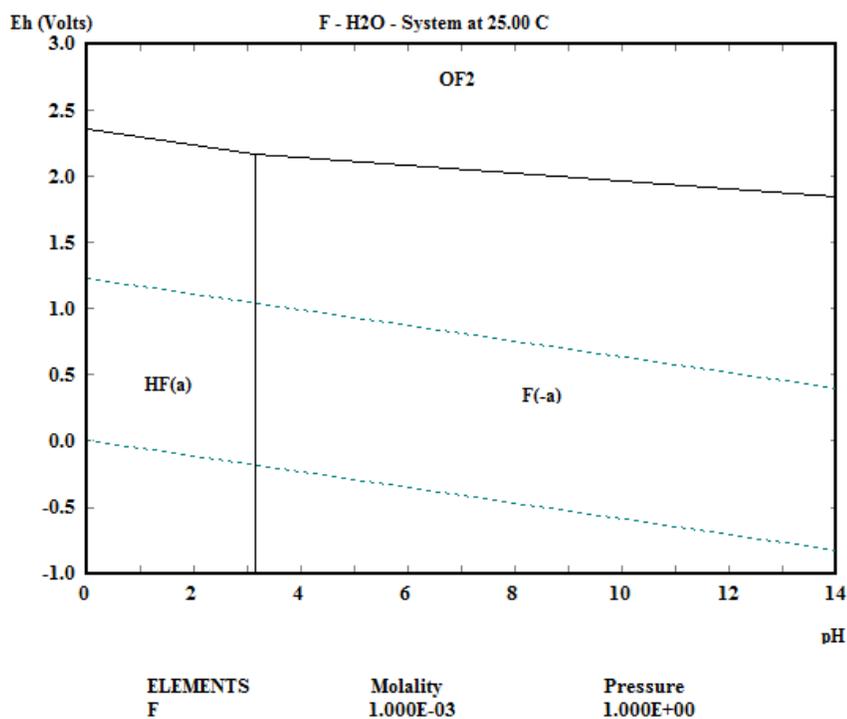


Figure 2.7 Eh-pH diagram for fluoride-water system at 25°C, 1 atm and 0.001 M fluoride by HSC 6.0

2.3.1 Fluoride analytical methods

A number of fluoride analysis methods have been developed, which are mass spectrometry, ICP-MS, AAS, MAS, electrochemical techniques fluorescence and UV-visible spectroscopy (Dhillon, 2016). For MS, ICP-MS, AAS and MAS, samples are needed to be evaporated or converted by laser to aerosol form. MS and ICP-MS are the same in that the detector is a mass spectrometer, where ions or species get separated in relation to their mass to charge ratio (m/z). As for AAS and MAS, the fluoride concentration is analyzed by radiation absorption of gas-phase free atoms (AAS) or molecular (MAS).

Fluoride ion-selective electrode provides highly selective measurement for fluoride ion in aqueous solution. When the electrode is immersed in to testing solution, the sensing element reacts with the fluoride ions in the testing solution and thus an electrode potential is developed. After that, the electrode potential is measured against the reference potential and reflected by a digital pH/mV meter. Figure 2.8 illustrates the structure of a 9609 BNWP fluoride combination electrode. (Fluoride Ion Selective Electrode–User Guide)

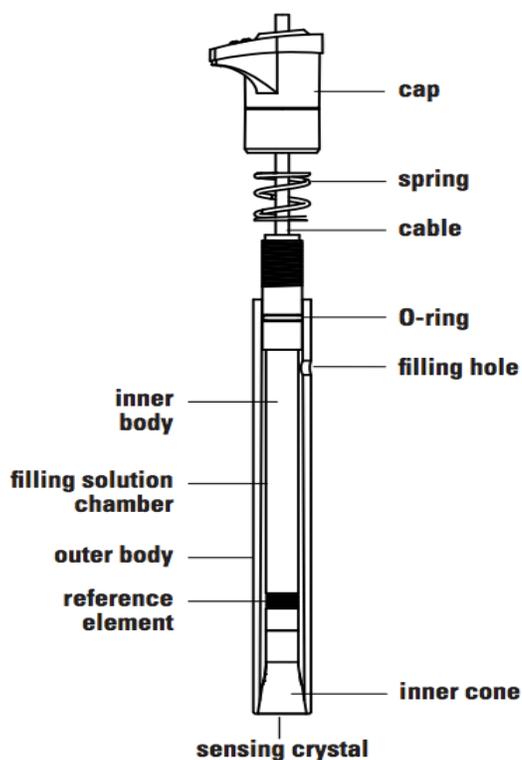


Figure 2.8 9609 BNWP Fluoride Combination Electrode

The measured potential corresponding to the level of fluoride ion in solution is described by the Nernst equation. The fluorescence technique requires a signaling unit that provides noticeable

physical change whereas UV-visible spectroscopy needs colorimetric sensor compounds, which convert to visible color after accepting fluoride ion. (Dhillon, 2016)

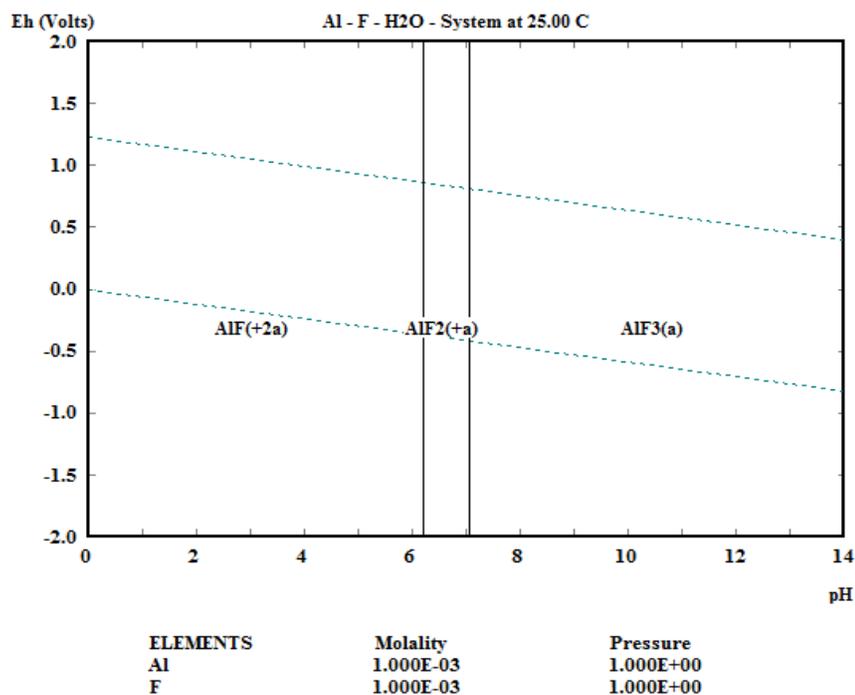


Figure 2.9 Eh-pH diagram for aluminum-fluoride-water system at 25°C, 1 atm, 0.001 M aluminum and 0.001 M fluoride by HSC 6.0

These methods have various selectivity for fluoride ions, variable reaction period and cost. All of the methods are sensitive to specific impurities like aluminum or iron. According to Lange's handbook, the solubility of aluminum fluoride is 5.6 g/L. (Lange's Handbook of Chemistry) Figure 2.9 shows the possible Eh-pH diagram of aluminum-fluoride-water system. The presence of aluminum in solution can form strong aluminum-fluoride complexes, which can be difficult to break.

2.3.2 Previous work of fluoride removal in aqueous solution

Previously, considerable attention focused on fluoride removal and various technologies were developed, including adsorption, ion exchange, precipitation and membrane techniques (Bhatnager et al, 2011).

Among these processes, precipitation by calcium and aluminum salts is the simplest and cheapest method. However, the utility of these salts cannot bring the fluoride concentration below 10 mg/L.

2.3.2.1 Activated alumina precipitation and other absorbents

For those processes that can bring fluoride concentration below the permissible concentration, precipitation by activated alumina is the most available and inexpensive process. Bishop reports the economical and efficient possibility of activated alumina on both batch and continuous flow bases. The result illustrated the fluoride concentration could be controlled as low as 0.1 mg/L. Also, the influences of pH and alkalinity were studied and the report showed both the increase of pH or alkalinity led to a decrease of fluoride capacity (Bishop, 1978). However, in order to maintain a high fluoride capacity, the treating pH and alkalinity should be controlled to relative low values. This led to difficulty for operation, higher cost and also accumulation of aluminum in treated water.

Other absorbents include charcoal, ash, rare earth oxides and mixed absorbents have been studied. For example, Bhargava reported a study using fishbone charcoal absorbent. Raichur illustrated that mixed rare earth oxides (La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , SmO_3) adsorption reaction was rapid with a high fluoride capacity as 12.5 mg F/g absorbent. Although, the drawbacks were: the stripping pH was as high as 12 and every regeneration of absorbent lost 2%-9% of the efficiency. For mixed absorbents, Sujana from Institute of Minerals and Materials Technology studied amorphous Fe/Al mixed hydroxides for fluoride removal. (Bhargava, 1992; Raichur, 2001; Sujana, 2010; Viswanathan, 2010)

2.3.2.2 Osmosis and nano-filtration

Alternative technologies that received considerable attention were reverse osmosis and nano-filtration. For reverse osmosis, it was observed by Ndiaye et al. that 98% fluoride was retained when osmosis membrane was considered fully regenerated. As for the nano-filtration, the overall recoveries were the same as the reverse osmosis (Ndiaye, 2005). However, the membrane used in nano-filtration has more pores. This leads to a lower resistance of solution passage, thus the lower pressure, less energy consumption and faster flows. There were many research results being devoted to the theoretical understanding of selection of membranes and optimization the operating conditions. Keba attributed the high selectivity of fluoride by the membranes mainly to steric and charge effects: the smaller diameter of fluoride ion leads to the higher charge density and which is more easily hydrated than other monovalent ions. These properties make fluoride ion more strongly retained on the membrane (Keba 2005). Tahaikt et al. tested the purification of

underground water by nano-filtration pilot plant with three commercial membranes in commercial models. In this report, the influences of factors were determined, such as simple pass, double pass with one type of membranes and combination of two types of membranes. Also, the water parameters were followed as a function of the running conditions (time, pressure, fluoride concentration, etc.). (Tahaikt, 2007)

2.3.2.3 Electrocoagulation

The last recommended method for fluoride removal is electrocoagulation. The conventional processes of electrocoagulation are conducted in batch reactors with constant current and magnetic stirring. Khatibikamal from the University of Tehran studied the behavior of fluoride removal from industrial wastewater using electrocoagulation. During the experiment, 2 aluminum electrodes and a potentiostat were settled to maintain a constant current of 1.32 A and a constant voltage of 30 V. Apart from that, the magnetic driver stirred at 400rpm and the volume of the batch vessel is 1.5 L. The results of this report show the fluoride can be removed from 4.84 ppm to 0.48 ppm within a rapid electrolysis time (5 minutes). Figure 2.10 indicates the evaluation of fluoride removal with electrolysis time. (Khatibikamal, 2010)

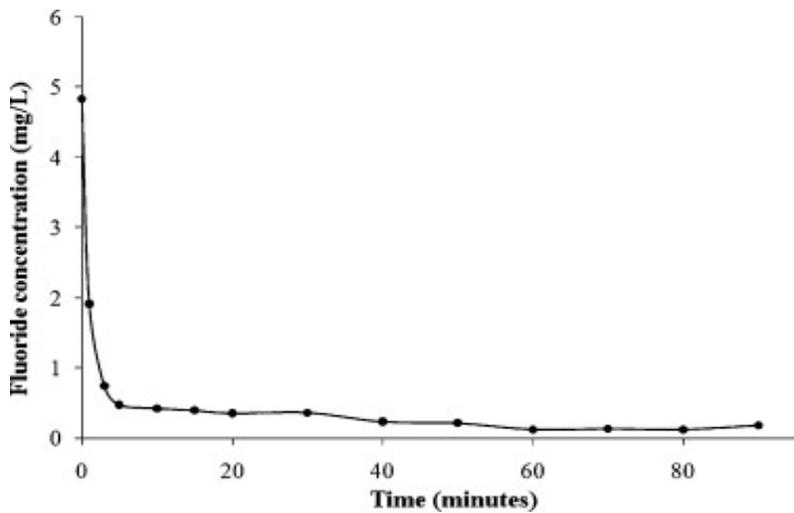
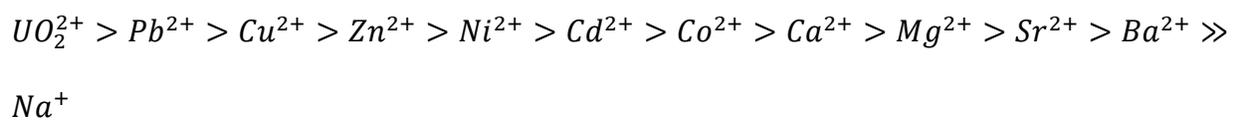


Figure 2.10 Evaluation of fluoride removal with electrolysis time at E=30V

2.4 Previous study on Lewatit® MonoPlus TP260 resin

Lewatit® MonoPlus TP 260 is a weakly acidic, macroporous cation exchange resin with chelating amino methyl phosphonic acid groups designed for the selective removal of heavy metal and alkaline earth cations. Divalent cations are removed from neutralized waters in following order (decreasing affinity):



As for the trivalent cations, the adsorption takes place, but desorption may be difficult. For instance iron (III) can only be desorbed by uneconomically high amounts of specific acid dosage. Additionally, aluminum (III) is less selectively absorbed than iron (III) but is reported to have higher selectivity than divalent cations.

The kinetic behavior of the resin leads to faster uptake of cations and a better utilization of capacity. Due to its modified polymer structure, most of the previous works were focusing on cation removal from neutralized solutions.

