IMPACT OF FILMING AMINE ON ION EXCHANGE RESIN FOR ULTRAPURE WATER APPLICATION

By

MARUFUL HASAN

Bachelor of Science in Chemical Engineering

Bangladesh University of Engineering and Technology

Dhaka, Bangladesh

2007

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 2013

IMPACT OF FILMING AMINE ON ION EXCHANGE RESIN FOR ULTRAPURE WATER APPLICATION

Thesis Approved:

Dr. Gary L Foutch

Thesis Adviser

Dr. Heather Fahlenkamp

Dr. A. H. Johannes

Name: MARUFUL HASAN

Date of Degree: DECEMBER, 2013

Title of Study: IMPACT OF FILMING AMINES ON EXCHANGE RESIN FOR ULTRAPURE WATER APPLICATION

Major Field: CHEMICAL ENGINEERING

Abstract:

Two types of proprietary filming amines were tested in laboratory experimentation to evaluate potential impacts on condensate polisher ion exchange resins (Dowex 650C and 550A). The properties of filming amines to coat surfaces within the steam cycle of a power plant may also block ionic mass transport or have chemical interactions with ion exchange resin. Experimentation was done with resins before and after exposure to filming amines and mass transfer coefficient (MTC) was compared to measure the impact. Comparative studies were also performed with octadecylamine (ODA). Results indicate a significant impact of Filming Amine-1 (FA-1) on cationic resin with reductions in MTC. MTC for cationic resin was partially recoverable. For anionic resins, MTC could be recovered with maximum strength regenerant. Effect of Filming Amine-1 (FA-2) was slightly higher than FA-1 in cation resin. But after regenerating, FA-2 exposed resin improved MTC higher than FA-1 exposed resin.

TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION 1

Ion Exchange and Ultrapure Water 1
Mass Transfer Coefficient (MTC) 2
Significance of Mass transfer coefficient 6
Ion exchange resin fouling mechanism 7
Filming Amine and its Impact in Power Plant Performance 8
Capacity loss of ion exchange resin due to filming amine 13

II. BACKGROUND OF THE STUDY 15

Scope of the work 15
Characterization of Resin Performance 16
Mass Transfer Coefficient determination 17
Performance Recovery of Fouled Resins 17
Regeneration Tests 17
Performance Recovery/Improvement of Cation Exchange Resin 18

III. EXPERIMENTAL 19

Apparatus 19
Experimental Procedure 23

Chapter Page

IV. RESULTS AND DISCUSSION....29

Continuous exhaustion....29
Repetitious exhaustion/ regeneration....33
Experiment with high concentration of FA-1....34
Experiment with very high concentration of FA-1....36
Experiment with low bed height....37
Cationic Resin exposed to ODA....37
Resin from Cation Column from Kentucky Power Plant....38
Resin FA-2 interaction....39
Resin FA-2 interaction(mixed bed)....43
Comparison of FA-1 and FA-2 exposure....44

V. CONCLUSION AND FUTURE STUDY....47

REFERENCES....49

APPENDICES....53

Error Analysis....53
Changes in MTC for Unused Old Resin....56
Sample Result....60
Proprietary Filming Amines....61

LIST OF TABLES

Table Page

3.1- List of auxiliary facilities..20

3.2- List of Chemicals..21

3.3- Properties of Resin...22

4.1- Comparison of FA-1 and FA-2 on ion exchange resin.......................................46

A.1- New cation resin (Dowex MS 650 C H) in mono bed..60

A.2- 25 ppm of FA-2 exposed cation resin in mono bed...60

A.3- 25 ppm of FA-2 exposed and regenerated cation resin in mono bed 60

A.4- 25 ppm of FA-1 exposed anion resin (Dowex 550 A OH) in mono bed............61

A.5- 25 ppm of FA-1 exposed and regenerated anion resin 61

A.6- General description of FA-2 V 217 62

LIST OF FIGURES

Figure Page

3.1- Gravity rinsing 25

3.2- Kinetic test apparatus (based on ASTM 6302-98) 26

3.3- MTC experimental set up 27

4.1- Effect of filming amine for sodium ion in cationic mono bed 30

4.2- Effect of filming amine for sulfate ion in anionic mono bed 31

4.3- Effect of filming amine for sodium ion in mixed bed 32

4.4- Effect of filming amine for sulfate ion in mixed bed 32

4.5- Repetitious exhaustion/ regeneration for cation mono bed 33

4.6- Repetitious exhaustion/ regeneration for anion mono bed 34

4.7- Repetitious exhaustion by 5 ppm filming amine for cationic mono bed 36

4.8- Changes of MTC in low bed height 37

4.9- Changes of MTC for exposure to ODA 38

4.10-25 ppm of FA-2 (50 BV) on cationic mono bed resin 40

4.11- 50 ppm of FA-2 (50 BV) on cationic mono bed resin 41

4.12- 250 ppm of FA-2 (50 BV) on cationic mono bed resin 42

4.13- Different concentration and amine solution volume on cation resin 42

4.14- Effect of FA-2 on cation resin of mixed bed 43

4.15- Effect of FA-2 on anion resin of mixed……………………………………………44

Figure Page

A.1- Error analysis for MTC experiment ……………………………………….… 55
A.2- Sodium MTC for old cationic resins at various influent concentrations............57
A.3- Chloride MTC for old anionic resins at various influent concentrations 57
A.4- Average MTC for old cationic dry resins of different age 58
A.5- Average MTC for old anionic dry resins of different age 58
A.6- Effect of storage condition of resins on MTC 59

NOMENCLATURE

a_s	Specific surface area of resin bead (m^2 m^{-3})
d_p	Harmonic mean diameter of spherical particle (m)
C_i	Fluid phase concentration (mg L^{-1})
C_i^f	Fluid phase concentration of feed (mg L^{-1})
C_i^{eff}	Fluid phase concentration of effluent (mg L^{-1})
C_i^*	Concentration at liquid solid interface (mg L^{-1})
F	Volumetric flow rate ($m^3 s^{-1)}$
FR	Volumetric fraction of resin (m^3 m^3 bed)
k_0	Overall mass transfer coefficient (m s^{-1})
k_f	Film mass transfer coefficient (m s^{-1})
k_p	Particle mass transfer coefficient (m s^{-1})
K	Distribution factor
$K_{f,i}$	Average film mass transfer coefficient (m sec^{-1})
q_i	Resin phase concentration (mg L^{-1})
t	Time (s)
u_r	Fluid velocity (m s^{-1})
Z	Bed depth (m)
ε	Porosity
Sh	Sherwood Number
Sc	Schmidt Number
Re	Reynolds Number
ODA	Octadecylamine

CHAPTER I

INTRODUCTION

Ion Exchange and Ultrapure Water

Ion exchange is a reversible reaction between two substances (usually an electrolyte solution in aqueous phase and ion exchanger material in solid phase) where ions of equally charged material interchange (Nasef et al., 2012). Ion exchange resins can purify large volumes of water economically. Mixed bed ion exchange resin, composed of anionic and cationic resin, can purify water to levels of parts per trillion.

Ion exchange materials are insoluble substances containing exchangeable ions which are able to be exchanged with other ions in solutions which come in contact with them. There are no physical changes in ion exchange material during the reaction (Alchin, 2005). Ion exchange resins are ion exchange material that have high molecular weight cross-linked polymer hydrocarbon matrix. There are two types of ion exchange resin- cationic resin and anionic resin. Anionic resin exchanges anion while cationic resin exchanges cation from solution of contact. Resin can be further classified as strong acid or weak acid cation resin or strong base or weak base anion resin. Different type of functional groups are used for cation and anion exchange resin. Such as carboxylic acids, sulfonic acid, phosphoric acid groups are used for cation resin while ammonium, phosphonium or sulphonium groups are used for anion resin. Non exchange site are made by polymerizing styrene with divinyl benzene (DVB). Degree of cross linkage determines important parameters of ion exchange resin (Drofner, 1971).

Ultrapure water can be effectively manufactured by mixed bed ion exchange along with other purification method. Standard of ultrapure water can be varied from industry to industry. But water having electrolyte conductivity less than 0.1 microsiemens per centimeter can be regarded as ultrapure water (Hussey & Foutch, 2004). Ionic concentration should be less than 20 parts per billion equivalent sodium chloride to be classified as ultrapure water. Many processing industries such as power, pharmaceutical, and chemical industries use ultrapure water to minimize corrosion (Gönder et al., 2006).

Mass Transfer Coefficient (MTC)

Fouling is indicated by a reduction in the ionic mass transfer coefficient (MTC) or effective capacity. MTC is defined as the rate at which ions move from the bulk solution to the exchange site and has the same units as velocity. MTC is a lumped parameter and numerous factors contribute to its value. In practice, a low MTC indicates that the rate at which ions are removed by exchange is too slow compared to the rate at which water flows through the bed (Foutch & Hussey, 2004). The concentration of ions in the feed water that leaves the bed without the opportunity for exchange is referred to as kinetic leakage. Beds that exhibit significant kinetic leakage are not effective for trace contaminant removal even if they have significant remaining exchange capacity. For equilibrium leakage, the effluent concentration depends on the regeneration efficiency of the mixed bed. Equilibrium leakage will occur at a specific flow rate until the bed saturates with ions in the feed that begin to break through into the outlet water stream. For any ion exchange bed, the flow rate can be increased until kinetic leakage begins. At this high flow condition the entire bed depth is the exchange zone. As the degree of fouling increases kinetic leakage will occur at lower flow rates. When the feed concentration is higher, equilibrium leakage concentration will not be affected but breakthrough will occur sooner, while kinetic leakage will be a function of both the feed concentration and the degree of fouling. The

MTC test method uses a high flow rate and sufficient concentration to ensure that the bed operates with kinetic leakage.

Unfouled ion exchange resin exhibits very low resistance to ionic mass transfer during processes and can be modeled by film diffusion in the water phase. When exchange is slowed by fouling, factors such as particle diffusion and exchange site reaction need to be considered (Lee et al., 1997). An overall mass transfer coefficient (MTC) can account for all factors and represents the quality of the ion exchange resin (Harries et al., 1984).

MTC is measured by simple laboratory experiment; a laboratory-scale exchange bed is prepared and a known concentration of salt water is fed to the column. The ionic concentration in the feed water that leaves the bed without the opportunity for exchange is referred to as kinetic leakage. The feed is pumped at sufficient flow rate to ensure that kinetic leakage is occurring as compared to equilibrium leakage. The influent and effluent ionic concentrations, flow rate and physical experimental parameters are used to calculate the MTC. The overall MTC experiment (ASTM D 6302-98) has two primary functions; a qualitative indication that a problem exists and the ability to quantify the current MTC of the resin. A numerical value of MTC can be used to calculate the expected performance of the resin in full-scale operation (Lee et al., 1997)

Lee et al. (1997) used MTC as an indicator of resin fouling. They analyzed samples of different ages of resin from two coal-fired power plants in Oklahoma. The older resin samples showed consistently lower MTC than newer resins. In addition, one of the plants showed greater fouling problems with the result traced to the presence of organics in river water downstream of oil refineries used in the condensers. They also investigated the MTC changes with various experimental conditions, such as influent flow rate and concentration and found as expected no strong correlation between them. So, MTC represents the resin quality well with difference between samples giving an indication of the degree of fouling.