Table 2.1 Properties of Lewatit® MonoPlus TP 260

Ionic form as shipped		Na ⁺	
Functional group		Aminomethylphosphonic acid	
Matrix		cross-linked polystyrene	
Structure		macroporous	
Appearance		beige, opaque	
			metric units
Total capacity	H-Form	2.4	min. eq/l
Uniformity Coefficient		1.1	max.
Mean bead size		0.63 (+/- 0.05)	mm
Bulk density	(+/- 5 %)	720	g/l
Density		1.2	approx. g/ml
Water retention		58 - 62	wt. %
Volume change	Na ⁺ --> H ⁺	-35	max. vol. %
Stability	at pH-range	0 - 14	
Storability	of the product	2	max. years
Storability	temperature range	-20 - +40	°C



Figure 2.11 Lewatit® MonoPlus TP 260

2.4.1 Water purification

The Lanxess Process involves the removal of fluoride in industrial effluent to meet the legal limitation of disposal, which is typically 1 ppm. The resin used has the functional group of an amino-methyl-phosphonic-acid-group, or AMPA-group. Before the removal of fluoride ions, the resin is activated or pre-loaded by AlCl_3 . Because of the high selectivity of aluminum on the phosphonic acid group, the operation will not result in much loss of the aluminum ions. When the aluminum pre-loaded resin is contacted with fluoride containing wastewater, the chloride ions that were bound with the aluminum ions will be replaced by the fluoride ions. After the resin is exhausted, AlCl_3 solution can be used to regenerate the resin, because the higher concentration of Al in solution will form complex with fluoride. Finally, the wastewater of the regeneration solution is treated by lime milk. Eq 2.7 to 2.11 illustrate the reactions involved in waster water

pretreating, aluminum preloading, fluoride removal, resin regeneration, and the spent regeneration solution treatment steps.(Kedar, 2012)

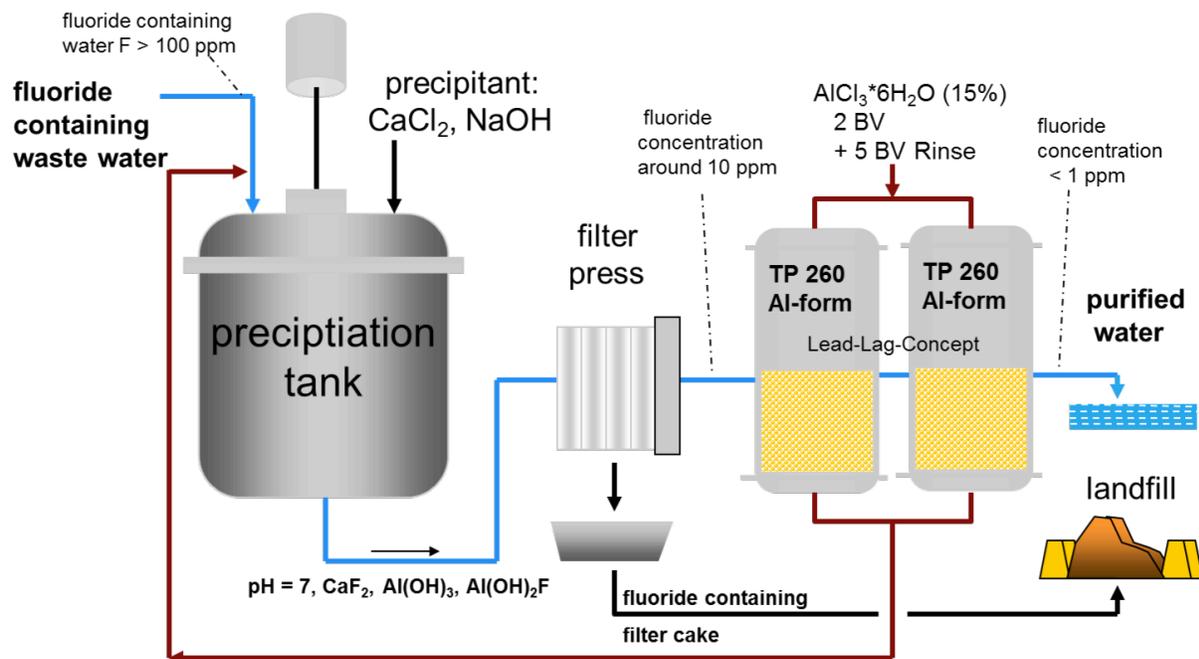
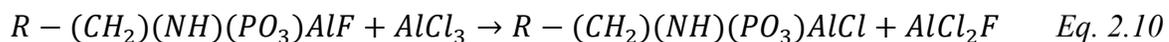
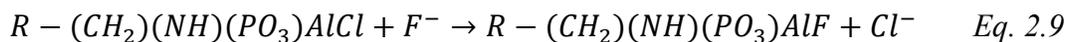
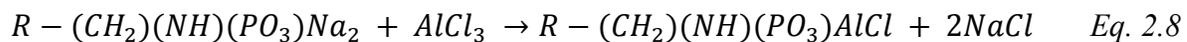
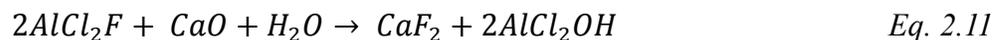


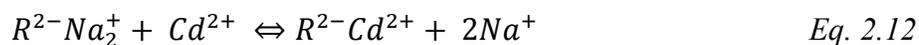
Figure 2.12 Flow sheet of fluoride removal from wastewater





2.4.2 Metallic impurities adsorption

F.J. Alguacil reported that cadmium could be effectively removed by Lewatit® TP 260 resin and the mechanism of the ion exchange reaction can be described as Eq. 2.12. In this study, equilibrium adsorption behavior was investigated by 0.5 g resin in 200 mL cadmium containing solution at 20 °C and pH 6.0. Also, the elution behavior was studied by using 0.25 M and 0.5 M sulfuric acid solutions.



Additionally, the kinetics of the adsorption were studied and modeled using Vermeulen's equation. The breakthrough capacities in different conditions are given in Table 2.2 and elution results are given in Table 2.3.

Table 2.2 Breakthrough capacities

Initial Cd concentration (g/L)	Flow rate (mL/min)	Cadmium capacity (mg/g resin)
0.2	1.5	14.1
0.1	1.5	>44.8
0.05	1.5	>45
0.05	3.0	25.7

Table 2.3 Elution of cadmium

H ₂ SO ₄ (M)	Time (min)	Elution rate (%)
0.25	5	77.4
	10	87.1
	30	91.4
	60	93.5
0.5	5	82.7
	10	92.0
	30	95.1
	60	95.1

2.5 Summary

As mentioned in section 2.2, 10-20 ppm fluoride is normally contained in zinc electrolyte. Even this level of fluoride causes sticking problems while most of previous fluoride removal works were focused on drinking water and ground water. Therefore, the objective of this thesis is to investigate the use of ion-exchange resin for fluoride removal from zinc electrolyte in order to create an economical method for zinc electrolyte purification.

Chapter 3: Possibility of Lewatit® MonoPlus TP260 Resin for Fluoride

Removal

3.1 Introduction

The purification of metallic impurities in zinc electrolyte solution has been studied since the 1900s using methods such as zinc dust cementation and solvent extraction as well as chelating ion exchangers. However, there are few published results, which concern the removal of non-metallic impurities such as fluoride. In addition, there is no research focusing on ion-exchange resin for fluoride removal from zinc electrolyte solution. Therefore, this thesis is a novel investigation of the application of ion-exchange resin for zinc electrolyte purification.

In this chapter, the experimental apparatus and procedures are illustrated in section 3.2. After that, the aluminum loading behavior and fluoride-loading behavior of Lewatit® MonoPlus TP 260 Resin in low concentration solution are reported (in section 3.3 and 3.4). Finally, some discussion and conclusions of this part are provided in section 3.5 and 3.6.

3.2 Experimental

3.2.1 Materials

All the solutions were prepared from reagent grade or analytical grade chemicals and deionized water without further purification. Aluminum chloride hexahydrate, sodium chloride, sodium fluoride and

TISAB II solution were provided by Sigma-Aldrich. The aluminum loading solution was prepared to be 55 g AlCl_3/L (11.13 g Al/L) by aluminum chloride hexahydrate and deionized water. This solution was chosen because it is the conventional Lanxess Process for fluoride removal. Sodium fluoride solution was prepared to be 10 ppm F (2.21×10^{-2} g NaF/L) and 5 g NaCl/L by sodium fluoride, sodium chloride and deionized water. The ion-exchange resin, Lewatit® MonoPlus TP260 resin, was provided by Lanxess.

3.2.2 Apparatus

The ion-exchange apparatus used during this study provided controlled conditions for fluoride removal by Lewatit® MonoPlus TP 260 resin. The apparatus used for carrying the ion-exchange experiments is shown in Figure 3.1 and Figure 3.2.



Figure 3.1 Apparatus for ion-exchange batch



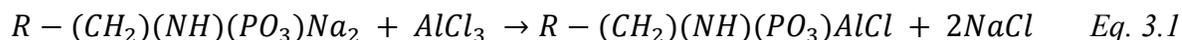
Figure 3.2 Apparatus for peristaltic pump

The ion-exchange batch test was carried out in a 50 mL class A burette provided by PYREX™. The peristaltic pump was Masterflex® Peristaltic Tubing Pump with pump driver and 14# L/S pump head which were provided by Cole-Parmer. The tubing was 14# L/S High-Performance Precision Pump Tubing that was also provided by Cole-Parmer.

3.2.3 Procedures

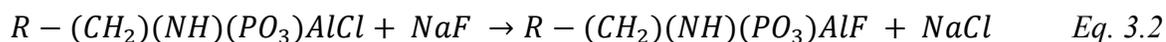
3.2.3.1 Aluminum pre-loading and fluoride-loading of TP260 resin

In order to convert the sodium form resin to aluminum chloride form, an aluminum pre-loading step before fluoride-loading step was necessary. After that, the fluoride in solution could replace the chloride, which had adsorbed on the resin; therefore the fluoride could be removed from the solution. The reaction involved in this part is shown as Eq. 3.1. (Kedar, 2012)



During the loading behavior test of TP260 resin, the reaction involved is indicated as Eq.

3.2.(Kedar, 2012)



3.2.3.2 Pretreatment of TP260 resin and preparation of chemicals

In order to test the precise volume of wet resin, the TP260 resin was immersed into deionized water for at least 8 hours. Apart from that, in order to prepare 10 ppm fluoride (which was 22.1 ppm sodium fluoride) solution, a standard sodium fluoride solution of 1000 ppm fluoride (as of 2.21 g NaF/L) had been prepared previously. For the solution used for aluminum pre-loading, a 55 g AlCl₃/L solution was prepared.

3.2.3.3 Procedures for aluminum pre-loading and fluoride-loading tests

The experimental procedure consisted of the following steps:

A) Aluminum pre-loading step

- a. At the beginning of the experiment the delivery rate of the pump had to be adjusted to 5 BV/hour (100 mL/hour)
- b. A sample of the feed solution was withdrawn and analyzed for the required parameters and labeled as FEED.
- c. A 20 ml of Lewatit® MonoPlus TP 260 resin sample was measured. The graduated cylinder (50 ml Capacity) was first filled with water to 40 % volume. Then a suspension of resin was poured into the graduated cylinder until the volume of the resin bed gets close to the target volume. Air was removed from the resin bed by stirring with a thin ceramic/glass rod. The resin bed was compressed by tamping the graduated cylinder bottom onto the rubber plate to settle the resin until the volume stays constant.
- d. The resin column was first filled with water and flushed with 1 L of deionized water. Water was passed in down flow direction.
- e. The resin sample was carefully washed out of the measuring graduate into the resin column by means of squeeze bottle and funnels set on the top of the column.
- f. The column head was sealed.

g. A 1 L solution of 55 g AlCl_3/L was prepared.

h. The AlCl_3 solution was passed through the resin bed at a flow rate of 5 BV/hour (100 mL/hour) for 2 hours.

i. The excess AlCl_3 solution was rinsed out from the column (by 1000 mL deionized water at a flow rate of 5 BV/hour for 10 hours)

B) Fluoride-loading step with low concentration feed solution

a. The aluminum pre-loaded resin was used.

b. A 10 ppm sodium fluoride solution was prepared by mixing 1000 ppm standard sodium fluoride solution and deionized water. This solution was labeled as input solution.

c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.

d. The fluoride concentration of the output solution was analyzed and plotted on the loading curve.

C) Fluoride-loading step with increased salt concentration

a. A solution of 10 ppm NaF in 5 g NaCl/L solution was prepared by mixing 1000 ppm standard sodium fluoride solution, sodium chloride solid and deionized water. This solution was labeled as input solution.

- b. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.
- c. The results were plotted on one diagram as the loading curve.
- d. The fluoride concentration of the input solution was analyzed over time.

3.2.3.4 Analytical methods

Figure 3.3 and Figure 3.4 illustrate the ICP-OES and Fluoride ISE, which were used for aluminum and fluoride analysis.



Figure 3.3 ICP-OES

The ICP-OES is a method of optional emission spectrometer. For aluminum analysis, the testing solution was evaporated at the first time and target ions were excited. As the excited aluminum released 4 different wavelength emission rays: 236.7 nm, 237.3 nm, 394.4 nm, and 396.2 nm. Therefore the intensity of the light with these four wavelengths reflected the concentration of aluminum in solution.

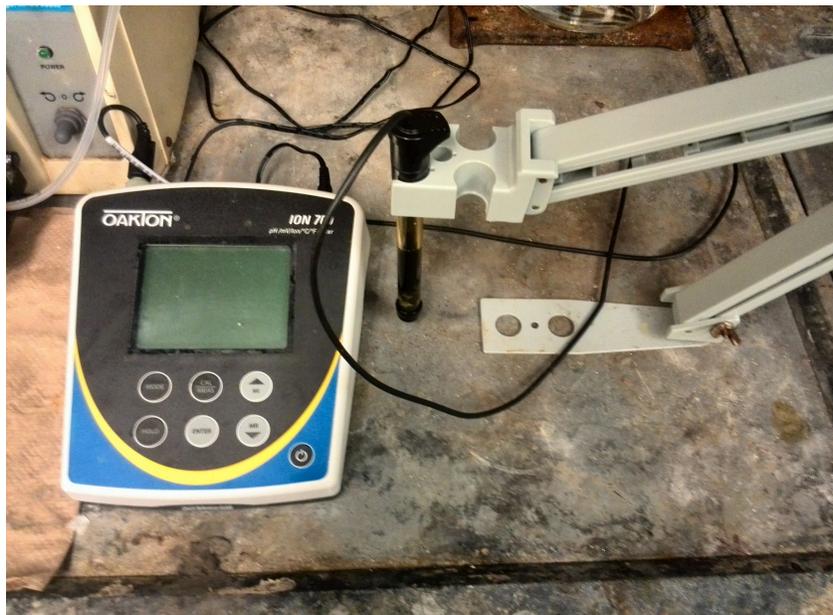


Figure 3.4 Fluoride ISE

The fluoride ISE contains an ion-selective membrane, which is a single crystal of Lanthanum Fluoride (LaF_3) doped with Europium Fluoride (EuF_2). When immersed into the testing solution, the negative fluoride ions pass through the ion-selective membrane till the concentration reached the same level. Then the build up of negative F ions on the inside of the membrane is compensated for by Cl ions in the internal reference solution becoming neutralized by combining

with the Ag/AgCl wire, and electrons are thus forced through the external wire to the voltage measuring device (ion meter or computer interface). The Fluoride ISE calibration procedure and the calibration results are given in Appendix A.

3.2.3.5 Evaluation factors

Pre-loaded aluminum and loaded fluoride on the resin are two key factors to evaluate the fluoride removal process. Eq. 3.3 listed below is used to calculate the aluminum pre-loaded on the resin as well as Eq. 3.4 is used to calculate the fluoride loaded on the resin.

$$N_{Al} = \frac{C_{Al,i} * V_{Al,i} - C_{Al,o} * V_{Al,o} - C_{Al,f} * V_{Al,f}}{V_{resin}} \quad Eq. 3.3$$

(N_{Al} is the mole per liter resin of aluminum which was pre-loaded on the resin; $C_{Al,i}$ is the concentration of aluminum which was in the input solution; $V_{Al,i}$ is the volume of the input solution which was pumped into the burette; $C_{Al,o}$ is the concentration of aluminum which was in the output solution; $V_{Al,o}$ is the volume of the output solution which was pumped out of the burette; $C_{Al,f}$ is the concentration of aluminum which was in the output flush water; $V_{Al,f}$ is the volume of the flush water which was pumped out of the burette and V_{resin} is the volume of the resin which was calculated as wet resin in sodium form.)

$$M_F = \frac{C_{F,i} * \sum V_F - \sum C_{F,o} * V_F}{V_{resin}} \quad Eq. 3.4$$

(M_F is the mass per liter resin of fluoride which was loaded on the resin; $C_{F,i}$ is the concentration of fluoride which was in the input solution; $C_{F,o}$ is the concentration of fluoride which was in the output solution; V_F is the volume of the output solution which was pumped out of the burette; V_{resin} is the volume of the resin which was calculated as wet resin in sodium form.)

3.3 Aluminum pre-loading on Lewatit® MonoPlus TP260 resin

A number of experimental variables were studied in order to understand the aluminum pre-loading behavior of TP260 resin. All the experiments were performed under ambient conditions unless otherwise noted separately. Aluminum pre-loading tests were repeated four times to ensure the reproducibility. The experiment conditions of aluminum pre-loading are summarized in Table 3.1.

Table 3.1 Conditions for aluminum pre-loading on TP 260 resin

	Temperature	Room temperature
	Form	Sodium form
Resin states	Pretreatment	Immersed in deionized water for 8 hours
	Dosage	20 mL (wet, Na form)
AlCl ₃ input solution	Concentration	55 g/L (11.13 g Al/L)
	Flow rate	5 BV/h
Flush water	Flow rate	5 BV/h

Table 3.2 Aluminum pre-loading results

Test No.	Volume (mL)	Al conc. (ICP test, ppm)	Dilution rate in ICP test	Al conc. (actual, g/L)	Al loaded (mol/L resin)	
1	Input	226	22.37	500	11.19	
	Output	219	16.35	500	8.18	1.013
	Flush water	884	0.43	500	0.22	
2	Input	209	22.30	500	11.15	
	Output	204	16.44	500	8.22	1.045
	Flush water	936	0.19	500	0.10	
3	Input	220	108.8	100	10.88	
	Output	216	81.63	100	8.17	1.049
	Flush water	993	0.64	100	0.06	
4	Input	261	105.8	100	10.58	
	Output	261	80.56	100	8.06	1.093
	Flush water	1041	0.65	100	0.07	

Table 3.2 indicates the result of aluminum pre-loading experiments. It was found the results of aluminum pre-loaded on the resin during the aluminum pre-loading step were around 1.05 mol Al/L resin that is approximately 28.3 g Al/L resin.

3.4 Fluoride-loading behavior of Lewatit® MonoPlus TP260 resin

Another number of experiments was carried to define the fluoride-loading behavior of TP260 resin. First, the loading behavior of fluoride in low concentration solution was tested and then the loading behavior of fluoride in increased salt concentration solution was studied. All the

experiments were performed under ambient conditions unless otherwise noted separately.

Fluoride-loading behavior tests were repeated three times to ensure the reproducibility. Table 3.3 shows the conditions of both fluoride-loading behavior of low concentration solution and increased salt concentration solution.

Table 3.3 Conditions for fluoride-loading behavior of TP 260 resin

		Low concentration feed solution test	Increased salt concentration test
	Temperature	Room temperature	Room temperature
Resin states	Form	Aluminum chloride form	Aluminum chloride form
	Dosage	20 mL (wet, Na form)	20 mL (wet, Na form)
	NaF Concentration	10 ppm F (22.1 ppm NaF)	10 ppm F (22.1 ppm NaF)
NaF input solution	NaCl concentration	0	5 g/L
	Flow rate	5 BV/h	5 BV/h
Flush water	Flow rate	5 BV/h	5 BV/h

Figure 3.5 illustrates the results of fluoride-loading behavior of TP 260 resin in low concentration solution. If the break through point was set as 1 ppm fluoride in output solution, it was found that the fluoride capacity in low concentration solution was about 0.4~0.5 g F/L resin.

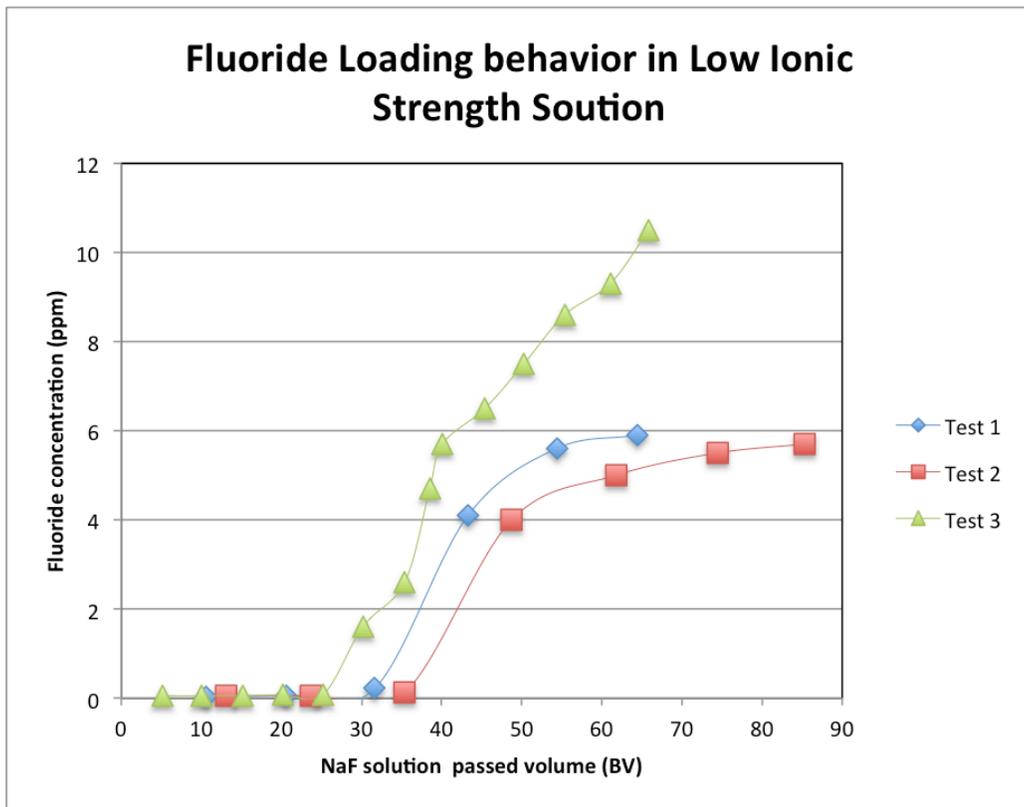


Figure 3.5 Fluoride-loading behavior in low concentration solution

Figure 3.6 illustrates the results of fluoride-loading behavior of TP 260 resin in a solution with an increased salt concentration solution. If the break through point was set as 1 ppm fluoride in output solution, it was found that the fluoride capacity in increased salt concentration solution was about 3.2~3.3 g F/L resin. The breakthrough point was set as 1ppm fluoride in eluent solution because this part of work was of repeating the Lanxess work so that the conditions in these experiments and results would be credible.

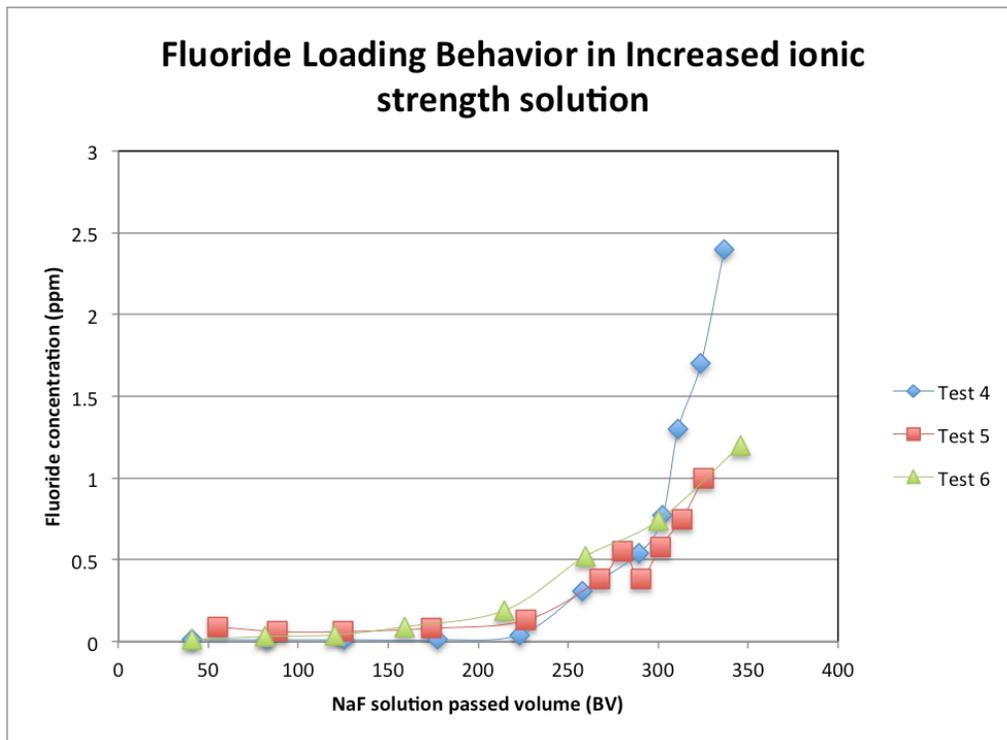


Figure 3.6 Fluoride-loading behavior in increased salt concentration solution

3.5 Discussion

There is a significant difference between the fluoride capacities of low concentration solution and sodium chloride addition solution. In the low concentration sodium fluoride solution experiment, the fluoride concentration of output solution is also as low as 0.02 ppm in the first 30 BV. While in the additional sodium chloride experiment, the fluoride concentration of output solution is also as low as 0.02 ppm in the first 200 BV. The mechanism of this difference is still unknown.

3.6 Summary

- 1) It was found that the aluminum pre-loading on TP 260 maintained a relatively stable value, which was about 1.05 mol Al/L resin. This means the aluminum pre-loading reaction fitted well to this result since the TP 260 resin is also around 1 mol/L as the reaction ratio of pre-loaded aluminum to resin was around 1:1. The stable pre-loading of aluminum meant the next step of fluoride-loading behavior test was possible.
- 2) The fluoride capacity in low concentration solutions remained the same at 0.4~0.5 g F/L resin. Whereas the capacity of fluoride in increased salt concentration solutions remained at 3.2~3.3 g F/L resin. Also, the fluoride capacities (about 0.5 g F/L resin) in low concentration solutions were much less than those (3.2 g F/L resin) in increased salt concentration solutions.

Chapter 4: Study on Lewatit® MonoPlus TP260 Resin for Fluoride Removal and Base Stripping in Zinc Sulfate System

4.1 Introduction

The possibility of fluoride removal by MonoPlus TP260 resin in low zinc concentration solution was confirmed in chapter 3. Therefore, it is important to understand the fluoride-loading behavior in zinc concentrated solution. The stripping behavior of several chemicals (NaOH, Na₂CO₃, NaHCO₃ and H₂SO₄) and influence of some impurities (aluminum, magnesium, and manganese) are also important to investigate to attempt to re-use the chemicals from loading.

In this chapter, the experimental apparatus and procedures are illustrated in section 4.2. In section 4.3, the results of fluoride-loading behavior in zinc sulfate system of aluminum pre-loaded resin are reported. After that the stripping behavior of several chemicals and fluoride-loading behavior by regenerated TP 260 resin are illustrated in section 4.4. The sodium hydroxide stripping test is listed in section 4.5. Finally, some discussions and conclusions of this part of work are provided in section 4.6 and 4.7.

4.2 Experimental

4.2.1 Materials and apparatus

All the solutions were prepared from reagent grade or analytical grade chemicals and deionized water without further purification. Aluminum chloride hexahydrate, sodium fluoride, sodium hydroxide, sodium carbonate, sodium bicarbonate, zinc sulfate heptahydrate and TISAB II solution were provided by Sigma-Aldrich. The aluminum pre-loading solution was prepared to be 55 g AlCl_3/L (11.13 g Al/L). Sodium fluoride standard solution was prepared to be 1000 ppm F (2.21g NaF/L). Fluoride in zinc sulfate solution was prepared to be 10 ppm F and 2 M ZnSO_4 . Sodium hydroxide solution was prepared to be 1 g NaOH/L . Sodium carbonate solution was prepared to be 1 g $\text{Na}_2\text{CO}_3/\text{L}$. Sodium bicarbonate solution was prepared to be 1 g NaHCO_3/L . The ion-exchange resin, Lewatit® MonoPlus TP260 resin, was provided by Lanxess.

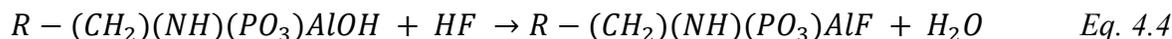
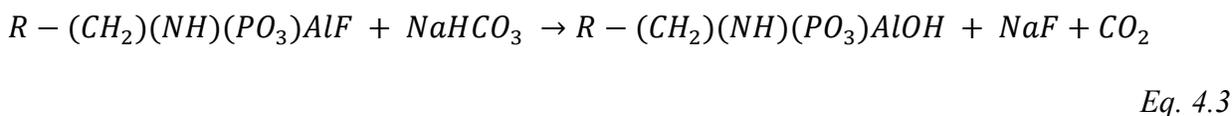
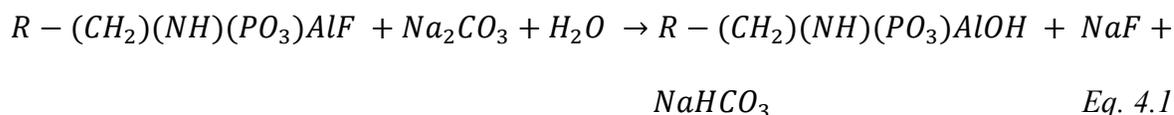
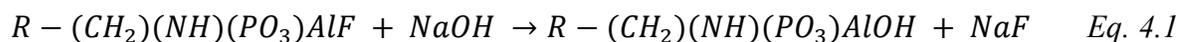
The experimental apparatus was the same as chapter 3.

4.2.2 Procedures

4.2.2.1 Base stripping behavior of fluoride loaded resin and fluoride-loading behavior of base stripped resin

The first 3 steps of TP 260 resin treatment were the same as chapter 3.

In order to reuse the fluoride loaded resin, it is important to strip the loaded fluoride. In this step, several kinds of base were tested as stripping reagent and the expected reactions involved in these steps are shown as Eq. 4.1 to 4.3. Assuming the stripping agents removed the loaded fluoride ions successfully, the resin could be reused in hydroxide form for the further fluoride removal in new feed solution. The reaction involved is illustrated as Eq. 4.4.



4.2.2.2 Pretreatment of TP260 resin and preparation of chemicals

In order to test the precise volume of wet resin, the TP260 resin was immersed into deionized water for at least 8 hours. Apart from that, 10 ppm fluoride (which was 22.1 ppm sodium fluoride) with concentrated zinc sulfate solution was prepared using a standard sodium fluoride solution of 1000 ppm fluoride (as of 2.21 g NaF/L) and zinc sulfate heptahydrate. For the

solutions used for base stripping, 1 g NaOH/L solution, 1 g Na₂CO₃/L solution and 1 g NaHCO₃/L solution were prepared.