Mass transfer coefficient for packed bed columns can be derived from the continuity equation. Continuity equation for species 'i' is given by:

$$\frac{\partial \mathrm{C_i}}{\partial \mathrm{t}} + \frac{\mathrm{u_r}}{\varepsilon}\frac{\partial \mathrm{C_i}}{\partial \mathrm{t}} + (\mathrm{FR})\frac{(1-\varepsilon)}{\varepsilon}\frac{\partial \mathrm{q_i}}{\partial \mathrm{t}} = 0 \tag{1-1}$$

The first term of this equation represents the change in bulk solution concentration with time; the second term indicates ionic movement within the bulk fluid and the third term is ionic sorption within the resin beads. If we assume that the experiment occurs over a differential increment so that ion accumulation in the bulk solution is negligible, we can ignore the first term and the equation becomes:

$$\frac{\mathrm{u_r}}{\varepsilon}\frac{\partial \mathrm{C_i}}{\partial \mathrm{t}} + (\mathrm{FR})\frac{(1-\varepsilon)}{\varepsilon}\frac{\partial \mathrm{q_i}}{\partial \mathrm{t}} = 0 \tag{1-2}$$

The result is that ionic loss from solution (first term) equals ionic gain on the resin (second term). If the liquid-film mass transfer is assumed to be the rate limiting step for normal exchange then the rate of sorption ($\frac{\partial \mathrm{q_i}}{\partial \mathrm{t}}$) can be calculated from the concentration gradient through the film (Equation 3):

$$\frac{\partial \mathrm{q_i}}{\partial \mathrm{t}} = \mathrm{K_{f,i}a_s(C_i - C_i^*)} \tag{1-3}$$

where $\mathrm{C_i}$ = localized bulk water concentration and $\mathrm{C_i^*}$ = water-resin interfacial concentration. For ultrapure water applications we assume the interfacial concentration to be zero.[6] Substituting equation 3 into equation 2 the resulting expression can be solved with the following boundary conditions:

$$\mathrm{C_i = C_i^f \text{ at } z = 0}$$

$$\mathrm{C_i = C_i^{eff} \text{ at } z = Z}$$

Integrating, we find the mass transfer coefficient for ion 'i':

$$\ln\left(\frac{C_i^{eff}}{C_i^f}\right) = (FR)\frac{-k_{f,i}\,(1-\varepsilon)z}{u} \tag{1-4}$$

For spherical beads we use $a_s d_p = 6$ and volumetric flow rate as $F = Au$, where A is the cross sectional area of the bed, the final mass transfer coefficient for ion ‘i’ is:[7]

$$\ln\left(\frac{C_i^{eff}}{C_i^f}\right) = (FR)\frac{-6k_{f,i}\,(1-\varepsilon)z}{d_p}\frac{\pi R^2 Z}{F} \tag{1-5}$$

Equation 5 is the basis of the MTC experiment (ASTM D-6302-98) where d_p is the harmonic mean size of the resin beads and is provided by the manufacturer.

In equation 5, $k_{f,i}$ represents the MTC and includes both particle and film diffusion and exchange site reaction (Pandey et al, 2008). For unfouled ion exchange resin only liquid side film diffusion controls the exchange rate; this value can be calculated from theory. For fouled resin the impact of all possible mechanisms slow the exchange. In that case MTC gives an overall rate and a measure of the quality for the resin. Note that the MTC value does not give an indication of the mechanism of fouling for the lower rate. Lee et al. (1997) showed that the total mass resistance is the summation of film and particle resistance and may be written in the following form. (Cussler et al., 1997)

$$\text{Total mass transfer resistance} = \text{resistance in film} + \text{resistance in particle}$$

This expression can be written in mathematical form as:

$$\frac{1}{k_0} = \frac{1}{k_f} + \frac{K}{k_p} \tag{1-6}$$

where, K = distribution factor. In this expression k_0 can be obtained by performing MTC experiments for used resin and k_f is approximately equal to the MTC value for unfouled resin. Lee et al. (1997) suggested that these two values may be used to obtain a more specific particle mass transfer coefficient (k_p) which in turn provides a quantitative indication to the ion exchange resin fouling or degradation. However, this analysis would require additional experimentation over a range of operating conditions.

Clean unfouled resin's mass transfer coefficient can be predicted theoretically (Chowdiah et al., 2003). Different theoretical approaches are available in the literature to estimate that. Reynolds number and Schmidt number can be correlated to Sherwood number which can provide mass transfer coefficient. Schmidt number is the ratio of kinematic viscosity to molecular diffusivity while Reynolds number is the ratio of internal to shear forces.

Chowdiah et al., (2003) investigated different correlations present in literature and found the following correlation most appropriate described by Dwivedi and Upadhaya (1977). This correlation is valid for Reynolds number between 0.01 and 15,000.

$$\mathrm{Sh} = Sc^{\frac{1}{3}} Re \left[\frac{0.765}{(\varepsilon Re^{0.82})} + \frac{0.365}{(\varepsilon Re^{0.386})}\right] \tag{1-7}$$

We can solve for Mass Transfer Coefficient from Sherwood number

$$K_i = \frac{D_i}{d_p} Sc^{\frac{1}{3}} Re \left[\frac{0.765}{(\varepsilon Re^{0.82})} + \frac{0.365}{(\varepsilon Re^{0.386})}\right] \tag{1-8}$$

Significance of Mass transfer coefficient

Ion exchange resin can be fouled and loss its quality in different ways. Degradation or fouling of resin results in more ionic leakage or quick breakthrough. Also degraded resin gives lower mass transfer coefficient than clean one as mass transfer coefficient depends on effluent results. So MTC actually does not say anything about the cause or mechanism of the fouling but it can predict the degree of degradation. So MTC can be a useful parameter in operational procedure of mixed or mono bed ion exchange purification procedure. Again shallow bed MTC experiments give the true MTC as this eliminates influence of resin saturation and intraparticle diffusion is eliminated. Keeping all parameter fixed, deep bed resin can also be used as comparison purpose as it is used in this study. Harries and Ray (1984) conducted MTC experiments in different condition and found the MTC is independent of influent concentration. But there can be a significant change in MTC in flow rate changes. High flow rate should be used to achieve necessary ionic leakage instead of equilibrium leakage. Both sulfate and chloride MTC lowered by the fouling of resin. Chloride MTC was lower than sulfate in the clean resin but the MTC deterioration rate was higher for sulfate. They believed that for clean resin mass transfer was exclusively controlled by film diffusion. But as the fouling begins particles diffusion take place along with film diffusion. They also noted that particle bead diameter also plays an important role in ion exchange mass transfer coefficient. Overall MTC can predict the performance of the bed and condenser leak.

MTC test can be done for both mono bed and mixed ion exchange bed. Different kind of combination in mixed bed (new cation with old anion, new anion and new cation, old cation and new anion) can be used to investigate the interaction by noting the MTC changes in different conditions. Again anion/ cation ratio, cleaning, regeneration and vessel flow distribution can affect the kinetic performance of ion exchange resin. McNulty et al. (1986) categorized the range of MTC and their physical performance in the actual operation. This classification can be used to proper performance prediction of condensate polisher in ion exchange operation.

Ion exchange resin fouling mechanism

Ion exchange resin can be fouled in different way such as organic foulants in feedwater, thermal degradation, incomplete separation or regeneration (McNulty et al., 1986). But all the factors can be broadly divided into two different category- losses of ion exchange site activity and non-ion exchange site fouling. Non ion exchange site fouling increases the physical resistance to ionic mass transfer from the bulk solution.

Adsorption is the main cause of cationic resin fouling. There are different types of absorbents like particulates, iron oxides or organics that foul cation resin. The fouling of cationic resin of particular ion exchange bed depends on feedwater history, flow distribution and other parameters related to the bed. Organics and others absorbents can accumulate in period to gradually degrade the cation.

Ion exchange species of higher functionality can replace the ion exchange site of anion and degrade the quality of anion resin. Strongly base site of anion resin can also be transformed to weakly base site which reduce functionality. For example, sulfonate of cation exchange resin can replace the one or more exchange site of anion resin. This can reduce the functionality of cation exchange and loss of site for anion exchange. The conversion from strong bas to weak base sites can be associated with thermal degradation.

Regeneration can take care of reversible fouling recovering the capacity of exchange resin. But some of this adsorption can be irreversible and cannot be recovered even with very strong regenerant. Resin can accumulate foulants in combination of different mechanism. Mass transfer coefficient can predict the overall extend to mechanism. As the industries goal is to have pure quality of water so any kind of fouling is unacceptable. So measurement of MTC can be very useful in predicting the extent of degradation.

Filming Amine and its Impact in Power Plant Performance

Filming amines (FA) are typically long-chain cationic surfactants that reduce corrosion of metal surfaces in aqueous systems. They often referred to as polyamines of fatty amines which general formula as $R^1 - [NH-(R^2)]_n-NH_2$. Here R^1 is an unbranched alchyl chain with 12 to 18 carbon atoms and R^2 is a short alkyl chain with 1 to 4 carbon atoms (Hater et al., 2008). Filming amine has one hydrophilic end and hydrophobic end. The hydrophobic end makes the surfaces unwettable by creating a physical barrier that prevents water, oxygen or other corrosive agents from reaching the metal surface. For power plant applications the amine formulation, entrained with water in the steam cycle has a high affinity for metal surfaces and deposits as a protective film. This film is a barrier for corrosive chemicals and dissolved gases, due to its hydrophobic characteristics, minimizes wettability. The organic end of the molecule is hydrophobic while the amine group is hydrophilic and adheres to the metal surface.

Distribution ratios and average surface coverage of filming amines are discussed by Voges and Hater (2010). An autoclave was filled with deionized water containing a particular concentration of filming amine to determine the distribution ratio. After achieving a certain pressure, water samples from the autoclave and condensate collector were analyzed with the concentration of filming amine measured by a Bengal Rose method. The distribution ratio is the quotient of concentration in the condensate to that in the autoclave. Experiments also determined which amines have highest distribution ratio and average surface coverage. Distribution ratio of oleyl propylenediamine was as high as 6 after 5 hours. Voges and Hater (2010) found that distribution ratio decreased as the operating pressure increased and increased as the operating pressure decreased. Distribution ratio was the maximum for oleyl propylenediamine within the homologous series of oleyl propylene oligoamines. The average surface coverage was not a strong function of operating pressure but did increase linearly as the initial concentration of filming amine increased. Average surface ratio was virtually constant within the homologous series of the oleyl propylene oligoamines.

Studies showed that filming amine increases heat transfer in shell boilers when compared with trisodium phosphate treatment (Topp et al., 2012). They used FA-2 as the representative filming amine. Also, more intense bubble formation occurred on the boiler wall with filming amine. Both phosphate and filming amine treatment formed a protective oxide layer, but for the filming amine treatment, the protective layer was more homogeneous, thinner, and had a lower degree of roughness. The authors also measured the critical heat flux density for both phosphate and filming amine treated heating surfaces. The critical heat flux measured for both filming amine and phosphate treated wall were similar in the range of value of wall treated by pure water. The behavior of heated surface during start up and shut down was also similar between filming amine treatment and phosphate treatment. Overdosing with filming amine gave similar results.

Filming amines helped prevent corrosion of power equipment at a cogeneration plant in standby. Chernyshev et al. (2006) studied the standby corrosion prevention by Octadecylamine (ODA). By analyzing eight hot water boiler stations, they showed that an ODA layer preserved most surfaces after a long term outage. ODA lowered the intensity of formation of scale in seasonal autumn and winter maximum load operation. ODA also had an inhibiting effect on pitting corrosion of stainless steel. Babler et al. (1999) studied the behavior of pitting corrosion at temperatures between 150^0C to 250^0C. They found the inhibiting effect of ODA is more marked at lower temperature.

Since filming occurs on all contacted surfaces, this study examines the impact of these amines on ion exchange resin performance. For optimal ion exchange resin performance, no limitations to ionic mass transfer from the bulk water to the anionic or cationic exchange site should exist. Filming amines reduce the efficiency of ion exchange resins by numerous mechanisms. These include: physical surface blockage of pore or gel structure, permanent filling of space within the resin beads, establishment of a surface charge or zeta potential that repulses diffusing ions, or permanent bonding of exchange sites within the beads that reduces effective exchange capacity. Even if bonding is non-permanent and the amine is removable – for a typical resin regeneration acid or caustic treatment – there may still be reduced. Organic amines have an impact within the power plant steam cycle; including, ion exchange resin performance.

Ideally, amines have a vapour-liquid partition coefficient that allows for effective transport throughout the steam cycle and results in deposition with the early condensate. Organic amines break down into organic acids that can contribute to materials problems. Influence of filming amines on boiling behaviour and heat transfer is discussed by Topp et al. (2012). The use of film-forming amine conditioning increases the heat transfer coefficient in low to medium heat flux, but the number of active bubble nucleation sites on the surface of the oxide layer decreases with the use of filming amines. Raught et al. (2005) hypothesized ion exchange resin fouling mechanisms by organic amines. One theory is that cation resin reacts with the amine, cleaving sulfonate fragments, which then deposit on the anion resin. The deposition blocks pores or utilizes exchange capacity on the anion resin permanently, reducing exchange of impurities.

In power plants filming amines counter the effects of oxygen corrosion and are used as a means of equipment protection during both operational and idle conditions. EPRI has conducted research of field operating conditions to demonstrate the effectiveness of the use of proprietary filming amines for metal components preservation in the steam/water cycle during shutdown. Testing to date has been promising and amine treatment may mitigate both single and two-phase flow accelerated corrosion mechanisms. A concern moving forward is whether filming amine application in systems with ion exchange condensate polishers have an impact on the performance, degrade and/or foul the ion exchange resins.

EPRI commissioned a field assessment of equipment layup protection with filming amine (octadecylamine ODA) to make a scientific assessment of the advantages and disadvantages of using a filming amine (mainly ODA) to protect idle equipment of the steam-water cycle in fossil units. All units (25 in total) in this field assessment ranging from 100 – 350 MW had condensate polishers which were removed from service (bypassed) during ODA dosing and the subsequent startup to prevent known fouling of the polisher resins. While ODA is not a filming amine of choice because of many undesirable attributes, its characteristics of hydrophobicity and impact on polisher resins serve as a “benchmark” for the examination of alternative filming amine products.

Some amines cause severe mechanical damage to certain types of ion exchange resins; kinetic impairment of anion resins is attributed to the effects of other amines. For polishers to perform satisfactorily, resins must remove impurities from condensate at the high velocities used in polishing plants, i.e. they must be “kinetically” sound. They must also be mechanically sound so as to minimize their breakdown. The possibility that an amine could either foul resins (reducing their kinetic ability) or damage them physically must be considered. Filming amines have strong affinity to surfaces.

There is little work on filming amine and ion exchange resin within the literature although ion exchange fouling due to secondary amine and organic matter were discussed in several papers. Gonder et al. (2006) discussed the fouling of anion exchanger by organic matter such as humic and fulvic acids. They argued that fouling of anion-exchange resins were mainly caused by degradation products of cation exchangers. They injected organic matters directly into anion exchange resin in a laboratory column and measured the SAK (spectral absorption coefficient) and DFZ (indexes of transparency). They also compared the breakthrough curve and capacity for fresh and fouled resin. For resin fouled by 0.13 mg/L humic acid, the capacity loss was 21%. For higher concentrations of humic acid, the capacity loss was as high as 30%. SAK and DFZ also reduced in similar manner.

Much work has been done to understand ethanolamine (ETA) and resin interaction. A survey developed by EPRI was conducted in various power plants in USA and Europe (Raught et al., 2005). Power plants operating at higher condensate temperature showed a strong correlation with the degree of resin fouling linked to the use of ETA. At that time, the mechanism was not well understood. Raught et al. (2005) confirmed that there is a chemical reaction between ETA and the cation resin backbone and the reaction appeared to involve the amine terminus of the pH control agent. The reaction could be delayed by using macroporous resin although the reaction between resin and ETA would continue. Both the evidence of physical degradation and oxygen consumption demonstrate that there was a synergism in the degradation of the anion resin that involves the cation resin.

Capacity loss of ion exchange resin due to filming amine

Ion exchange capacity decreases due to saturation of filming amine in ion exchange resin (Foutch et al., 2013). Both FA-1 and ODA, reduced the ion exchange capacity of Dowex 650C(H) resin to a significant amount of the original value but this capacity was regained by regeneration in the case of FA-1. Since the MTC experiments demonstrated that regenerated resins had reduced kinetics versus the unexposed resin (Foutch et al., 2013) it must be concluded that while regeneration frees the ion exchange sites, it does not remove all of the filming amine so kinetic impairment remains. Testing has determined that the filming amines adsorb onto the cation resin by both ion-exchange and physisorption to the resin backbone. In the case of ODA, regeneration failed to recover all of the ion exchange capacity. Fresh TCD-1(H) resin showed a greater loss of ion exchange capacity when saturated with ODA than when it was exposed to FA-1. All of the capacity could be recovered by regeneration in the case of FA-1 but not for the ODA-exposed resin.

Dowex 550 A(OH) resins adsorbed significantly less filming amines than the cation resins but the exposure led to significant losses in ion exchange capacity that could not be completely recovered by regeneration. FA-1 curtailed the ion-exchange capacity by 27.5% while ODA reduced it by 14.7%. These numbers are not strictly comparable since the sorption of ODA from isopropyl alcohol (used as a solvent due to solubility issues) was too small to be quantified yet it clearly had a dramatic effect on the resin's chemical properties.

The hydrophobic nature of the filming amines generally reduces the moisture content of the resin beads. As a result, the beads are less swollen and are measurably smaller than the pristine resins. The exception is the ODA-saturated DOWEX 650C (H) beads that are larger than the unreacted beads. Presumably this is due to swelling with the large amount of ODA that is adsorbed. Filming amines were also associated with a higher proportion of cracked beads.

The rapid uptake of filming amines by cation and anion resins and their strong negative effects on the capacity, kinetics, and physical properties of the resins suggest that all exposure of the resins to filming amines should be avoided. While some kinetics and capacity can be regained by strong regeneration, there is permanent irreversible damage. Therefore, it would be best that condensate polishers should be taken out of service during addition of filming amines. Otherwise the amine would be removed by the resins and not be available to protect surfaces, and also would impact the ability of the resin to remove contaminants in the event of a condenser leak.

CHAPTER II

BACKROUND OF THE STUDY

Scope of the work

The scope of this study was to evaluate the impact of filming amines on ion exchange (condensate polishing) resins with consideration for the use and application of these products (amines) in power plant steam cycles. Evaluation of resin properties most likely to be affected by filming amines include the ionic mass transfer coefficient (MTC) that is associated with the effectiveness in ion exchange (ionic contaminant removal), the effective (dynamic) capacity and service time, as well as affecting the ability to separate and regenerate the resins. The ability to recover these properties by normal regeneration was confirmed in some cases. In others cases the residual and/or cumulative effective on permanent capacity or kinetic losses and resin fouling was determined.

The scope of work was to evaluate these effects through a series of laboratory experiments to measure the resin MTCs through multiple simulated cycles. The impact and consequence of accidental or intentional overdosing of the filming amine to a condensate polisher was evaluated by performing experimentation over a range of filming amine concentrations. These tests aid in determining the increased challenges associated with removal of the film forming amines from the resin with subsequent loading cycles.

Specific experimental tasks exposed the resins to defined concentrations of amines at known operating conditions. These resin-amine interactions were performed in laboratory test columns. Variables included amine concentration, operating temperature, and water flow rate and contact time. Test columns were removed from service and the resins analyzed. Specific tasks included measuring the resin properties that define their performance; including,

a) MTC (mass transfer coefficient)

b) Regenerability

c) Analysis of the data to define the influence of filming amines on these properties.

d) Performance Recovery of Fouled Resins

Characterization of Resin Performance

A simulated feed solution was defined and prepared for use in sequential iterative resin column test cycles. Influent solution was consisting of various concentration of sodium sulfate solution from 0.2 to 7.2 ppm and filming amine (5 ppm to 1500 ppm as product). A mixture of cationic and anionic resins for each test columns (CP commercial grade, e.g. Dowex 650C/550A) was prepared to match the cation to anion balance of the solution (alternatively, concentrations can be adjusted to match a specific cation to anion resin ratio). Influent and effluent concentration was measured by ion chromatograph.

The total number of interactive cycles conducted depended on the nature and degree of impact of the filming amine on the resin performance (i.e. negligible or severe impact limits the number of cycles required, however gradual and/or cumulative impact increases the number of cycles.)

Mass Transfer Coefficient determination

Samples from the top and bottom of the bed represent the limits of amine exposure in that test column. The top of the bed operated through the amine break while the bottom of the bed was primarily in the hydrogen form. MTC was measured, as outlined in the procedure provided in Appendix A. After MTC measurements, samples were placed in solution for equilibrium measurements of total capacity. The results led to experimental hypotheses. The resins were reused through several cycles to evaluate trends of long-term exposure to amines to provide verification of the appropriate hypothesis.

Performance Recovery of Fouled Resins

The typical low solubility of the filming amines makes removal of the amines from resins by an aqueous washing procedure highly difficult if not improbable. This problem can be solved in two ways, a chemical reaction to convert the amines to more water-soluble compounds or the use of organic solvents into which the amines will dissolve. The failure of regeneration procedures to remove the filming amines from cation exchange resins suggests that simple acidification is not sufficient to have the amines dissolve as the corresponding hydrogen sulfates or hydrochlorides.

Regeneration Tests

Regeneration of the test columns is performed in accordance with the regeneration procedure outlined by resin manufacturer. Monitoring of the resin separation and regeneration over numerous cycles conducted to give an indication of the ability of the resin to return to an acceptable performance level after a service cycle in the presence of filming amines. MTC samples between multiple regenerations should achieve an acceptable performance level – typically $2.0\text{x}10^{-4}$ m/s. MTC values significantly below this performance level indicate the requirement to evaluate processes to restore performance.

Performance Recovery/Improvement of Cation Exchange Resin

Cation exchange resin is used for determination of acid conductivity which may be negatively impacted by the use of filming amines. Typically the use of this resin for analytical purpose is on a one-time basis and as such the most significant impact on performance is the ionic kinetic exchange and kinetic leakage. If these are negatively impacted corrective actions for this condition was explored.

CHAPTER III

EXPERIMENTAL

Apparatus

The experimental system is based on the ASTM 6302(98) (2009). The system is composed of mainly carboys, pumps and a test column. A branch line is used to deliver filming amine to the main line. Figure 2-2 represents the Mass Transfer Coefficient (MTC) testing apparatus. In addition to MTC apparatus, auxiliary units were used for regeneration of resin and filming amine exposure. An ion chromatograph and computer were used to analyze the sample concentration. All the facilities are listed in Table 2-1. Information on the chemicals utilized in the resin testing is provided in Table 2-2.

Test column

The experimental column used in this study was made of Pyrex glass. The columns were transparent and resin can be seen from outside. These columns were used by previous investigator to study the incomplete regeneration of cationic resin (Lee, J., 2012). Two fritted disks were attached to both ends of the column so that resin cannot pass from the column. The inside diameter of the column was 1 inch and length of the column was 24 inch.

Ion Exchange Resins

Strong anionic and cationic resins were used for the experiment. New and three years old unused resins were used in the experiment. These were Dowex Monosphere 650 C (H) cationic and Dowex Monosphere 550 A (OH) anionic resin manufactured by the Dow Chemical Company. Physical properties of these resins were listed in Table 2-3. All the resins used were regenerated and rinsed with ultrapure water prior to experimentation.

Ion Chromatograph

The influent and effluent samples were analyzed by Metrohm 790 personal IC. The chromatograph uses RS232 interface with a personal computer (PC). The PC can be used to evaluate and record the chromatograph operation and make operational change. An injection valve is used for individual sample or DI water injection. A low pulsation double piston high pressure pump is used to deliver a flow range of 0.2 to 2.5 ml/min at maximum pressure of 25 MPa. Column chamber is insulated to ensure thermally stable condition for separation column and shield the system against electromagnetic interface. A cationic column and an anionic column with suppressor are used in the chromatograph. The suppressor module is pressure resistant and can regenerate automatically. An integrated two channel peristaltic pump with a flow rate of 0.5 ml/minute was used to regenerate and rinse the suppressor module. Conductivity detector is used at 40°C and varies by less than 0.01°C.