4.2.2.3 Procedures for fluoride-loading behavior in 2 M zinc sulfate solution and base stripping tests

The aluminum pre-loading step was the same as it in chapter 3 and is not repeated here.

Therefore the experimental procedures consisted of the following steps:

A) Fluoride-loading in 2 M zinc sulfate solution

- a. A volume of 20 mL of the aluminum pre-loaded resin was placed in the burette.
- b. A 10 ppm sodium fluoride in 2 M zinc sulfate solution was prepared by mixing 1000 ppm standard sodium fluoride solution, zinc sulfate heptahydrate and deionized water. This solution was labeled as input solution.
- c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.
- d. The fluoride concentration of the output solution was analyzed and plotted as loading curve.

B) Sodium hydroxide stripping and fluoride-loading cycle

- a. The fluoride-loaded resin was prepared.

b. A 1g/L sodium hydroxide solution was prepared by mixing sodium hydroxide solid and deionized water. This solution was labeled as stripping solution.

c. The stripping solution was passed through at a flow rate of 5 BV/h (100 mL/hour) for 8 hours.

d. The sodium hydroxide stripped resin was flushed by deionized water at a flow rate of 5 BV/h (100 mL/h) for 2 hours.

e. A second fluoride-loading step was repeated the same as A).

C) Sodium carbonate stripping and fluoride-loading cycle

a. The fluoride-loaded resin was prepared.

b. A 1g/L sodium carbonate solution was prepared by mixing sodium carbonate solid and deionized water. This solution was labeled as stripping solution.

c. The stripping solution was passed through at a flow rate of 5 BV/h (100 mL/hour) for 8 hours.

d. The sodium carbonate stripped resin was flushed by deionized water at a flow rate of 5 BV/h (100 mL/h) for 2 hours.

e. A second fluoride-loading step was repeated the same as A).

D) Sodium bicarbonate stripping and fluoride-loading cycle

a. The fluoride-loaded resin was prepared.

- b. A 1g/L sodium bicarbonate solution was prepared by mixing sodium bicarbonate solid and deionized water. This solution was labeled as stripping solution.
- c. The stripping solution was passed through at a flow rate of 5 BV/h (100 mL/hour) for 8 hours.
- d. The sodium bicarbonate stripped resin was flushed by deionized water at a flow rate of 5 BV/h (100 mL/h) for 2 hours.
- e. A second fluoride-loading step was repeated the same as A).

E) Sodium hydroxide stripping test

- a. The first fluoride-loaded resin was used.
- b. A 1 g/L sodium hydroxide solution was prepared by mixing sodium hydroxide and deionized water. This solution was labeled as stripping input.
- c. The stripping solution was passed at a flow rate of 5 BV/h (100 mL/hour) for 6 hours. The aluminum and fluoride concentration in the output solution was analyzed every half hour. The volume of the output solution was measured and set as the volume passed through the resin.
- d. The results were plotted on one diagram as the loading curve.

4.2.2.4 Analytical methods and evaluator factors

The analytical methods were the same as those listed in chapter 3. The key factor of loaded fluoride is the same as reported in chapter 3.

4.3 Fluoride-loading behavior of Lewatit® MonoPlus TP260 resin in 2 M zinc sulfate solution

A number of experiments were carried to define the fluoride-loading behavior of TP260 resin in 2 M zinc sulfate solution. The experiments were performed under ambient conditions unless otherwise noted separately. Fluoride-loading behavior tests were repeated three times to ensure reproducibility. Table 4.1 shows the conditions of fluoride-loading behavior in 2 M zinc sulfate solution.

Table 4.1 Conditions for fluoride-loading behavior of TP 260 resin

	Temperature	Room temperature
Resin states	Form	Aluminum chloride form
	Dosage	20 mL (wet, Na form)
	NaF Concentration	10 ppm F (22.1 ppm NaF)
NaF input solution	ZnSO ₄ conc.	2 M
	Flow rate	5 BV/h
Flush water	Flow rate	5 BV/h

Figure 4.1 illustrates the results of fluoride-loading behavior of TP 260 resin in 2 M zinc sulfate solution. If the break through point was set as 10 ppm fluoride in output solution, it was found that the fluoride capacities of test 4 to test 6 in 2 M zinc sulfate solution were 7.53 g F/L resin, 5.57 g F/L resin and 8.62 g F/L resin. The breakthrough points in this chapter and chapter 5 were set as 10 ppm fluoride in the eluent solution because the complete fluoride-loading curve is essential to the results of this work

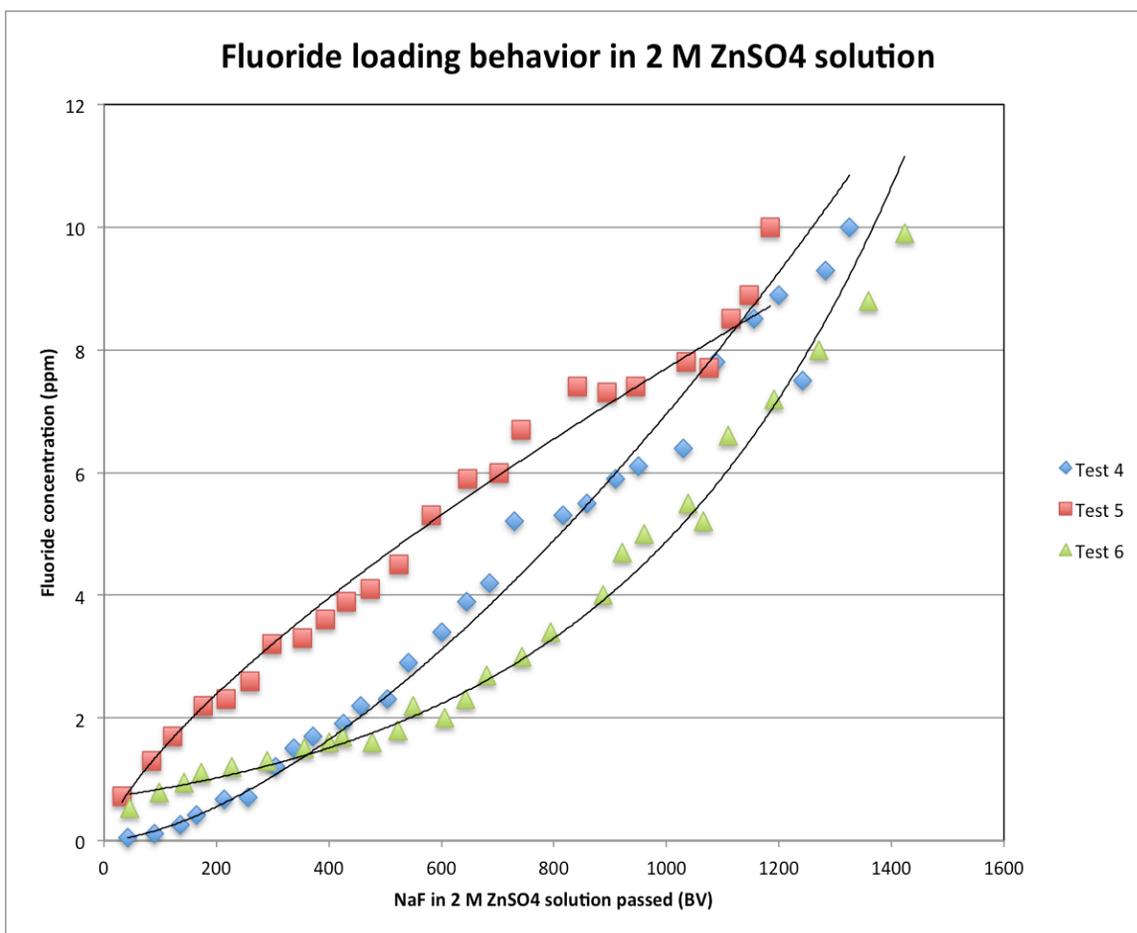


Figure 4.1 Fluoride-loading behavior in 2 M zinc sulfate solution

4.4 Base stripping and fluoride-loading cycles

Another numbers of experiments were carried to define the base stripping behavior of TP260 resin in 2 M zinc sulfate solution. The experiments were performed under ambient conditions unless otherwise noted separately. Table 4.2 shows the conditions of base stripping behaviors and fluoride-loading cycle in 2 M zinc sulfate solution.

Table 4.2 Conditions for base stripping behaviors of TP 260 resin

		NaOH stripping	Na ₂ CO ₃ stripping	NaHCO ₃ stripping
Temperature		Room temperature	Room temperature	Room temperature
Resin states	Form	Aluminum fluoride	Aluminum fluoride	Aluminum fluoride
	Dosage	20 mL (wet, Na form)	20 mL (wet, Na form)	20 mL (wet, Na form)
Base solution	Base conc.	1g NaOH/L	1 g Na ₂ CO ₃ /L	1g NaHCO ₃ /L
	Flow rate	5 BV/h	5 BV/h	5 BV/h
Flush water	Flow rate	5 BV/h	5 BV/h	5 BV/h

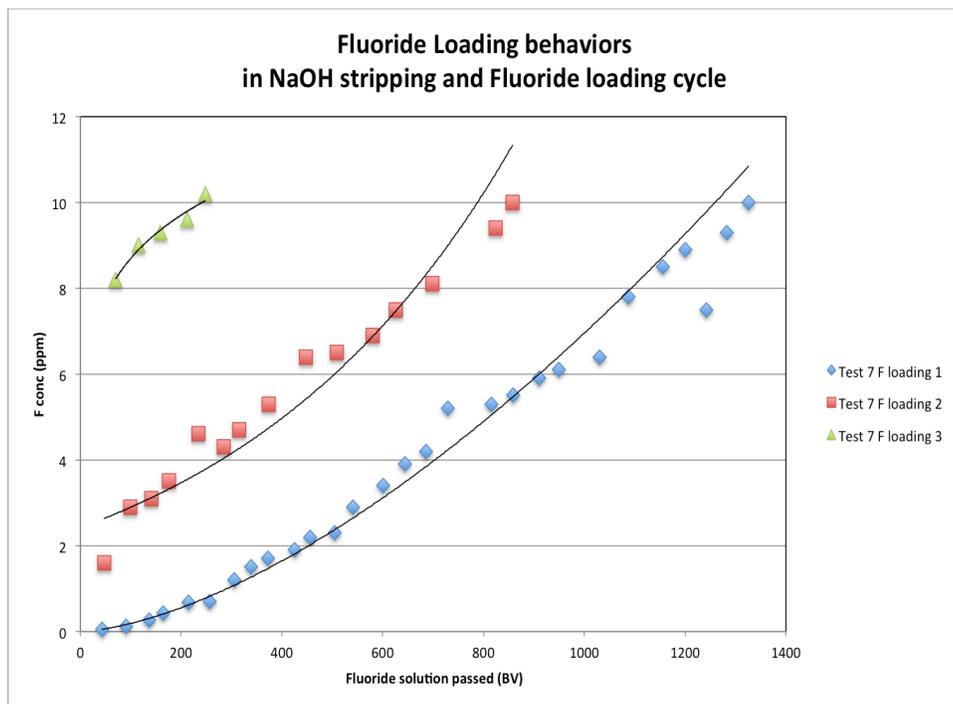


Figure 4.2 Fluoride-loading behaviors in sodium hydroxide stripping and fluoride-loading cycle

Figure 4.2 illustrates the results of sodium hydroxide stripping behavior of TP 260 resin in 2 M zinc sulfate solution. If the break through point was set as 10 ppm fluoride in output solution, it

was found that the fluoride capacities of fluoride-loading 1 to 3 were 7.53 g F/L resin, 3.11 g F/L resin and 0.22 g F/L resin.

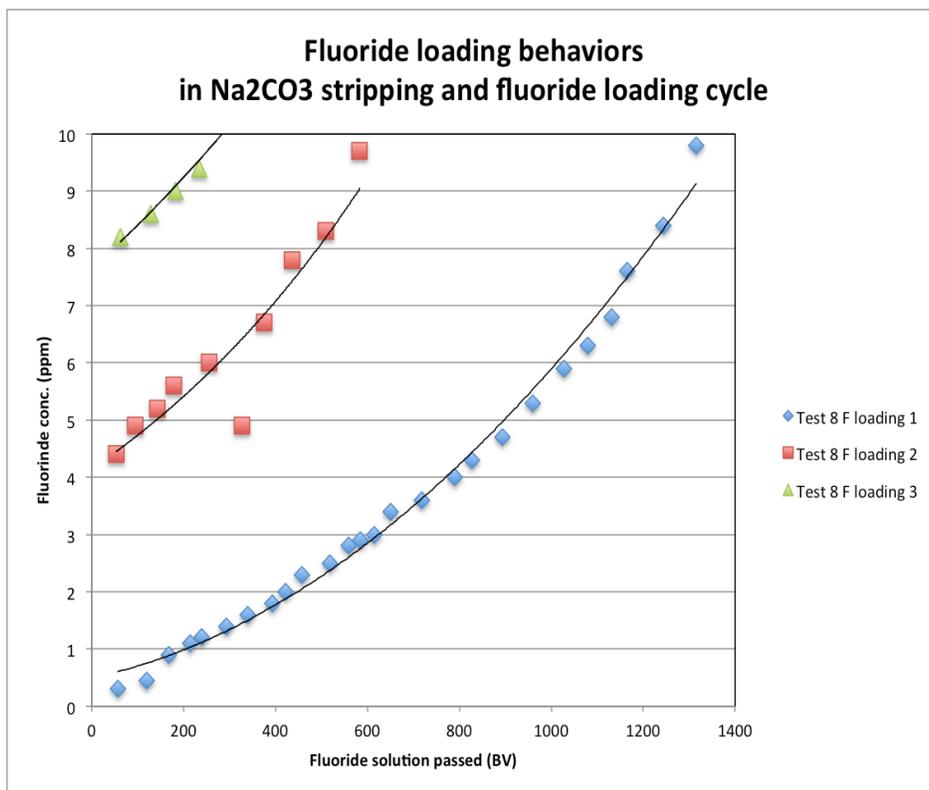


Figure 4.3 Fluoride-loading behaviors in sodium carbonate stripping and fluoride-loading cycle

Figure 4.3 illustrates the results of sodium carbonate stripping behavior of TP 260 resin in 2 M zinc sulfate solution. If the break through point was set as 10 ppm fluoride in output solution, it was found that the fluoride capacities of fluoride-loading 1 to 3 were 7.99 g F/L resin, 2.01 g F/L resin and 0.27 g F/L resin.