Table 3.1

List of auxiliary facilities

Facility	**Unit**	**Capacity**	**Model No. / Manufacturer**
Carboy	2	20 L	Nalgene
	2	10 L	Nalgene
Piston pump	1	4.4 gal/min max	WMD-30RLZT/ Iwaki Walchem

Metering pump	1	0.4 ml/pulse	PHP-167/ Omega Eng. Corp.
Static Mixer	1		318-40C-4-6-2/ Coflo Corp.
Flow meter	1		Ki Instruments
Conductivity meter	2		Sension 5/ Hach
Ion chromatograph	1		790 personal IC/ Metrohm
Personal computer	1		Power Edge 1400 SC/ Dell

Table 3. 2

List of Chemicals

Chemical	**Purity**	**Manufacture**	**Comments**
Sodium hydroxide	97.0%	EM Science	Regeneration
Sulfuric acid	95-98%	Pharmaco	Regeneration
Hydrochloric acid	35-38%	Pharmaco	Regeneration
Sodium bicarbonate	99.7%	EM Science	IC eluent
Sodium carbonate	99.5%	EM Science	IC eluent
PDCA	>99.5	Fluka	IC eluent
Sodium Sulfate	99%	Spectrum Quality Products Inc.	Feed to the column
Octadecylamine	95%	Alfa Aesar	Filming Amine
FA-1	NA	FA-1	Filming Amine
0.1 N Hydrochloric acid		Fisher	Titrant
0.2 N Sodium hydroxide		Fisher	Titrant
Anion and cation standard solution		Fluka	Calibration of IC

Table 3-3
Properties of Resin

	Dowex MS 650 C(H)	**Dowex MS 550 A (OH)**	unit
Physical Form	Dark amber spherical beads	White to cream spherical beads	
Matrix	Styrene-DVB gel	Styrene-DVB gel	
Functional group	Sulfonic acid	Quaternary amine	
Total volume capacity	2.0	1.1	Eq/L
Moisture retention capacity	46-51%	55-65%	
Particle size			
▪ Harmonic mean diameter	650 ±50	590 ±50	µm
▪ Uniformity coefficient, max	1.1	1.1	
▪ >850 µm, max	5	5%	
▪ <300 µm, max	0.5	0.5%	
Whole uncracked bead, min.	95%	95%	
Friability average, min	500	359	g/bead
Ionic conversion			
▪ OH^-	99.7 %	94% min	
▪ Cl^-		0.5% max	
▪ CO_3^-		6 % max	
Trace metals, dry resin, max.	Na (100); Fe (50); Al (50); Heavy metals [as ppb] (20)	Na (50); Fe (80); Al (40); Heavy metals [as ppb] (20)	
Total swelling	7 (Na^+ to H^+)	25%(Cl^- to OH^-)	
Particle density	1.22	1.08	g/mL
Maximum Operating temperature	265 °F	140/212 °F	

pH range	0-14	0-14
Total rinse requirement	3-6 Bed Volume	2-5 Bed Volume
Regenerant	1-10 % H_2SO_4 or 4-8% HCl	4-8% NaOH

Experimental Procedure

Several resin bed heights in the test column were used during the experimentation. Also mono bed and mixed bed experimentation were carried out. The experimentation procedure for 15 inch mixed bed column is described here.

Separation of anion and cation resin

Mixed resin was taken into separation apparatus. Then the mixed bed was backwashed with DI water to separate the phases. Backwash flow rate was sufficient to give a 50% bed expansion. Next, the anion resin on the top was removed using an aspiration assembly while cation resin was taken out from bottom. The middle layer of mixed resin was not taken to minimize cross contamination. The procedure was then repeated to give satisfactory separation.

Regeneration

New, separated or old unused resins were tested for kinetics in the study. Regeneration was done for all the resins prior to starting the final experiment. 200 ml of cationic resin was measured by coring. Then the resin was transferred to the column as slurry. This was done slowly and carefully to minimize air bubbles in the column. Then the resin was rinsed by DI water for 30 minutes at 50 ml/minute. 6.5% of sulfuric acid (standard regeneration) or 8.5% of sulfuric acid (strong regeneration) was used as the regenerant solution. Up to four bed volume of regenerant solution was passed through the resin at 25 ml/minute.

100 ml of anionic resin was measured by coring and transferred as slurry to another column. The same procedures were followed for anionic resin as cationic resin. 5% sodium hydroxide was used as standard regenerant and 8% sodium hydroxide was used as strong regeneration.

Rinsing

Rinsing was done by the use of gravity. The column was connected with an overhead carboy containing DI water. The effluent was collected in a waste carboy. The flow rate of DI water was controlled by the valve of carboy. At first the flow rate was adjusted to give approximately 5 mm of water on the top of resin. After 15 minutes, the flow rate of DI water increased to 100 ml/minute. The effluent sample was taken and its conductivity was measured by conductivity meter. The rinsing procedure continued until the conductivity of effluent concentration was less than 5µS/cm. Figure 2-1 shows the process of gravity rinsing.

Resin mixing and column preparation

150 ml of cationic resin and 75 ml of anionic resin were transferred by coring into the plastic storage container. Extra water was decanted and the resins were mixed thoroughly with a glass rod. Then the mixed resin was transferred to the test column as slurry. This was done slowly to minimize air pockets. A small amount of DI water was used the rinse the resin attached to the side of the column. The water level was kept not more than 5 mm above the resin surface to minimize the separation. After the resin loading, the column was installed into the kinetic test unit.

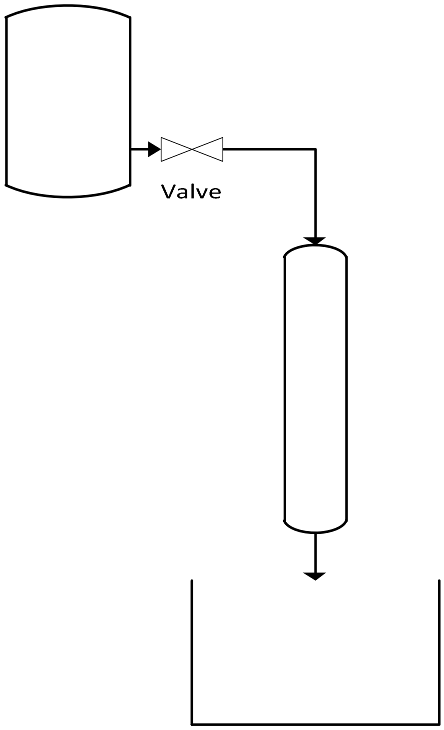


Figure 3-1

Gravity rinsing

MTC experimentation

Figure 2-2 shows the experimental procedure for MTC experimentation. Feed carboy-1 was used as salt/solution DI water feed. A centrifugal pump was used to pump the feed solution up to 1 liter per minute. Flow rate was controlled by the valve-1 next to the pump measured by a flow meter attached online with the system. Flow rate was also measured manually by collection the effluent and measuring the time taken by stop watch.

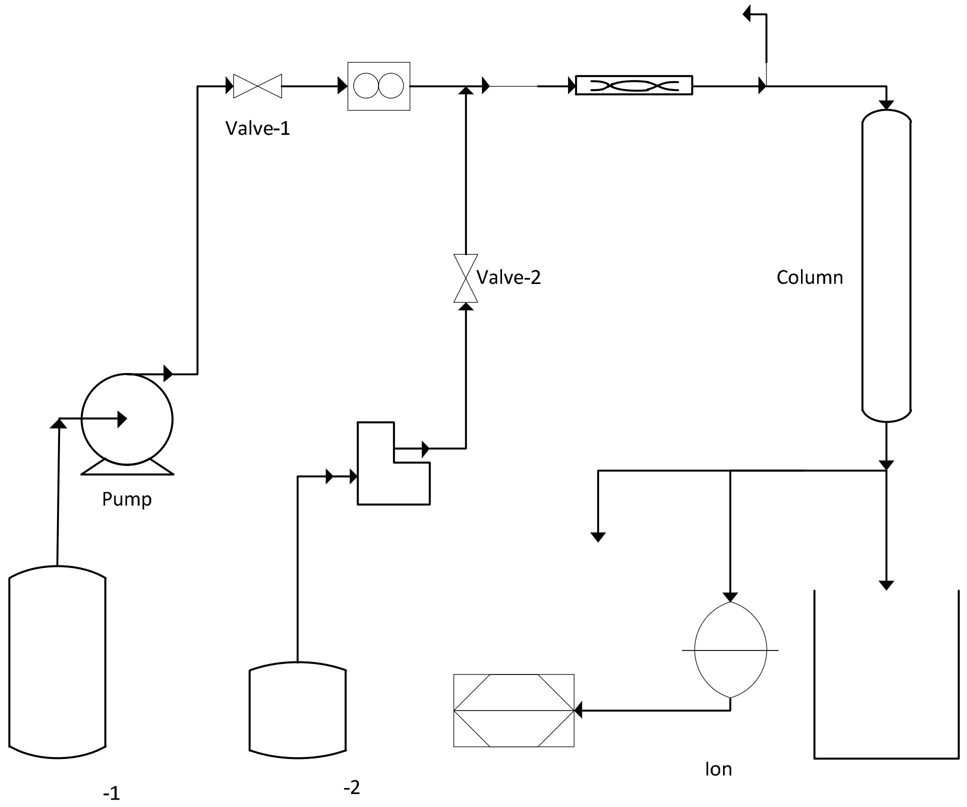


Figure 3-2

Kinetic test apparatus (based on ASTM 6302-98)

Filming amine solution was made in another 1 liter carboy (carboy-2). Due to the strong affinity of filming amines for surfaces, the filming amine solution was injected right before the column. A metering pump was used to pump the filming amine solution into the main feed line. The branch line can be closed by valve-2. The speed of the metering pump was adjusted to make the correct concentration of filming amine solution that will be injected to the column. A static mixer was used to mix the DI water from main feed line and filming amine solution from the branch line. Then the mixed solution entered the test column. The effluent was then collected in a waste tank. There was a sample collection provision before the column. This sample collection branch also helped to vent the air during the startup of the experiment and allowed continuous solution flow. High flow rate (~1 liter/minute) was used to have kinetic leakage in the column. The influent and the effluent sample were taken to measure the concentration of certain ion. A photograph of the experimental equipment represented by Figure 2-2 is depicted in Figure 2-3.

Figure 3-3

MTC experimental set up

The summary of experimental conditions for MTC testing is listed in Table 2-4. The associated results are presented in Chapter 3 and identified as appropriate figures listed in column 1 of Table 3-4

Ion chromatograph procedure

A 3.2 mmol of sodium carbonate and 10 mmol of sodium bicarbonate solution were used for anion eluent solution. Cation eluent solution was 2 mmol of nitric acid and 0.7 mmol of 2,6-pyridinecarboxylic acid. A 100 mmol of sulfuric acid was used for regeneration and DI water was used for rinsing. The base line was set for 70 minutes and then the chromatograph was calibrated using standard solutions ranging from 0.01 ppm to 10 ppm. The sample from the experiment was injected and the chromatograph detected the concentration automatically.

Exposing with filming amine

Filming amine exposing to the resin is problematic due to the filming amine's strong affinity to surfaces. Therefore, the filming amine was introduced to the column as lately as possible for minimizing loss of amine on the apparatus surface. One of the exposure procedures was using gravity. Filming amine solution was made in a LDPE carboy which was then connected to the test column containing the resin. Amine solution was slowly passed through the column. Another procedure was to make a small amount (~50 ml) of filming amine solution and directly inject it into the resin on the test column. Subsequently, DI water was passed slowly to the column by gravity for 3 hours. The experimental setup for resin exposure and titration studies are in presented in Figure 3-4.