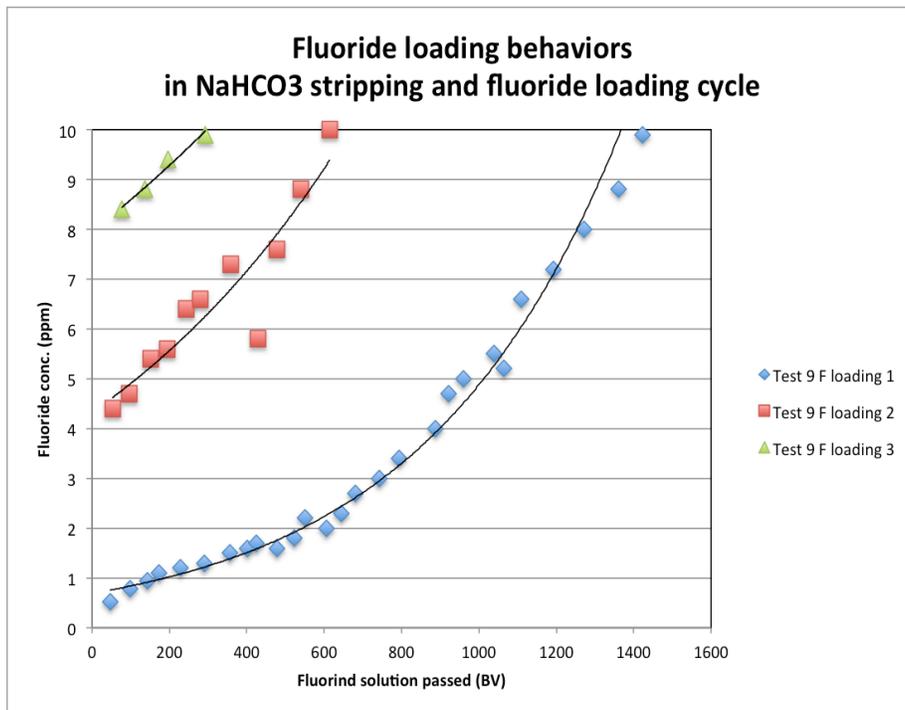


Figure 4.4 Fluoride-loading behaviors in sodium bicarbonate stripping and fluoride-loading cycle

Figure 4.4 illustrates the results of sodium bicarbonate stripping behavior of TP 260 resin in 2 M zinc sulfate solution. If the break through point was set as 10 ppm fluoride in output solution, it was found that the fluoride capacities of fluoride-loading 1 to 3 were 8.62 g F/L resin, 1.97 g F/L resin and 0.24 g F/L resin.

4.5 Sodium hydroxide stripping behavior of aluminum fluoride pre-loaded resin

As the results of base stripping and fluoride-loading cycle tests, the fluoride capacity of aluminum pre-loaded resin is dropped dramatically. These results show the three kinds of base have a similar influence on fluoride ions, which loaded on the TP 260 resin. Also, these results

illustrate the hydroxide ions stripped not only fluoride ion but also the aluminum ions loaded on the resin which cause the aluminum lost which also implies an increase of financial cost.

Therefore an experiment of sodium hydroxide stripping behavior is necessary. The experiment conditions were the same as the sodium hydroxide stripping test in section 4.4.

Figure 4.5 illustrates the results of sodium hydroxide stripping behavior of first fluoride loaded TP 260 resin. It was found that the fluoride stripped was 1.74 g F/L resin and the aluminum stripped was 0.05 mol Al/L resin.

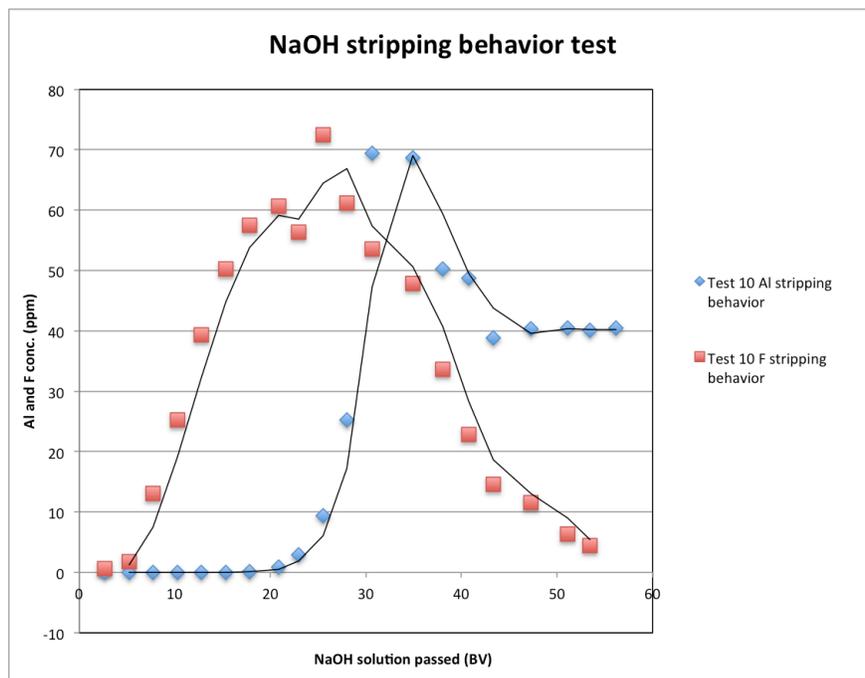
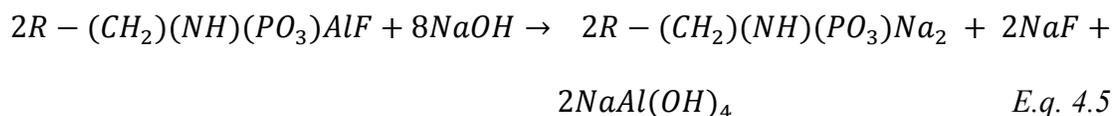


Figure 4.5 Sodium hydroxide stripping behavior

4.6 Discussion

The fluoride stripped by sodium hydroxide stripping was 1.74 g F/L resin and the aluminum stripped in this step was 0.05 mol Al/L resin. As for the fluoride loaded in the first fluoride-loading which was 7.5 g F/L resin and pre-loaded aluminum was 1.05 mol Al/L resin. This results indicates the aluminum loss during the stripping step and 1 g/L sodium hydroxide solution may be not able to strip all the fluoride loaded on the resin. Also, this result matches the fluoride capacity decreasing in second and third fluoride-loading step. During the sodium hydroxide stripping test, the results show the aluminum is partially stripped which can be described as Eq. 4.5.



4.7 Summary

- 1) It was found that the aluminum pre-loaded resin has a relatively stable fluoride capacity in zinc sulfate system, which is around 7.5 g F/L resin. The sodium hydroxide stripping and fluoride-loading cycle reduce the fluoride capacities from 7.53 g F/L resin to 3.11 g F/L resin and then 0.22 g F/L resin at last. The sodium carbonate stripping and fluoride-loading cycle drop the fluoride capacities from 7.99 g F/L resin then 2.01 g F/L resin and 0.27 g F/L resin in the third fluoride-loading step. The sodium bicarbonate stripping and fluoride-loading

cycle also decrease the fluoride capacities from 8.62 g F/L resin to 1.97 g F/L resin and 0.24 g F/L resin at last.

- 2) It was found that all the 3 kinds of chosen base, sodium hydroxide, sodium carbonate and sodium bicarbonate can be used to strip the fluoride loaded on the aluminum pre-loaded resin. Also, the base stripped resin can be reused for fluoride-loading again. Whereas the fluoride capacities decreased with successive loading and stripping cycles and the choice of base stripping dramatically and the difference of base has little influence on the fluoride capacity decrease.
- 3) It was found that the sodium hydroxide not only strips the fluoride loaded on the resin but also strips the aluminum from on the resin, which causes aluminum loss and also increasing of financial cost.

Chapter 5: Study on Commercial Aluminum Pre-loading and Stripping Process in Zinc Sulfate System and the Influence of Impurities

5.1 Introduction

As it is shown in chapter 4, aluminum is believed to be lost as long as the base stripping continues. Therefore a commercial aluminum pre-loading and fluoride stripping cycle is necessary to be studied. In this trial, aluminum sulfate was chosen as the aluminum pre-loading reagent and sulfuric acid was chosen as the stripping acid. Acid was used to convert the resin to its hydrogen form during stripping and elution and then sodium hydroxide was used to convert the hydrogen form resin to its sodium form. As the resin was originally in the sodium form when received from Lanxess, the next step would be another cycle of aluminum pre-loading so the resin could be re-used for fluoride removal.

In this chapter, the experimental apparatus and procedures are illustrated in section 5.2. In section 5.3, the fluoride-loading behavior of aluminum sulfate pre-loading is reported. In section 5.4 the aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration are reported. After that the influences of several impurities are illustrated in section 5.5 and 5.6. Finally, some discussions and conclusions of this part of work are provided in section 5.7 and 5.8.

5.2 Experimental

5.2.1 Materials and apparatus

All the solutions were prepared from reagent grade or analytical grade chemicals and deionized water without further purification. Aluminum sulfate octadecahydrate, sulfuric acid, sodium hydroxide, zinc sulfate heptahydrate, magnesium sulfate, manganese sulfate monohydrate, sodium fluoride and TISAB II solution were provided by Sigma-Aldrich. The aluminum sulfate pre-loading solution was prepared to be 71 g $\text{Al}_2(\text{SO}_4)_3/\text{L}$ (11.19 g Al/L) by aluminum sulfate octadecahydrate and deionized water. For the study of aluminum sulfate pre-loading trial, fluoride input solution was prepared to be 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate by sodium fluoride, zinc sulfate heptahydrate and deionized water. For the experiments of aluminum influence, the fluoride input solution was prepared to be 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate solution and 100 ppm Al (0.634 g $\text{Al}_2(\text{SO}_4)_3/\text{L}$, by sodium fluoride, zinc sulfate heptahydrate, aluminum sulfate octadecahydrate and deionized water. As for the experiments of aluminum and other impurities influence, the fluoride input solution was prepared to be 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate solution with 100 ppm Al (0.634 g $\text{Al}_2(\text{SO}_4)_3/\text{L}$, 20 g/L Mg (99.03 g MgSO_4/L) and 5 g/L Mn (13.74 g MnSO_4/L) by sodium fluoride, zinc sulfate heptahydrate, aluminum sulfate octadecahydrate magnesium sulfate, manganese sulfate monohydrate and deionized water. The ion-exchange resin, Lewatit® MonoPlus TP260 resin, was provided by Lanxess.

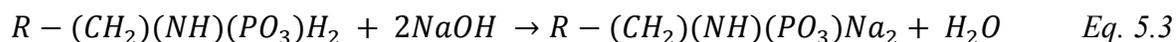
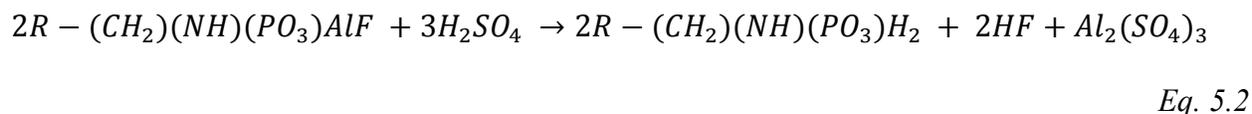
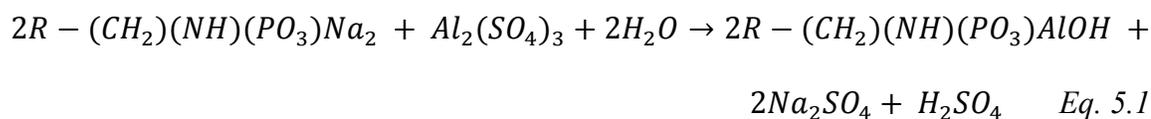
The experimental apparatus was the same as chapter 3.

5.2.2 Procedures

5.2.2.1 Aluminum sulfate pre-loading, sulfuric acid stripping and sodium hydroxide regeneration cycle

The pretreatment of TP 260 resin was preformed in the same way as in chapter 3.

In this step, aluminum sulfate was used as a preloading reagent, and sulfuric acid and sodium hydroxide were used for stripping and the reactions involved in these steps are shown as Eq. 5.1 to 5.3.



5.2.2.2 Pretreatment of TP260 resin

In order to test the precise volume of wet resin, the TP260 resin was immersed into deionized water for at least 8 hours.

5.2.2.3 Procedures for aluminum sulfate pre-loading behavior and stripping tests

The experimental procedures consisted of the following steps:

A) Aluminum sulfate pre-loading step

- a. The DI water immersed resin was used.
- b. A 71 g $\text{Al}_2(\text{SO}_4)_3/\text{L}$ (11.19 g Al/L) aluminum sulfate solution was prepared by mixing aluminum sulfate octadecahydrate and deionized water. This solution was labeled as input solution.
- c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour) for 2.5 h.
- d. The aluminum pre-loaded resin was flushed with DI water at a flow rate of 5 BV/h for 8 h.

B) Sulfuric acid stripping and sodium hydroxide regeneration step

- a. The fluoride-loaded resin was prepared.
- b. A solution of 10 g/L sulfuric acid was prepared by mixing concentrated sulfuric acid (98%) and deionized water. This solution was labeled as input acid solution.
- c. The input acid solution was passed through the fluoride-loaded resin at a flow rate of 5 BV/h for 10 hours. The fluoride and aluminum concentration in the output solution were analyzed as 2, 4, 6, 8, 10, 20, 30, 40 and 50 BV solution passed. The volume of the output solution was measured and set as the volume passed through the resin. The results were plotted on one diagram as the sulfuric acid stripping behavior curve.
- d. The resin was then flushed with deionized water at a flow rate of 5 BV/h for 8 hours.

- e. A 1 g/L sodium hydroxide solution was prepared by mixing sodium hydroxide and deionized water. This solution was labeled as input base solution.
- f. The input base solution was passed through the resin at a flow rate of 5 BV/h. The fluoride and aluminum concentration in the output solution were analyzed as 2, 4, 6, 8, 10, 20, 30, 40 and 50 BV solution passed. The volume of the output solution was measured and set as the volume passed through the resin. The results were plotted on one diagram as the sodium hydroxide stripping behavior curve.
- g. The resin was then flushed by deionized water at the flow rate of 5 BV/h for 8 hours.

C) Fluoride-loading step

- a. A volume of 20 mL of the aluminum pre-loaded resin was placed in the burette.
- b. A solution of 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate was prepared by mixing sodium fluoride, zinc sulfate heptahydrate and deionized water. This solution was labeled as input solution.
- c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.
- d. The fluoride concentration of the output solution was analyzed and plotted as loading curve.

D) Fluoride-loading step for the influence in Al impurity test

- a. A volume of 20 mL of the aluminum pre-loaded resin was placed in the burette.

- b. A 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate solution and 100 ppm Al was prepared by mixing sodium fluoride, zinc sulfate heptahydrate, aluminum sulfate octadecahydrate, and deionized water. This solution was labeled as input solution.
- c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.
- d. The fluoride concentration of the output solution was analyzed and plotted as loading curve.