CHAPTER IV

RESULTS AND DISCUSSION

Continuous Exhaustion

Monobed continuous experiments were first performed with unused three-year old Dowex MS 650C (H) cationic resin and Dowex MS 550A (OH) anionic resin. Figure 4-1 shows the impact of FA-1 on the MTC for cationic monobed. After passing 10 liters of FA-1 solution (50 ppm as product, 52 bed volume), the average MTC for sodium ion was 18% lower than the fresh cationic resin. After passing an additional 10 liters of amine solution through the column, the MTC decreased to 38%. After regeneration of cationic resin with 6.5% sulphuric acid, the MTC improved but was still approximately 15% lower than the unexposed cationic resin. Conducting a subsequent regeneration at a higher concentration of sulphuric acid, 8.5%, did not result in a significant improvement in the MTC indicating a permanent reduction in the MTC. Figure 4-2 shows the impact of FA-1 on an anionic monobed. The results indicate higher effect on the MTC than for cationic resin. After passing 10 liters of 50 ppm as product solution (52 bed volumes) through the resin column, the sulphate ion average MTC was 34% lower than the unexposed anionic resin value. Another 10 liters of 50 ppm FA-1 was passed through the ion exchange column.

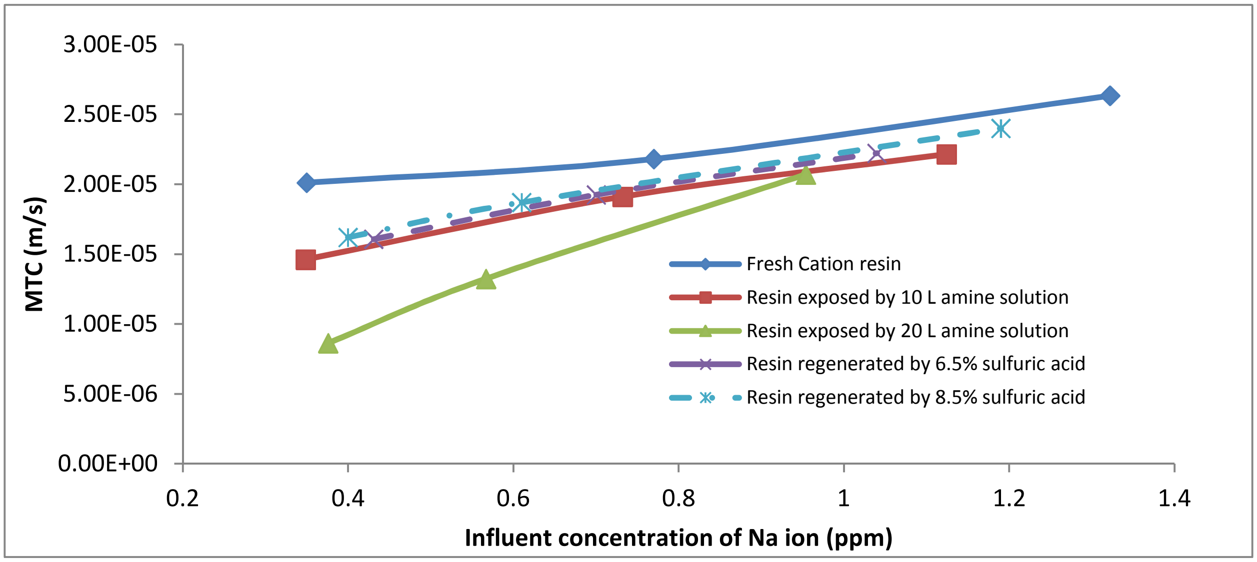


Figure 4-1

Effect of FA-1 for sodium ion in a cationic monobed (15-in. [381-mm] bed height)

However, doubling the amount of the solution did not result in any significant further reduction in the MTC. After regenerating with 5% sodium hydroxide, the sulfate ion average MTC was 24% lower than the unexposed resin. However, when the resin was regenerated with 8% sodium hydroxide, the MTC improved and nearly matched the value of the unexposed anionic resin, indicating that the amine could be removed by the higher regenerant concentration. This result indicates that MTC was recoverable for anionic resin at high regenerant concentration.

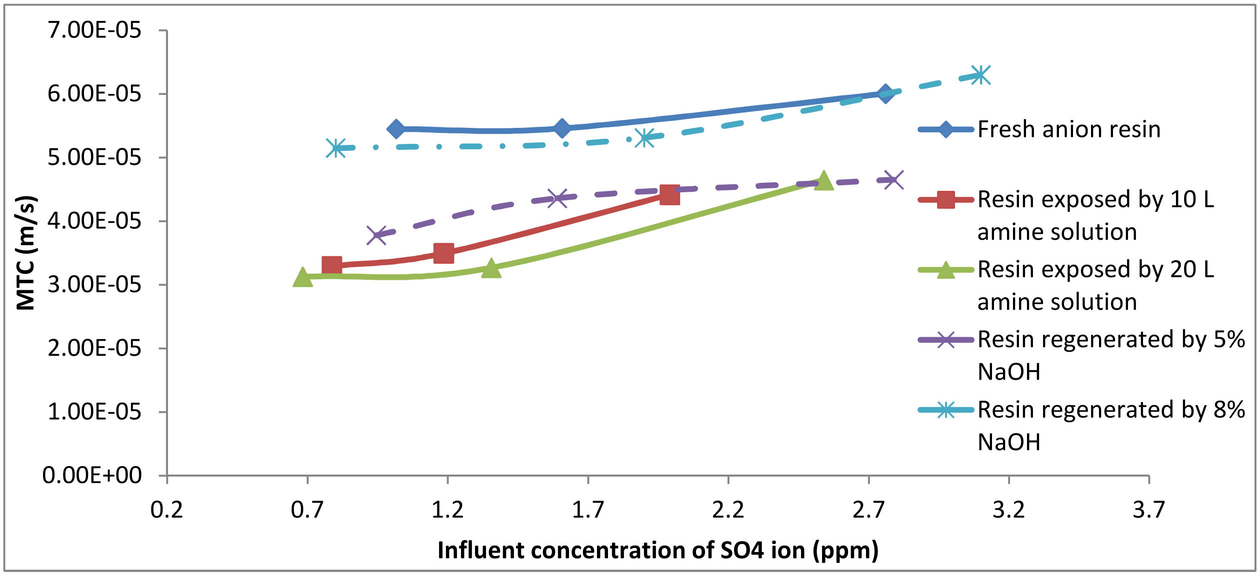


Figure 4-2

Effect of FA-1 for sulfate ion in an anionic monobed (15-in. [381-mm] bed height)

For mixed-bed experiments, new Dowex MS 650C (H) and Dowex MS 550A (OH) resins were used. The resins were regenerated separately and then mixed for exposure to the amine solution. After exposure, the resins were tested for the MTC, and both resin types showed about the same MTC reduction percentage. After exposure to 50 ppm as product 10-liter amine solution (52 bed volumes), the MTC of both the anionic and the cationic resin was about 24% lower than fresh, unexposed resins. An additional 10-liter amine solution resulted in further MTC deterioration for both anionic and cationic resins an additional 5-10%. Exposed cationic resin was regenerated by 6% sulfuric acid and showed only partial recovery of the MTC (to allow comparison to the monobed from Figure 4-1. The anion resin regenerated with 5% caustic showed almost a complete recovery of the MTC compared to unexposed resin which would indicate the fouling was reversible. Figures 4-3 and 4-4 show the impact of FA-1 on cationic resin and anionic resin on a mixed bed.

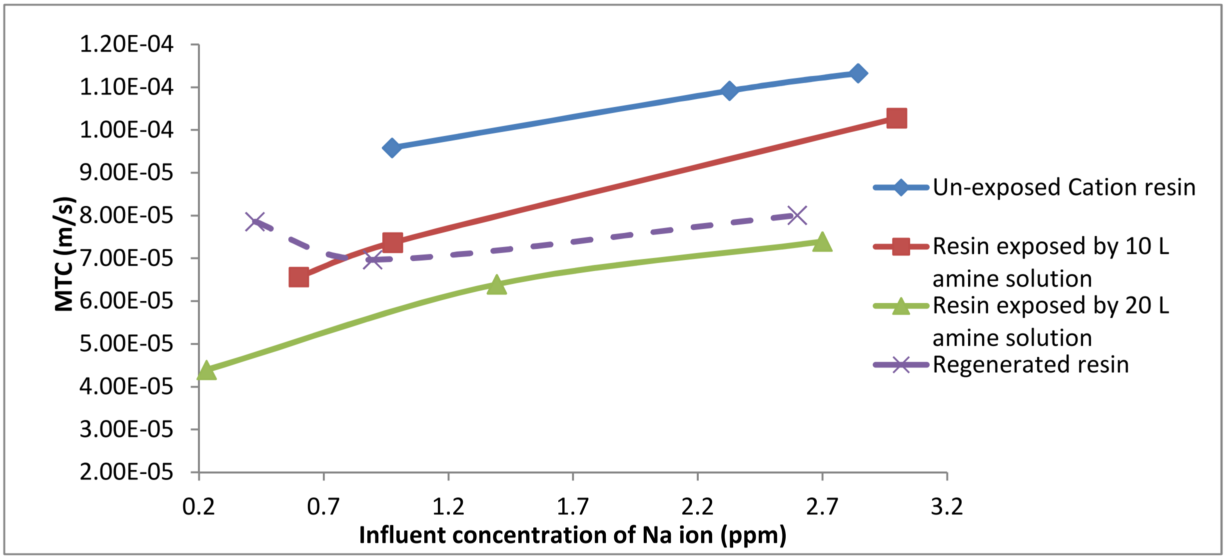


Figure 4-3

Effect of FA-1 for sodium ion on cation resin in a mixed bed (15-in. [381-mm] bed height)

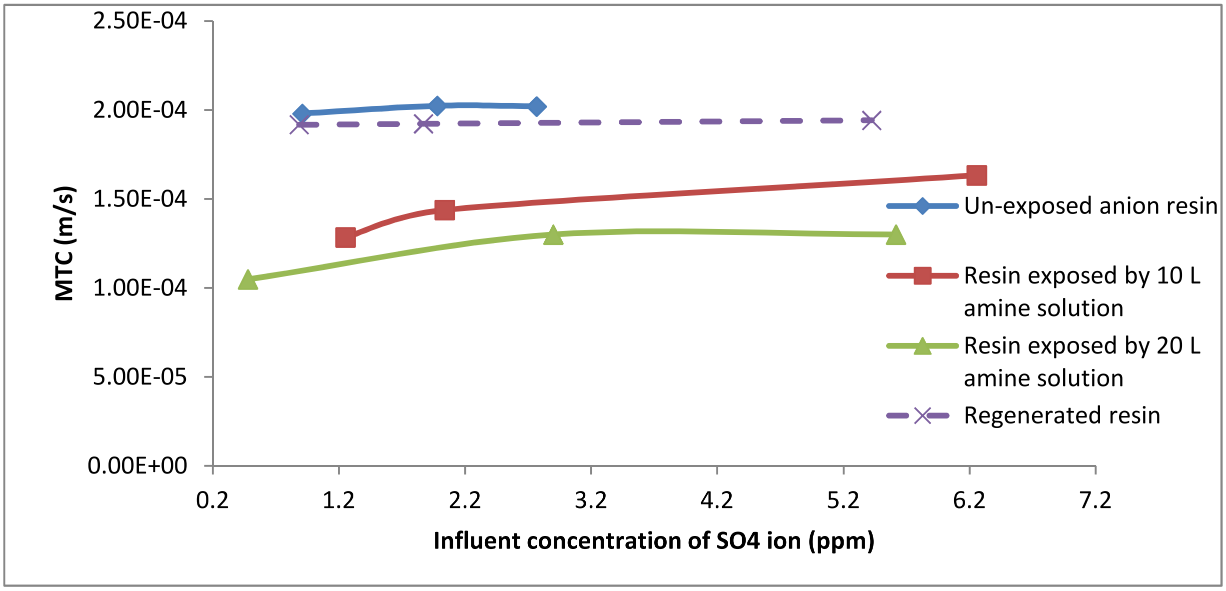


Figure 4-4

Effect of FA-1 for sulfate ion on anion resin in a mixed bed (15-in. [381-mm] bed height)

Repetitious Exhaustion/Regeneration

A volume of 190 ml of new regenerated cation was exposed to 10 liters of FA-1 solution (25 ppm as product, 53 bed volumes). The MTC was reduced by 17% compared with unexposed resin MTC. After the regeneration with 6% sulfuric acid, the MTC was 12% lower than the unexposed resin MTC. Further exposure of amine did not further reduce the MTC in a significant amount. Regeneration for the second time increased the MTC. The final MTC was about 90% of the unexposed MTC. Figure 4-5 shows the impact of filming repeated cycle of exhaustion and regeneration.