E) Fluoride-loading step for the influence of Al, Mg, Mn impurities test

- a. A volume of 20 mL of the aluminum pre-loaded resin was placed in the burette.
- b. A 10 ppm F (2.21×10^{-2} g NaF/L) with 2 M zinc sulfate solution, 100 ppm Al, 20 g/L Mg and 5 g/L Mn was prepared by mixing sodium fluoride, zinc sulfate heptahydrate, aluminum sulfate octadecahydrate, magnesium sulfate, manganese sulfate monohydrate and deionized water. This solution was labeled as input solution.
- c. The input solution was passed through at a flow rate of 5 BV/h (100 mL/hour). The fluoride concentration in the output solution was analyzed every 8 hours. The volume of the output solution was measured and set as the volume passed through the resin.
- d. The fluoride concentration of the output solution was analyzed and plotted as loading curve.

F) Aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step cycle

- a. Aluminum pre-loaded resin was used.

- b. A fluoride-loading step was processed as C)
- c. The fluoride-loaded resin was flushed by DI water at a flow rate of 5 BV/h for 8 hours.
- d. A sulfuric acid stripping and sodium hydroxide regeneration step was processed as B)
- e. An aluminum sulfate pre-loading was processed as A)
- f. An aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step cycle was repeated.

G) The influence of Al impurity test

- a. Aluminum pre-loaded resin was used.
- b. A fluoride-loading step was processed as D)
- c. The fluoride-loaded resin was flushed by DI water at a flow rate of 5 BV/h for 8 hours.
- d. A sulfuric acid stripping and sodium hydroxide regeneration step was processed as B)
- e. An aluminum sulfate pre-loading was processed as A)
- f. An aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step cycle was repeated.

H) The influence of Al, Mg and Mn impurities test

- a. Aluminum pre-loaded resin was used.
- b. A fluoride-loading step was processed as E)
- c. The fluoride-loaded resin was flushed by DI water at a flow rate of 5 BV/h for 8 hours.
- d. A sulfuric acid stripping and sodium hydroxide regeneration step was processed as B)
- e. An aluminum sulfate pre-loading was processed as A)

f. The cycle of aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step was repeated.

5.2.2.4 Analytical methods and evaluator factors

The analytical methods were the same as those listed in chapter 3 and 4.

5.3 Fluoride-loading behavior of aluminum sulfate pre-loading

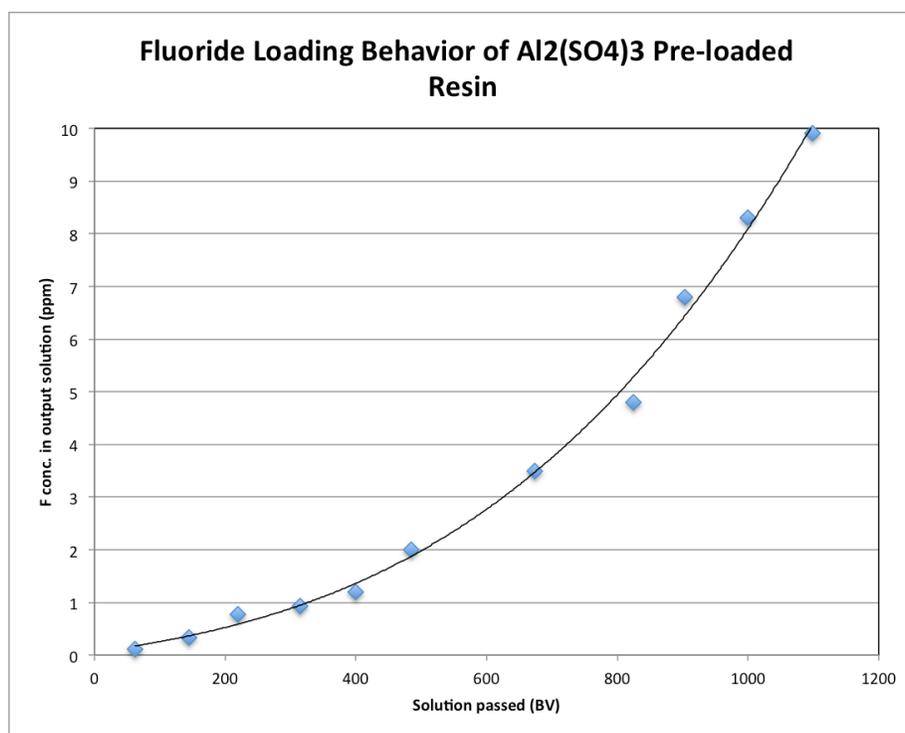


Figure 5.1 Fluoride-loading behavior of aluminum sulfate pre-loaded resin

Figure 5.1 illustrates the results of fluoride-loading behavior of aluminum sulfate pre-loaded resin. It was found that the fluoride capacity was 7.27 g F/L resin which is similar to aluminum

chloride pre-loaded resin (7.5 g F/L resin). Thus aluminum sulfate can be used to pre-load aluminum to the TP 260 resin.

5.4 Sulfuric acid stripping and sodium hydroxide regeneration step behavior

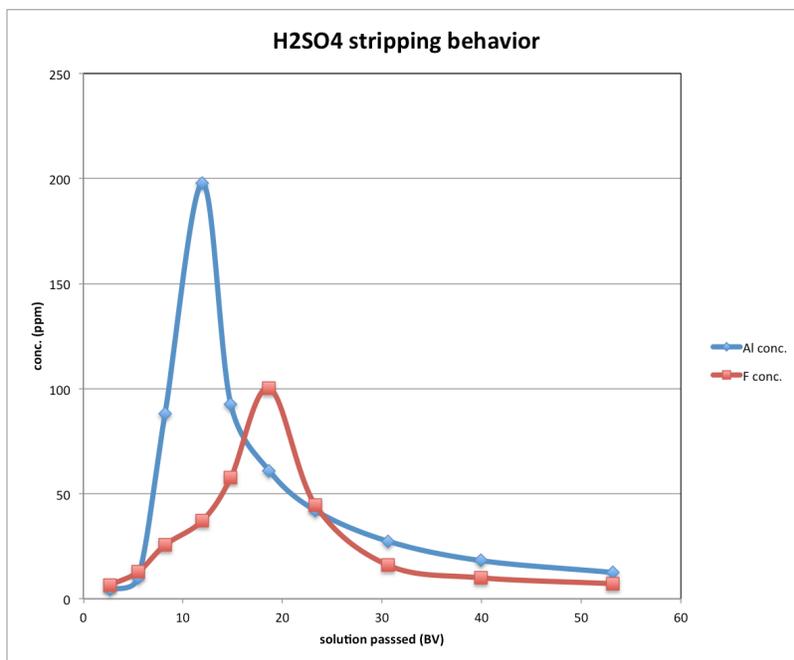


Figure 5.2 Sulfuric acid stripping behavior

Figure 5.2 and 5.3 illustrate the results of the sulfuric acid stripping and sodium hydroxide regeneration step behavior test. It was found that the total fluoride stripped during this test was 1.325 g F/L resin in sulfuric acid stripping along with 0.044 g F/L resin during sodium hydroxide regeneration. Meanwhile, the aluminum stripped was 0.083 mol Al/L resin in sulfuric acid stripping, and 0.00026 mol Al/L resin is stripped during sodium hydroxide regeneration.

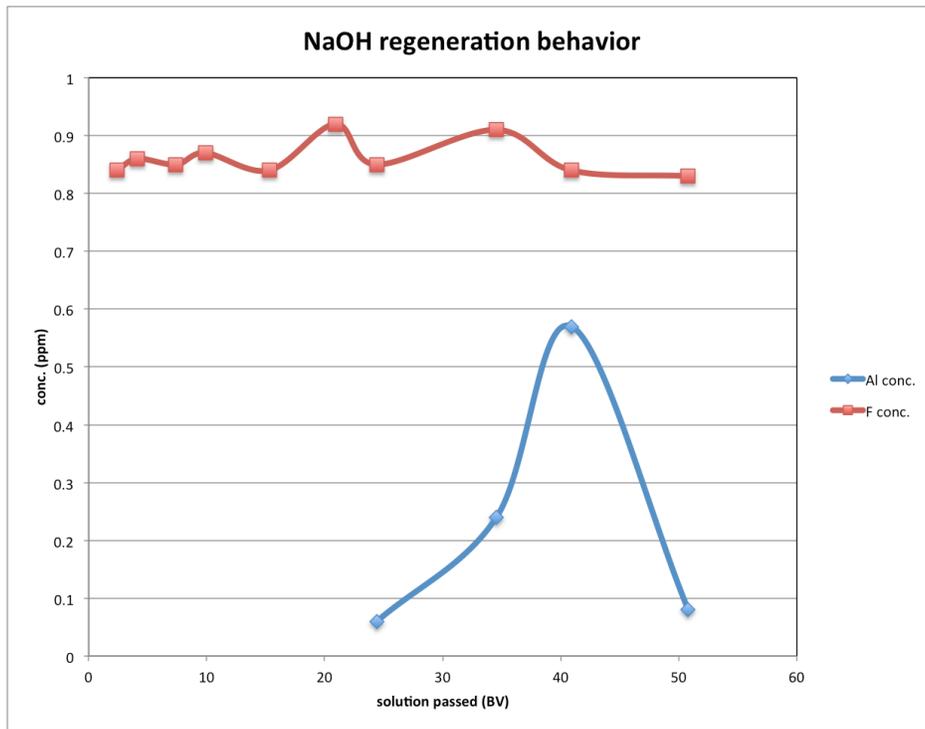


Figure 5.3 Sodium hydroxide regeneration behavior

Table 5.1 indicates the aluminum and fluoride stripped in sulfuric acid and sodium hydroxide regeneration step. The results show the total aluminum stripped in the sulfuric acid stripping step, sodium hydroxide regeneration and flush water is 0.085 mol Al/L resin. As for the fluoride stripped, the total fluoride stripped in the sulfuric acid stripping step and sodium hydroxide regeneration is 1.475 g F/L resin. It is necessary to perform further study on the mass balance for fluoride-loading and elution. It is believed that the fluoride analysis of the acid strip solution may be in error.

Table 5.1 Aluminum and fluoride concentration in flush water after sulfuric acid stripping and sodium hydroxide regeneration

	Flush water volume (mL)	Aluminum concentration (ppm)	Aluminum stripped (mol/L resin)	Fluoride concentration (ppm)	Fluoride stripped (g/L resin)
After sulfuric acid stripping	1360	0.13	0.0003	2.2	0.1496
After sodium regeneration	1685	0.16	0.0005	0.02	0.0017

5.5 Fluoride-loading behavior of aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step

Figure 5.4 illustrates the results of fluoride-loading behavior of aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration step test. It was found that the fluoride capacities were 7.27 g F/L resin and 7.21 g F/L resin in the first and second fluoride-loading steps.

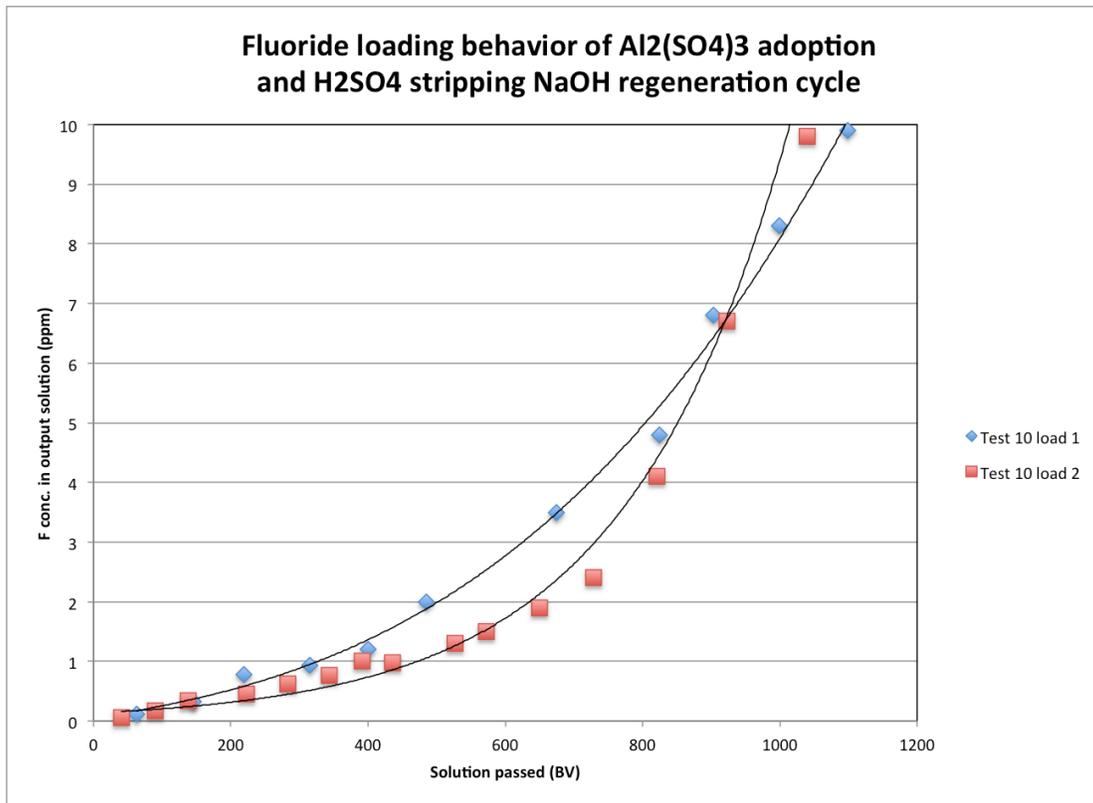


Figure 5.4 Fluoride-loading behavior of aluminum sulfate pre-loading and sulfuric acid stripping and sodium hydroxide regeneration cycle

5.6 Impurity influences of aluminum, magnesium and manganese

Some of the impurities such as aluminum, magnesium and manganese can influence the performance of MonoPlus TP 260 resin and analytical results of fluoride. For example, fluoride complexes may exist in the solution (AlF^{2+} , MgF^+ and MnF^+) as well as react with the resin. Therefore, it is important to understand the fluoride-loading behavior and resin performance under the influence of these impurities. The magnesium concentration in zinc sulfate electrolyte is as high as 15-25 g Mg/L and the manganese concentration is often on the range of 4-8 g Mn/L.

Therefore, the feed solution for aluminum influence was prepared to be 2 M zinc sulfate, 100 ppm Al as aluminum sulfate, and 10 ppm F as sodium fluoride while the feed solution for aluminum, magnesium and manganese influence was prepared to be 2 M zinc sulfate, 100 ppm Al as aluminum sulfate, 20 g Mg/L as magnesium sulfate, 5 g Mn/L as manganese sulfate and 10 ppm F as sodium fluoride.