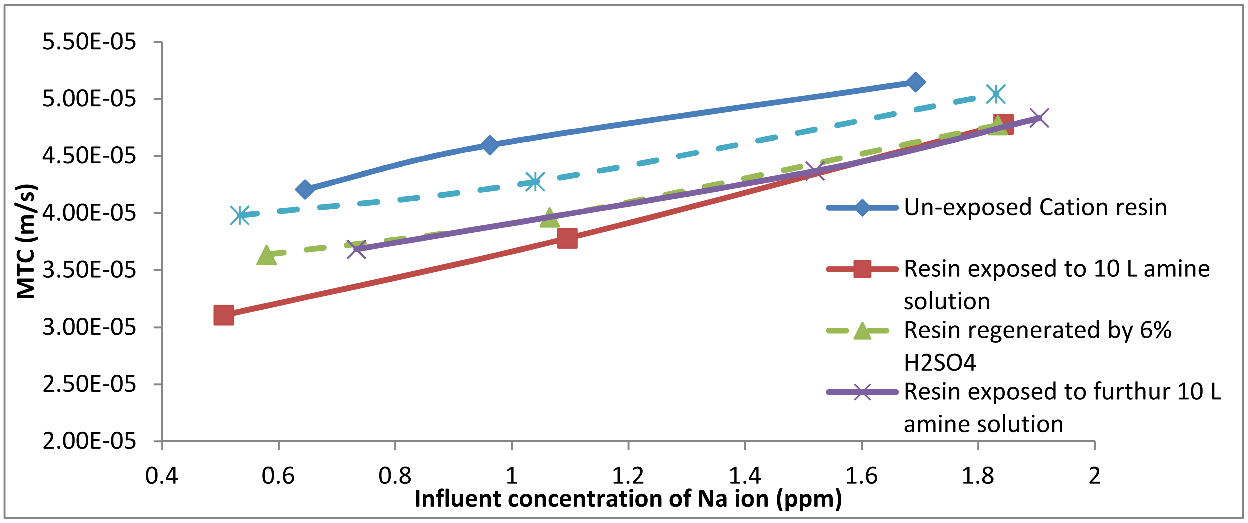


Figure 4-5

Repetitious exhaustion/regeneration for the cation monobed (15-in. [381-mm] bed height)

A volume of 185 ml of new anion resin was exposed to 10 liters of FA-1 solution (25 ppm as product, 54 bed volumes). The MTC was reduced by about 25% for this exposure; however, the regeneration with 8% sodium hydroxide improved the MTC to nearly the original value. Further exposure and regeneration did not change the MTC in a significant amount. Figure 4-6 shows the impact of a repeated cycle of exhaustion and regeneration with the FA-1 on the anionic resin.

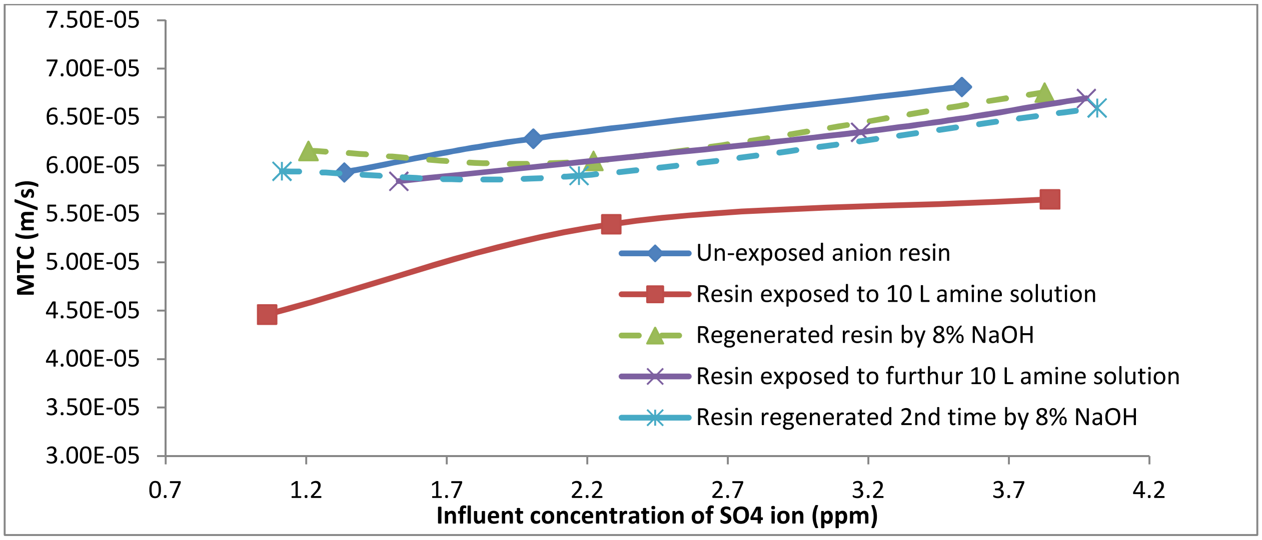


Figure 4-6

Repetitious exhaustion/regeneration for the anion monobed (15-in. [381-mm] bed height)

Experiments with High Concentration of FA-1

Filming amine can coat surfaces and make the experiment difficult. The initial experimental procedure was to prepare a solution of filming amine and pass it through ion exchange resin. A lower concentration (5 ppm) of FA-1 solution, made in the carboy, was passed through the resin. An MTC experiment did not show significant loss on kinetic ability. In addition to having no effect at low concentrations, it is also possible that filming amine is adsorbed on the surface of the carboy and supply line. As a result of this possibility a different experimental approach was used for comparison. An amount of filming amine was directly injected in the mouth of the resin. The outlet valve was closed to allow the resin to contact the solution. After 1 minute, the outlet valve was opened and 50 bed volumes of deionized water were passed through the resin. To accomplish this, the carboy was set above the resin column to perform gravity rinsing. The washing flowrate was approximately 40 ml/min. The exposed resin column was then used to perform a mass transfer coefficient experiment. Capacity calculations of filming-amine exposed, ion-exchange resin shows a significant amount of exchange sites used by the amine. These used exchange sites can result in reduced kinetic ability of ion exchange resin by shortening the exchange zone in the MTC calculation. For comparison, a stoichiometric equivalent of filming amine to ion exchange resin could be exposed to the resin, then an MTC test would confirm how the reduction in exchange sites impact kinetics. However, this type of experiment was not possible due to the lack of stoichiometric information of the proprietary filming amine.

The amount of filming amine varied over a group of experiments. A different amount of filming amine was used to define the extent of fouling as a function of exposure. In previous experiments, FA-1 was mixed with deionized water to make a defined concentration of FA-1. With the filming amine injected as product, a different approach was used to estimate or simulate the actual concentration. The ratio of filming amine injected to the volume of DI water used to wash the resin is the same as if a solution had been prepared by combining the amine with water. This staged process of FA followed by rinse ensures that the mass of amine exposure is known and consistent, while concentration calculations by this experimental method are assumed inaccurate.

A 250 ppm solution of FA-1 as product was prepared to perform this experiment. A 3.5-year-old unused strong cationic resin (Dowex MS 650C (H)) was used in this experiment. The experimental column was exposed to 50 bed volumes (2 liters) of 250 ppm FA-1 solution. The calculated average MTC was 24% lower than unexposed resin. After regeneration of resin by 6.5% sulfuric acid, the MTC improved, but, still, it was about 13% lower than unexposed resin. Further exposure of FA-1 lowered the MTC at about the previous exposed value. Further regeneration again improved the MTC and slightly above the previous regeneration. Figure 4-7 shows the effect of a high concentration of FA-1 on the cation resin. When considering the monobed cationic experiments, there was a 17% reduction in the MTC for 25 ppm FFA, 18% reduction for 50 ppm FFA, and 24% reduction for 250 ppm FFA (the three amine concentrations are as product). No strong correlation between amine concentration and MTC reduction was apparent. For direct comparison with another proprietary FA-1, FA-2, data are presented in Chapter 4, additional experiments were performed with FA-1 injected at the start of the test column and then washed through the bed with 50 volumes of deionized water.

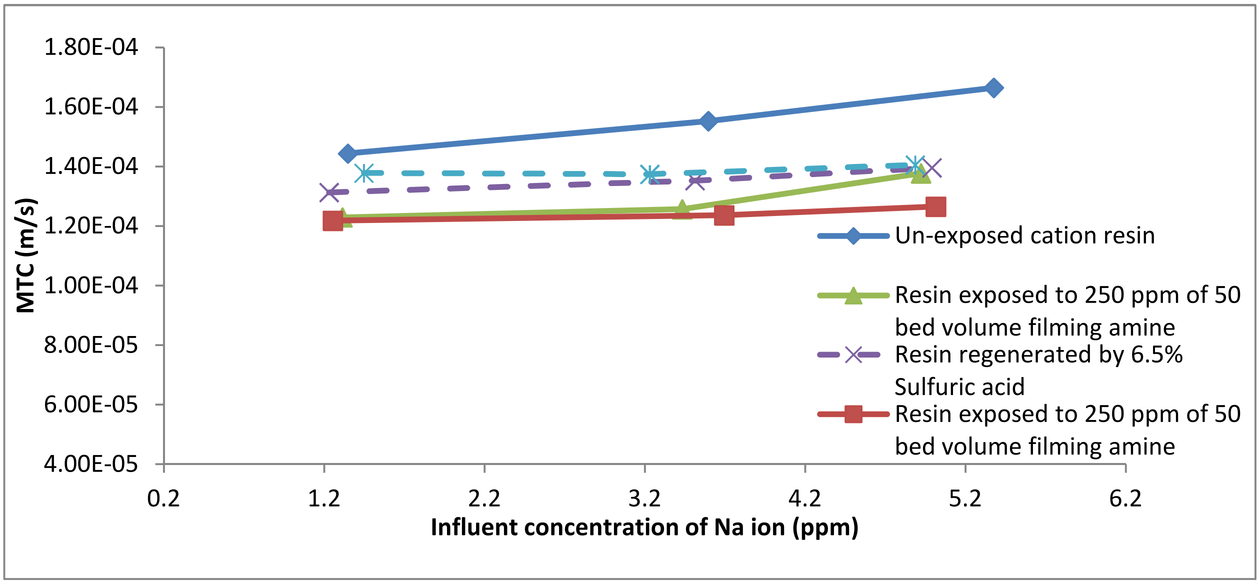


Figure 4-7

Repetitious exhaustion by 250 ppm FA-1 for the cationic monobed (3.1-in. [78.7-mm] bed height)

Experiments with Very High Concentration of FA-1

A 50 bed volume (2.5 liters) of 1500 ppm of FA-1 solution as product and 3.5-year-old cation resin with a 4-in. [104.1-mm] bed height was used for this experiment. Unexposed resin gave an MTC of 1.595 E -04 m/s, and exposed resin gave an MTC of 1.085 E -04 m/s; the MTC of the exposed resin was 32% lower than unexposed resin. For 50 ppm FA, exposed resin showed an 18% lower MTC than the unexposed resin. FA-1 can be adsorbed in the resin to reduce the kinetic ability. Hater [19] showed that alkalizing amines are completely absorbed by strong cation resin. Cation resin can also adsorb filming amine quickly at high concentration and result in significant loss of kinetic ability. At lower concentrations of filming amine for longer period the total mass exposed to the resin is achievable.

Experiments with Low Bed Height

Keeping other factors fixed, the MTC value was higher for lower bed height. This is expected because the shorter the bed, the more accurate the assumption that the bed acts as a differential exchange zone. Figure 4-8 shows the changes of the MTC at a low bed height of 4.1 in. [104.1 mm]. With higher bed depth, the exchange zone is more integral and can have some portion of the height operating in equilibrium rather than kinetic mode. The MTC reduction resulting from exposure to FA-1 was about the same percentage for different bed heights. After exposing the cationic resin to 25 ppm as product of the FA-1 solution 48 bed volumes (2.5 liters), the average MTC was 19% lower than the unexposed resin. After regenerating with 6.5% sulfuric acid, the average MTC improved and was about 10% lower than unexposed resin.

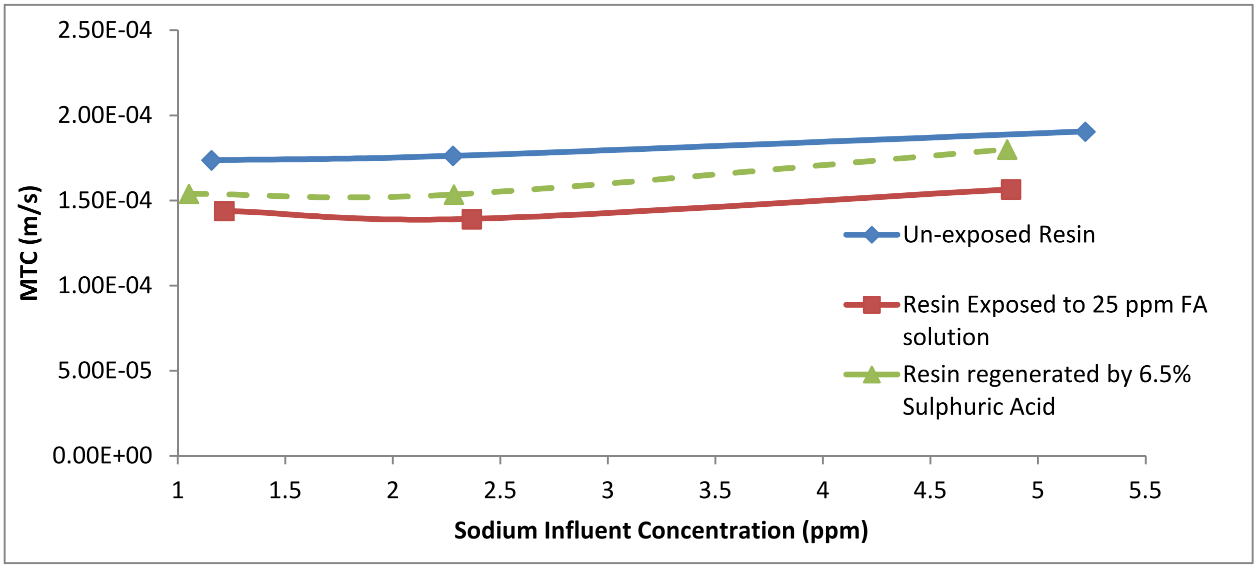


Figure 4-8

Changes of the MTC in the low bed height (4.1-in. [104.1-mm] bed height)

Cationic Resin Exposed to ODA

Figure 4-9 depicts the impact of ODA on cationic resin. An ODA solution of 0.5 ppm was made in isopropanol. Although solubility is not limiting in isopropanol, the concentration chosen was based on solubility of ODA in water. To compensate for the low concentration, additional solution was passed through the resin sufficient to saturate with ODA stoichiometrically. The resin was exposed to 3 bed volumes (0.3 liters). The average MTC was about 20% lower than unexposed resin. After regeneration by 6.5% sulfuric acid, the MTC was still about 12% lower than the original unexposed MTC.

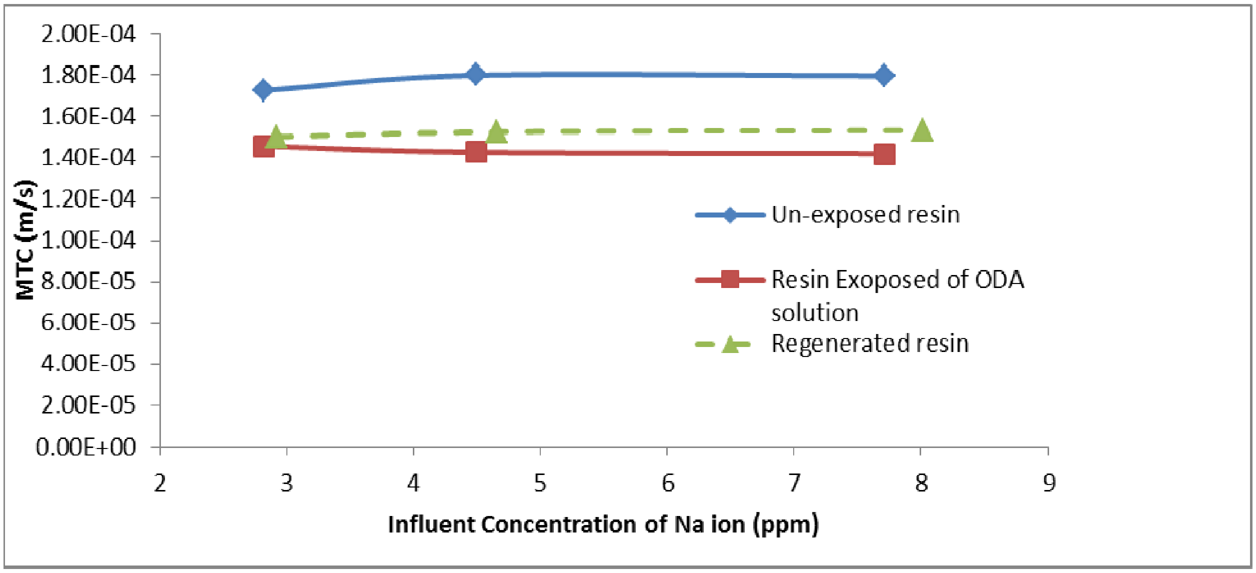


Figure 4-9

Changes of the MTC for exposure to ODA of cation (8-in. [203.2-mm] bed height)

Resin from Cation Column from Kentucky Power Plant

Resin from a cation column exposed to various concentrations of FA-1 during layup dosing trials was received for evaluation from a power plant located in Kentucky. For 4-in. (101.6-mm) resin bed height, as received, and 2.9 ppm of input concentration, the MTC was 9.648E-06 m/s and ion-exchange capacity was 0.268 eq/l. After regenerating with 6.5% sulfuric acid, the resin sample changed color from brown-black to purple, and the MTC was 8.672E-05 m/s, which is about nine times higher than without regeneration. However, the MTC was still 38% lower compared with the value of the new resin MTC, which was 1.412E-04 m/s. Some plants have an

MTC specification. While plant specific, an MTC of 2.0E-04 m/s is a nominal value that may indicate that the resin should be replaced.

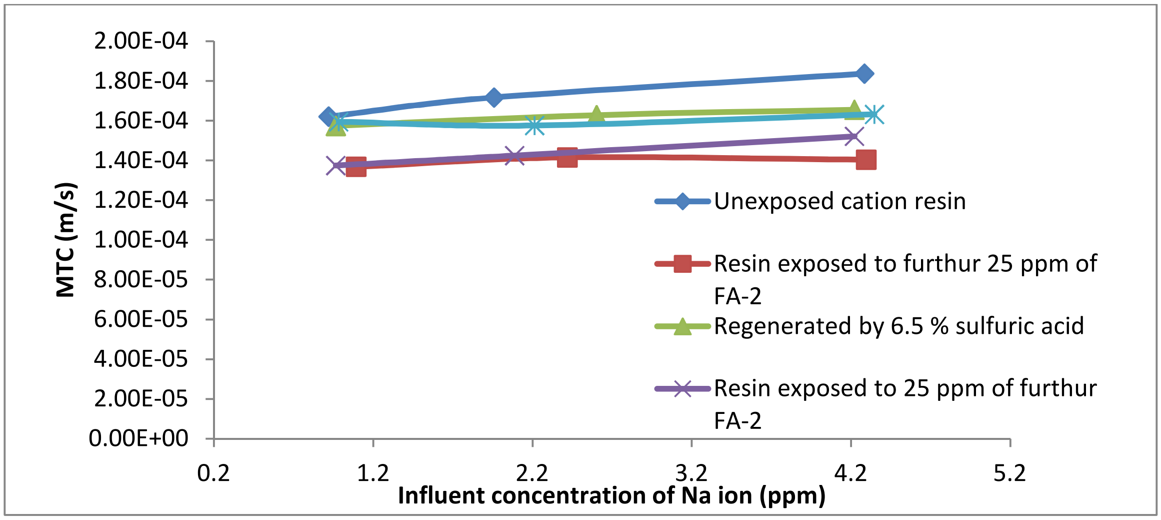
Resin FA-2 interaction (Cation Mono Bed)

FA-2 V219 is a combined neutralizing and filming amine product developed by BK Guilini (BKG) for use in layup of steam generator equipment to minimize offline corrosion. The component protection is provided by a combination of elevated pH from the alkalizing, neutralizing, amine and a monomolecular film by a filming amine that provides a barrier on the surfaces from that acts as a barrier between metal and water.

Both anion and cation mono bed were tested for impact of FA-1. For both the cases resin MTC reduced, but anion resin MTC was recovered by regeneration. FA-2 experiments were performed on cationic resin mono beds. One mixed bed experiment was also performed for FA-2.

All experiments followed the same test procedures conducted with FA-1. Initially a dilution was prepared to match the experiments with FA-1; however, for FA-2 no filming amine was observed entering the column. This was attributed to filming on the container and the column entry lines. Alternatively, FA-2 was added directly ahead of the column and experiments with FA-1 at the same concentrations were repeated following the same procedure. This best matched the FA-2 manufacturer’s direction of no dilution prior to application of the filming amine. Specifically, resin was exposed to selected concentrations of FA-2 within a column followed by about fifty bed volumes of deionized water. Amount of FA-2 injected on the mouth of the column and the amount of deionized water used to wash determined the concentration. Cation resin was regenerated with 6.5% sulfuric acid and anion resin was regenerated with 5.5% sodium hydroxide. The MTC was calculated for unexposed, exposed and regenerated resin for comparison.

Figure 4-10 shows the effect of FA-2 exposure on cationic mono bed. First, 2.5 liters of 25 ppm FA-2 were exposed to the resin. The MTC was 19% lower than unexposed resin. After regenerating with 6.5 % sulfuric acid, MTC improved to about 6% lower than unexposed resin. Further exposure dropped the MTC to 17% below unexposed resin. Repeated regeneration improved MTC back to about 7% below unexposed resin. The repeated experiment showed that similar recovery was observed after each exposure. Based on these data FA-2 appears to have similar impact on MTC at the same concentration as FA-1. No visual damage of the resins was observed by these exposures.



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Effect of 25 ppm FA-2 (50 BV) on cationic mono bed resin (4 inch bed height)

Figure 4-11 shows the results of 50 ppm FA-2 exposure on cation mono bed. A 2.5 liter solution of 50 ppm FA-2 showed an MTC decrease of 20%. Regeneration with 6.5% sulfuric acid returned MTC to 7% below the unexposed value. Repeating the experiment with 250 ppm FA-2 showed MTC dropped by 25%. Repeated regeneration again improved MTC to 6% below the unexposed value.

The results in Figures 4-11 and 4-12 indicate that there is some initial MTC impact from FA-2, but that recovery is consistent regardless of the exposure concentration.