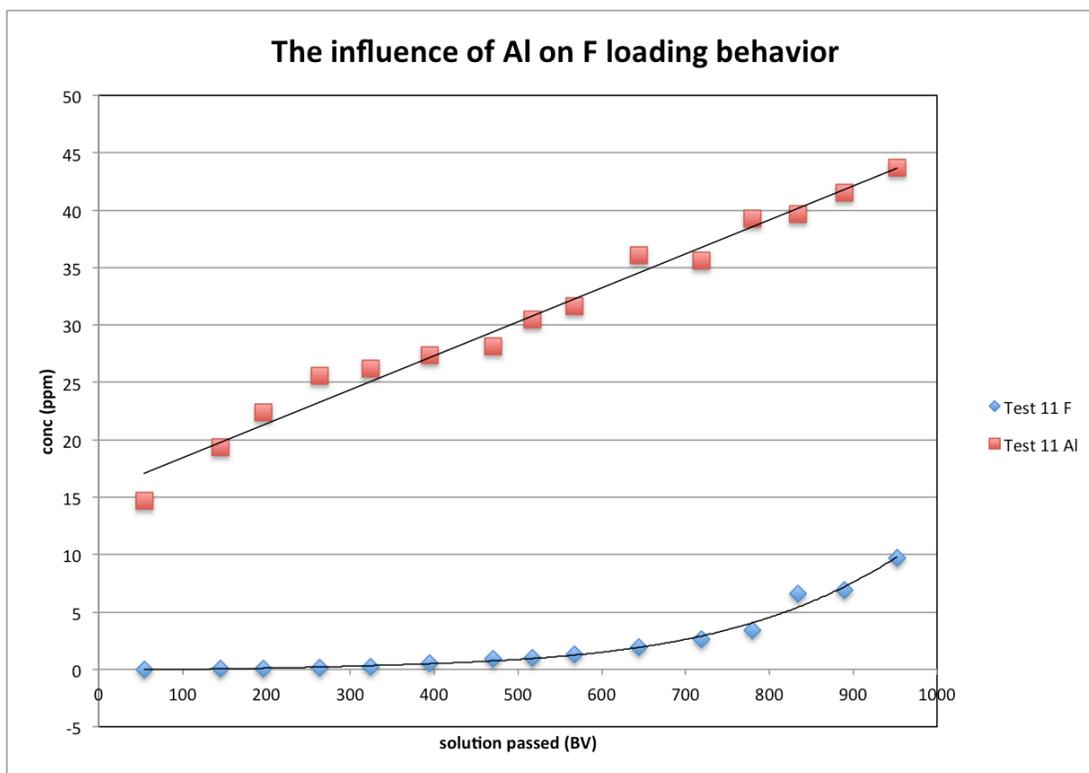


Figure 5.5 Influence of aluminum on fluoride-loading behavior

Figure 5.5 illustrates the results of aluminum influence test. The aluminum concentration in solution was increasing to approximately 40 ppm and the capacity of fluoride was 7.37 g F/L resin. Figure 5.6 illustrates the results of the influence of all three kinds of impurities. The

aluminum concentration in solution was increasing to approximately 30 ppm and it could also be found that the capacity of fluoride was 7.30 g F/L resin.

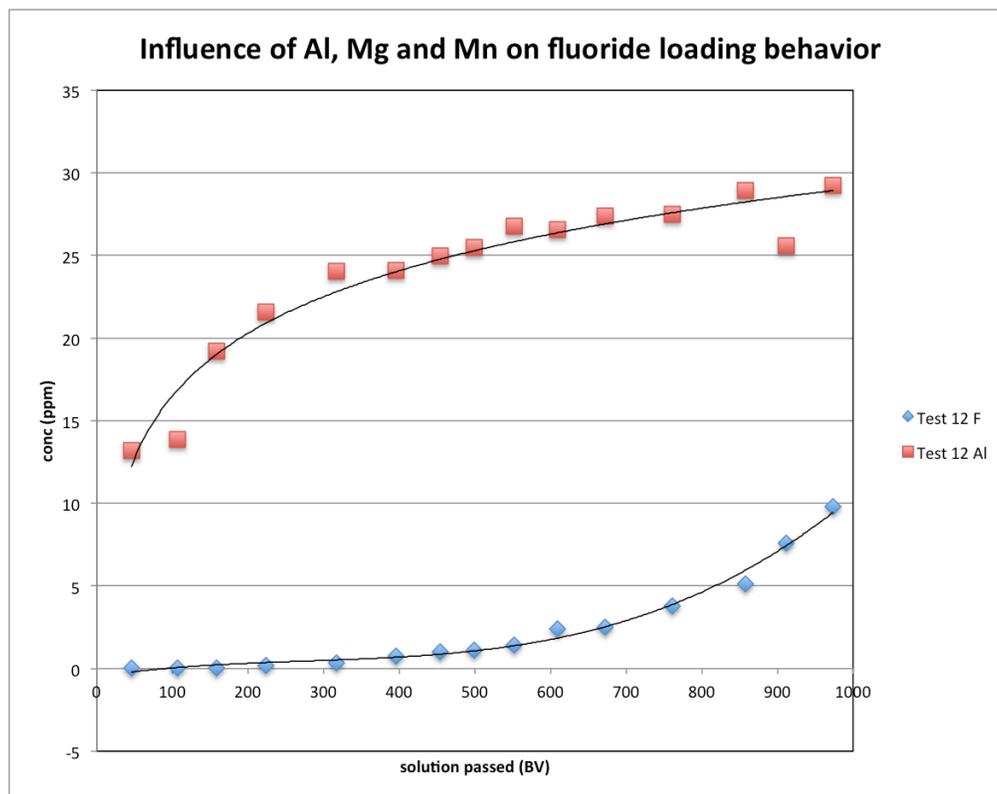


Figure 5.6 Influence of Al, Mg and Mn on fluoride-loading behavior

5.7 Discussion

The fluoride loaded on the aluminum pre-loaded resin was 7.27 g F/L resin during the first fluoride-loading step, however the fluoride stripped during sulfuric acid stripping and sodium hydroxide regeneration was only 1.475 g F/L resin (subject to further investigation). This illustrates the concentration of sulfuric acid solution and sodium hydroxide solution used in this

experiment was relatively low because the fluoride and aluminum loaded couldn't be completely stripped. However, the fluoride-loading capacity in the second fluoride-loading step was 7.21 g F/L resin which was similar to the fluoride capacity in the first fluoride-loading step. This may illustrate that in the second aluminum sulfate loading step, both the aluminum loading reaction and fluoride stripping reaction took place since concentrated aluminum sulfate solution had a relatively low pH. Eq. 5.4 describes the probable reaction involved in the second aluminum sulfate loading step that is not listed in section 5.2.2.1.



During the influence of impurities tests, the initial aluminum concentration prepared in the feed solution was 100 ppm. Therefore the aluminum removed from the zinc sulfate solution in the influence of aluminum on fluoride-loading behavior test was 56.33%, the aluminum removed from the zinc sulfate solution in the influence of aluminum, magnesium, and manganese on fluoride-loading behavior test was 70.77%.

5.8 Summary

- 1) It was found that aluminum and fluoride was stripped from the resin during both sulfuric acid stripping and sodium hydroxide stripping while the total fluoride stripped during this test was 1.475 g F/L resin and the aluminum stripped was 0.085 mol Al/L resin.

- 2) It could also be found that the fluoride capacities are 7.27 g F/L resin and 7.21 g F/L resin in the cycle of aluminum sulfate pre-loading, fluoride-loading and sulfuric acid stripping and sodium hydroxide regeneration. Also, the flooding curves of the two loading steps were similar as well as the fluoride capacity and breakthrough point.
- 3) It was found that the impurities of aluminum, magnesium and manganese have slight influences on the fluoride capacities of aluminum sulfate pre-loaded resin. The fluoride capacity of aluminum influence test is 7.37 g F/L resin whereas the fluoride capacity in aluminum, magnesium and manganese influence experiment is 7.30 g F/L. Additionally, the aluminum concentration in the solution reached to 40 ppm and 30 ppm in the two experiments.

Chapter 6: Conclusions and Recommendations

6.1 Summary of the results

Fluoride removal from zinc sulfate electrolyte solution by Lewatit® Monoplus TP260 resin was studied with variation of experimental conditions. The results from this work can be summarized as below:

- 1) Aluminum chloride can be pre-loaded onto the Lewatit® Monoplus resin in the sodium form and the aluminum capacity of fresh resin was about 1.05 mol/L resin. Additionally, the fluoride capacity in low concentration solution (10 ppm F and 5 g /L NaCl solution) was about 3.2 g F/L resin when the breakthrough point was set as 1 ppm in eluent solution whereas the fluoride capacity in 10 ppm F in DI water solution was less than 0.5 g F/L resin.
- 2) The aluminum chloride pre-loaded resin may also be applied to the fluoride removal in zinc sulfate electrolyte system. The results in this part of work illustrate the fluoride capacities were approximately 7.5 g F/L resin. However, when three different kinds of basic stripping steps were included in the fluoride removal cycle, the fluoride capacities decreased dramatically to around 2.5 g F/L resin and then about 0.22 g F/L resin. The ICP test for sodium hydroxide stripping behavior also showed that pre-loaded aluminum would be also stripped (0.05 mol Al/L resin) as well as the fluoride (1.74 g F/L resin).
- 3) An aluminum-loading step was necessary to be applied prior to the fluoride removal cycle. Aluminum sulfate was chosen as an alternative reagent because of potentially lower cost than

the aluminum chloride used in the Lanxess process and the better compatibility with the zinc electrowinning process. the chloride ion was undesirable in the zinc plating system due to concerns around anode corrosion. The results of the first fluoride-loading test showed that aluminum sulfate could be applied to replace aluminum chloride for aluminum pre-loading. The fluoride capacity of aluminum sulfate pre-loaded resin was measured as 7.27 g F/L resin and was similar to that achieved for the aluminum chloride pre-loaded resin. Also, the results of sulfuric acid stripping and sodium hydroxide regeneration illustrated that the total fluoride stripped was 1.475 g F/L resin and the total aluminum stripped was 0.085 mol Al/L resin. After that, the fluoride capacity of second fluoride-loading was 7.21 g F/L.

- 4) The influence of additional impurities (aluminum, magnesium and manganese) in the zinc sulfate solution were also studied and the results indicated that the influences of these impurities on fluoride capacity were slight and the fluoride capacity remained at 7.3 to 7.4 g F/L resin.

6.2 Conclusions

Therefore, the conclusion of this work can be summarized as below:

- 1) Aluminum can be successfully pre-loaded onto the Lewatit® Monoplus TP260 resin with a good reproducibility of aluminum capacity. The resin can also be used for the fluoride removal from low concentrated solution but not as low as 10 ppm NaF solution.

- 2) The three kinds of base, sodium hydroxide, sodium carbonate and sodium bicarbonate can be used for the stripping of fluoride and also aluminum pre-loaded on the resin. These bases have similar influences on the fluoride capacities. The fluoride-loading capacity decrease with each successive base stripping and fluoride-loading cycle.
- 3) Aluminum sulfate can be used to replace aluminum chloride for aluminum pre-loading. Sulfuric acid stripping and sodium hydroxide regeneration can also be used for fluoride stripping while an aluminum pre-loading step is required prior the further fluoride-loading step.
- 4) The cycle of aluminum sulfate pre-loading, fluoride-loading, sulfuric acid stripping and sodium hydroxide regeneration step and then aluminum sulfate pre-loading can be successfully used for fluoride removal in zinc sulfate system even if impurities exist.
- 5) Impurities of aluminum, magnesium and manganese have only a slight influence on the fluoride removal cycle.

6.3 Recommendations for future work

This work leaves a number of unexplained results and there are still helpful future works that can have the fluoride removal process optimization:

- 1) The mechanisms of most of the reactions involved in this work are still unclear; therefore SEM-WDS studies can substantiate the resin structure and cross-section, which is helpful to understand the reaction that is taking place during the fluoride removal cycle.

- 2) There are still some factors, which have significant influences on fluoride-loading reaction such as flow rate, aluminum concentration in pre-loading step and pH in the zinc sulfate system. Additionally, temperature is another significant factor and studies are also needed in this direction.
- 3) The fluoride removal process should be pilot tested to determine the fully cycle mass balance and show that the resin can be used for many cycles of aluminum pre-loading, fluoride-loading and stripping and resin regeneration.
- 4) The fluoride removal process should be tested with industrial solutions.

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Appendices

Appendix A Calibration of Fluoride ISE

- 1) Solutions and chemicals used in the calibration experiments

Solutions: TISAB II; Optimum Results A Fill Solution for Cadmium, Calcium, Fluoride and Sulfide ISE; 100 ppm Fluoride Standard Solution. These solutions are provided by ThermoFisher Scientific.

Chemicals: Zinc sulfate heptahydrate and sodium fluoride. These solid chemicals are provided by Sigma Aldrich.

- 2) The fluoride ISE calibration procedure is given by the fluoride ISE user guide and is consisted of the following steps:
 - a. The filling solution is first added into the electrode up to the filling hole.
 - b. A 0.1 ppm fluoride standard solution is prepared by 100 ppm Fluoride Standard Solution and DI water, so as a 1 ppm fluoride standard solution and a 10 ppm fluoride standard solution.
 - c. A 10 mL of 0.1 ppm fluoride standard solution and a 10 mL of TISAB II solution are added in a 30 mL beaker and is stirred thoroughly.

- d. The electrode is rinsed and then placed into the prepared solution in step c. When a stable reading is displayed, the electrode potential is recorded as 0.1 ppm fluoride.
 - e. Step c. and d. are repeated for 1 ppm and 10 ppm fluoride.
- 3) Fluoride ISE calibration and fluoride standard solutions recalibration lines

The calibration curve of Fluoride ISE is shown in Figure A.1 and the recalibration curve of fluoride standard solutions is illustrated in Figure A.2.

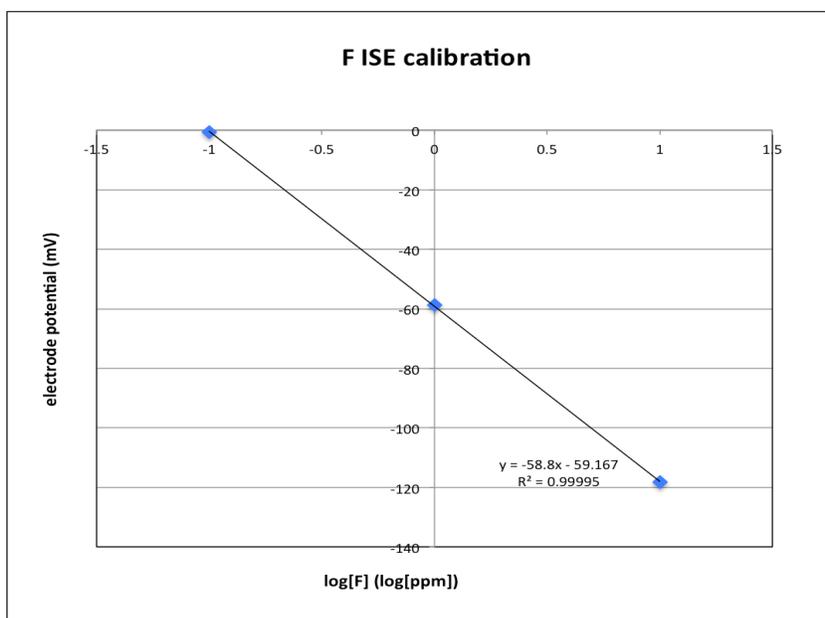


Figure A.1 Fluoride ISE calibration line

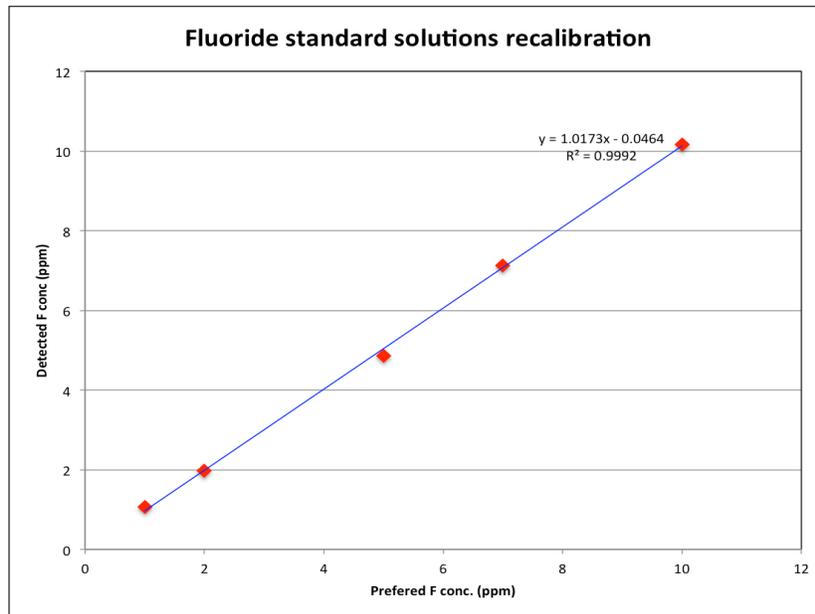


Figure A.2 Fluoride standard solution recalibration line

- 4) The Fluoride ISE calibration in 2M ZnSO₄ solution procedure is consisted of the following steps:
- a. The filling solution is first added into the electrode up to the filling hole.
 - b. A 0.1 ppm fluoride in 2M zinc sulfate standard solution is prepared by 100 ppm Fluoride Standard Solution, zinc sulfate heptahydrate and DI water, so as a 1 ppm fluoride in 2M zinc sulfate standard solution and a 10 ppm fluoride in 2M zinc sulfate standard solution.
 - c. A 10 mL of 0.1 ppm fluoride in 2 M zinc sulfate standard solution and a 10 mL of TISAB II solution are added in a 30 mL beaker and is stirred thoroughly.
 - d. The electrode is rinsed and then placed into the prepared solution in step c. When a stable reading is displayed, the electrode potential is recorded as 0.1 ppm fluoride.

- e. Step c. and d. are repeated for 1 ppm and 10 ppm fluoride.
- 5) Fluoride ISE in 2M ZnSO₄ calibration and fluoride standard solutions recalibration lines
- The calibration curve of Fluoride ISE in 2M zinc sulfate solutions is shown in Figure A.3 and the recalibration curve of fluoride in 2M zinc sulfate standard solutions is illustrated in Figure A.4.

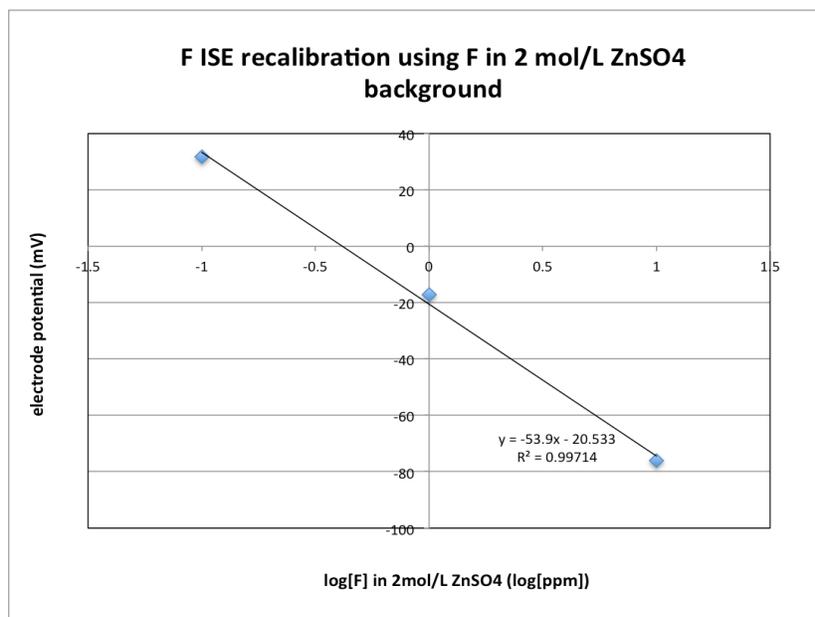


Figure A.3 Fluoride ISE calibration line in 2M ZnSO₄ background solutions

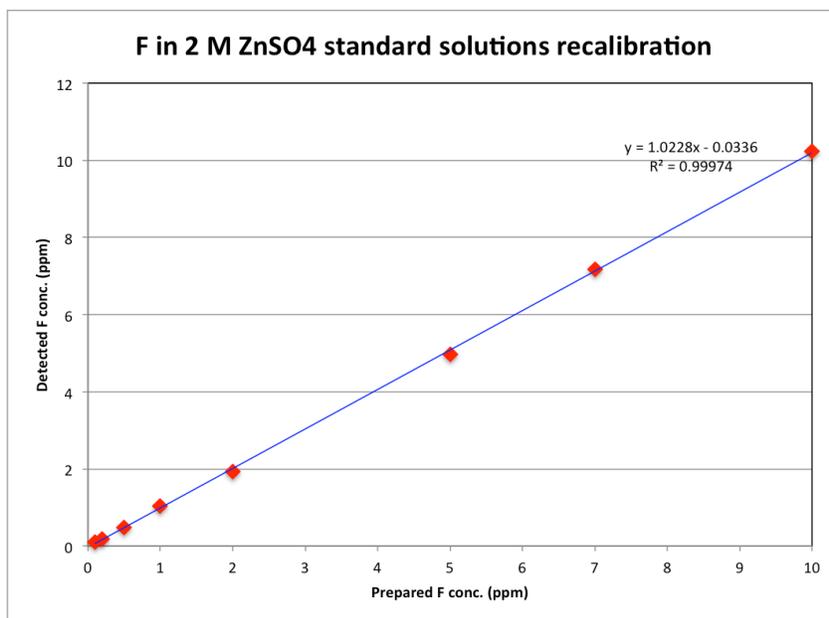


Figure A.4 Fluoride in 2M ZnSO₄ standard solutions recalibration line

6) Theoretical uncertainty

Basically, the Fluoride ISE is assumed to follow the Nernst equation:

$$E_F = E_F^\circ - \frac{2.303RT}{F} \lg(a_F) \quad \text{Eq. A.1}$$

E_F is the potential of Fluoride ISE; E_F° is the standard potential of Fluoride ISE; R is ideal gas constant; T is the temperature; F is the Faraday constant and the a_F is the activity of Fluoride ions.

$$a_F = \gamma_F C_F \quad \text{Eq. A.2}$$

γ_F is the activity coefficient of Fluoride ion and the c_F is the concentration of Fluoride ion.

Therefore, theoretically, the testing result is affected by several factors as follow:

a. Temperature

In the fluoride concentration level of this experiment (10^{-6} mol/L) and standard temperature (308.15K), the error of 1 K change can be calculated as below (assume $\gamma_F = 1$):

$$E = E_F^\circ - \frac{2.303RT}{F} \lg(c) \quad \text{Eq. A.3}$$

$$E = E_F^\circ - \frac{2.303R(T+\Delta T)}{F} \lg(c + \Delta c) \quad \text{Eq. A.4}$$

$$\text{Eq. A.3} - \text{Eq. A.4}: \frac{2.303R(T+\Delta T)}{F} \lg(c + \Delta c) - \frac{2.303RT}{F} \lg(c) = 0$$

$$\lg(c + \Delta c) = \lg(10^{-6} + \Delta c) = \frac{T + \Delta T}{T} \lg(c) = \frac{308.15 + 1}{308.15} * \lg(10^{-6})$$

$$\Delta c = -4.38 * 10^{-8} \text{ mol/L}$$

Therefore the error here is $error = \frac{|\Delta c|}{c} = 4.38\%$

b. Complexion:

For hydrogen ion (H^+), in low pH solution, hydrogen complexes with fluoride to form H_2F_2 for which its $pK_a = 3.20$ (Lange's Handbook of Chemistry). Figure A.5 illustrate the probable fraction of fluoride species when complexion with hydrogen.

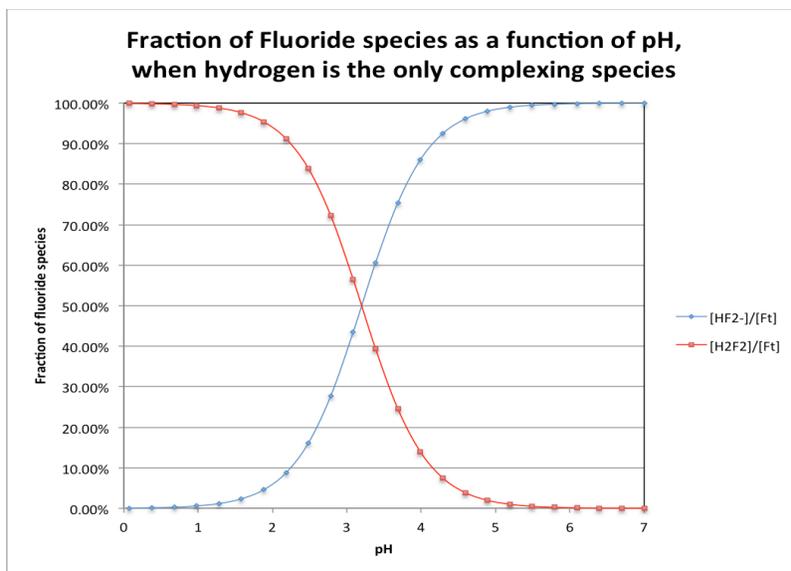


Figure A.4 Fraction of Fluoride Species as a Function of pH

It can be found that the percentage of free fluoride ion (HF_2^-) is higher than 98.44% when $pH=5$. Therefore the error from hydrogen complexion with fluoride is 1.56%.

For hydroxide group, it interferes with the electrode response of fluoride ions when the concentration of hydroxide is higher than one-tenth the fluoride concentration. Figure A.5 shows the response of the electrode to the alkaline solutions. (Fluoride Ion Selective Electrode–User Guide)

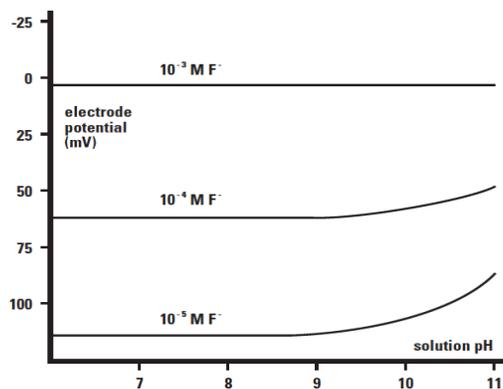


Figure A.5 Electrode Response to Alkaline Solution

For other ions, fluoride complexes with some polyvalent cations such as aluminum ($pK_1=6.10$), iron (III) ($pK_1=5.28$) and manganese (II) ($pK_1=5.48$). According to previous works, 5-sulfosalicylic acid, citric acid, tartaric acid, Tiron, EDTA, CDTA and also TISAB I, TISAB II, TISAB III can be used as complexing agents for masking such cations (Sun et al, 2010; Harwood, 1969; Hawkings, 1978). As for the recommendations by the user's guide, TISAB III is applied to for the aluminum masking when aluminum concentration is lower than 5 ppm in 1 ppm fluoride level. In 1 ppm level fluoride sample, TISAB IV is recommended as the complex agent which can complex more than 100 ppm aluminum. However, 200 ppm aluminum can cause 5% error (Fluoride Ion Selective Electrode–User Guide).

c. Meter:

According to Orion Laboratory Products Catalog, the relative accuracy is $\pm 0.2 \text{ mV}$ (Orion Laboratory Products Catalog). Therefore the error from meter can be calculated as below:

$$E = E_F^\circ - \frac{2.303RT}{F} \lg(c) \quad \text{Eq. A.5}$$

$$E + \Delta E = E_F^\circ - \frac{2.303RT}{F} \lg(c + \Delta c) \quad \text{Eq. A.6}$$

$$\text{Eq. A.6} - \text{Eq. A.5}, \frac{2.303RT}{F} \lg(c) - \frac{2.303RT}{F} \lg(c + \Delta c) = \Delta E$$

$$\frac{2.303RT}{F} \lg\left(\frac{c}{c + \Delta c}\right) = \Delta E$$

when $\Delta E = 0.2 * 10^{-3} V$

$$\frac{c}{c + \Delta c} = 10^{\Delta E F / 2.303RT} = 1.0078$$

Therefore $error = \frac{|\Delta c|}{c} = 0.78\%$

7) Actual uncertainty test

Table A.1 illustrates the calibration data of the standard fluoride solution in 2 mol/L ZnSO₄ background solution and the Table A.2 shows the 10 ppm fluoride in 2 mol/L ZnSO₄ solution uncertainty test results. It can be found the actual error exists in this experiment is 4.20%.

Table A.1 Calibration of the standard fluoride solution in 2 mol/L ZnSO₄ background solution

F conc. (ppm)	log[F]	Electrode potential (mV)
1	0	-100.6
10	1	-162.1
100	2	-217.1

Table A.2 10 ppm fluoride in 2 mol/L ZnSO₄ solution uncertainty test

Test Num.	Electrode potential (mV)	log[F]	F conc. (ppm)
1	-162.1	1.04	10.90
2	-160	1.00	10.03
3	-161.4	1.03	10.60
		Mean	10.51
SD	0.44	Error	4.20%

Figure A.6 illustrates the results of the calibration line and the uncertainty tests.

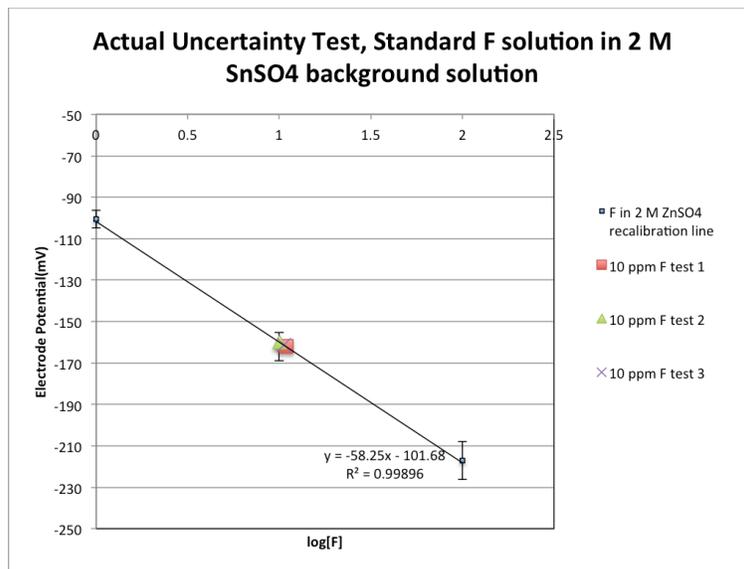


Figure A.6 Actual uncertainty test results of 10 ppm fluoride in 2 M zinc sulfate solution