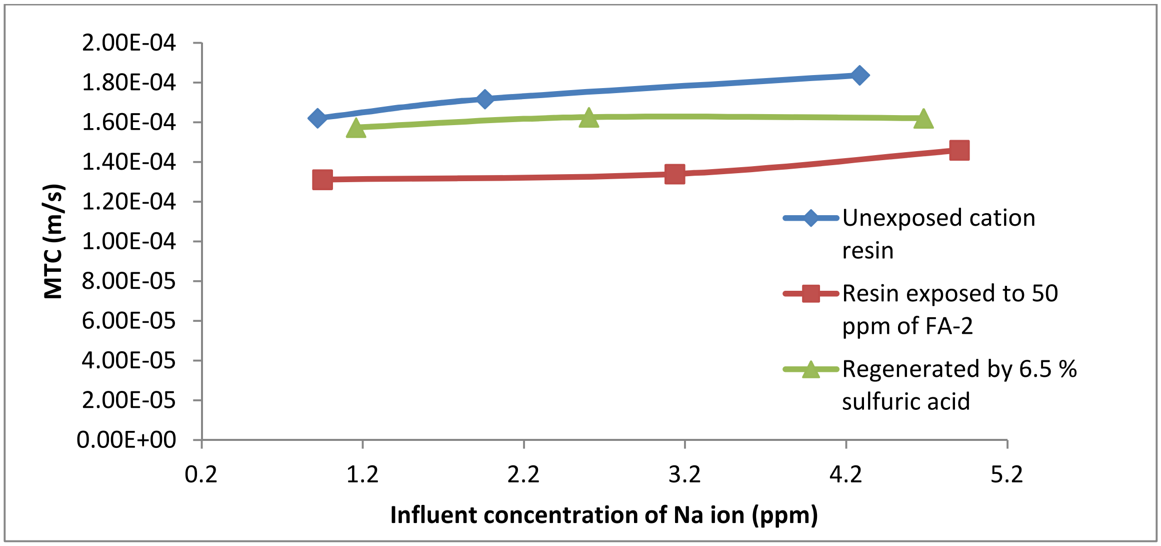

Figure **Error! No text of specified style in document.**4-11

Effect of 50 ppm of FA-2 (50 BV) on cationic mono bed resin (4 inch bed height)

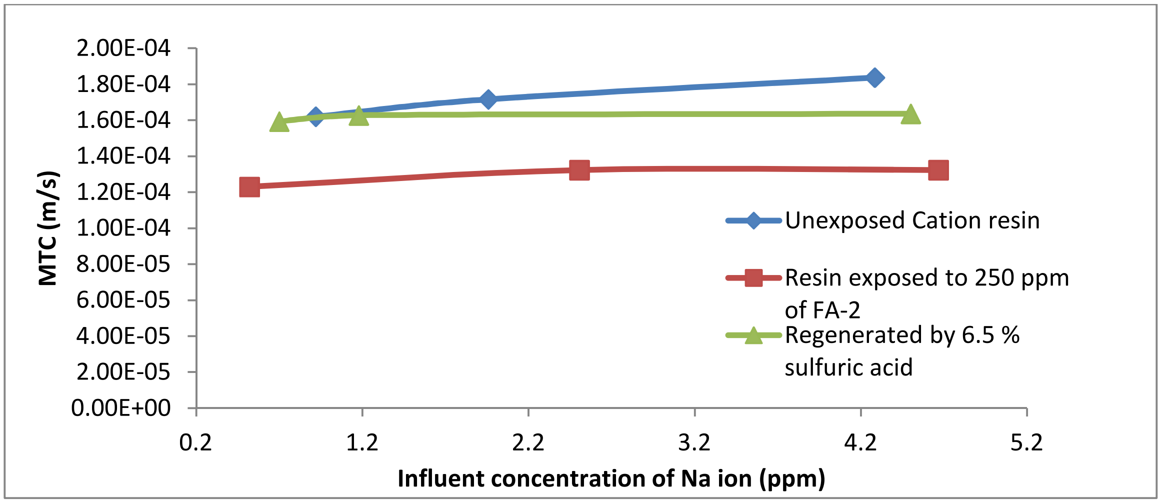

Figure **Error! No text of specified style in document.**4-12

Effect of 250 ppm of FA-2 (50 BV) on cationic mono bed resin (4 inch bed height)

Figures 4-11and 4-12 results raise the question about whether filming amine effects will be the same if the exposure amount is the same but the volume of the solution is different. To address this question, 0.0635 ml of FA-2 was mixed with 2.5 liter and 12.5 liter of water, respectively. Both solutions were passed through 50 ml of cation resin and MTC measured. However, the results for both experiments showed little reduction in MTC. A possible reason might be that FA-2 deposited as a film on the walls of the carboy and supply line. To overcome this possibility, an experimental procedure modification was made. First, 0.0125 ml of FA-2 was injected at the entrance of the 50 ml cation resin column. Then 2.5 liter (50 BV) of deionized water flowed through the column and the MTC measurement repeated. An additional 2.5 liters of deionized water were used and MTC measured again. Figure 4-13 shows the result of the experiment. After FA-2 exposure and the first 2.5 liters of water, MTC dropped 8.3% from its unexposed value. After passing the additional 2.5 liters of water, MTC did not change significantly and measured at 8% lower than the unexposed value. This experiment indicates that the amount of filming amine determines the total impact on the resin and not the volume of water processed. The only difference in water usage among these experiments was the amount used for rinsing.

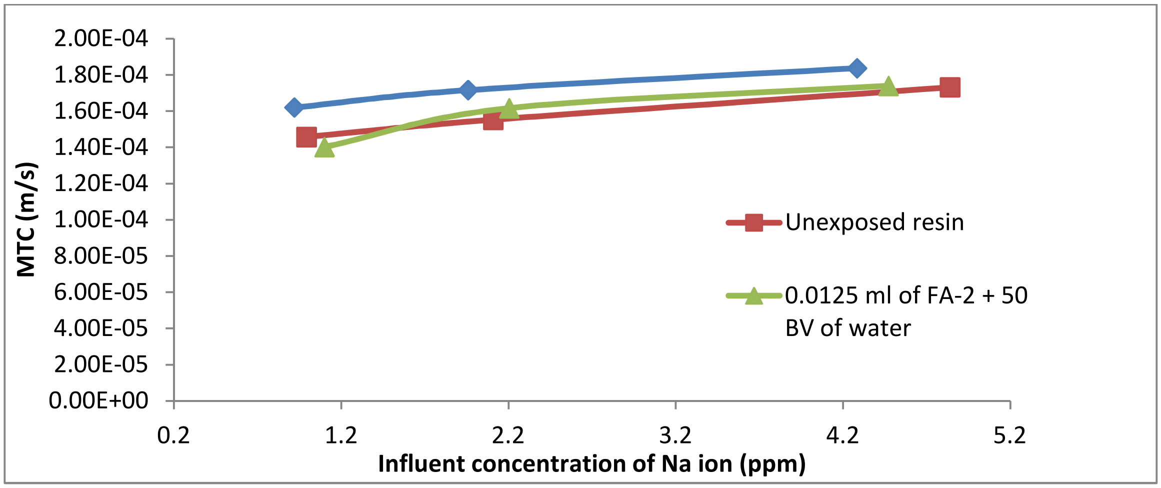

Figure **Error! No text of specified style in document.**4-13

Effect of different concentration and amine solution volume on cation resin (4 inch bed height)

Resin FA-2 interaction (Mixed Bed)

A mixed resin column was prepared that had a total bed volume 50% greater. FA-2 was injected to minimize amine absorption on the carboy wall and feed line. This column was exposed to 25 ppm of FA-2 followed by 50 bed volumes of water. After the experiment, the resins were separated and MTC values were determined for each resin type. The cation resin (Figure 4-14) showed a 12% drop in MTC from the unexposed value; while the anion resin (Figure 4-15) gave a 5% reduction in MTC unexposed values.

The impact on cationic MTC was approximately the same with both mono-cationic and mixed beds. Although the fouling percentages are slightly lower with the mixed bed they are not statistically significant and within experimental error. Also, note that the anionic resin was affected less than the cationic resin, as expected, due to the impact of charge repulsion (Donnan exclusion) between the positively charged amine and the positively charged anionic resin beads.

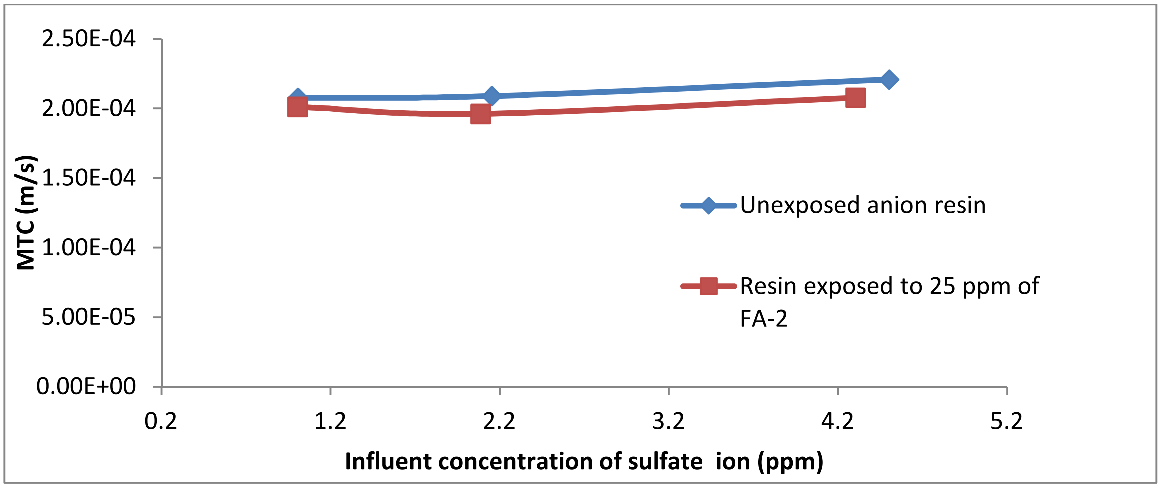

Figure **Error! No text of specified style in document.**4-14

Effect of FA-2 on cation resin of mixed bed (6 inch bed height)

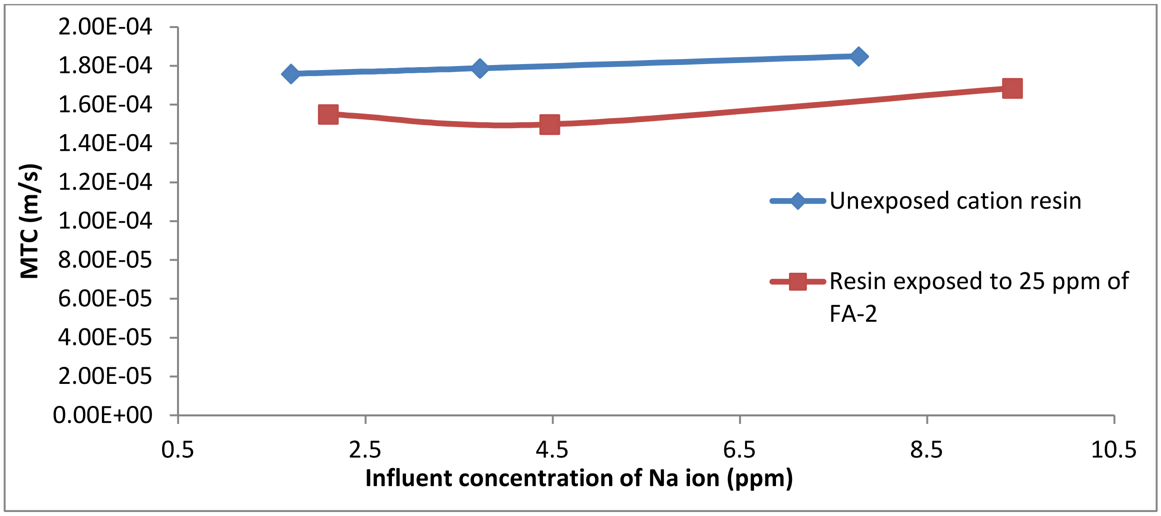

Figure **Error! No text of specified style in document.**4-15

Effect of FA-2 on anion resin of mixed bed (6 inch bed height)

Comparison of FA-1 and FA-2 Exposure on MTC

Very low dosing (0.5 ppm of FA-1 as product) of film-filming amine is recommended by the manufacturers for continuous application. However, over time, film-forming amine may accumulate in and on the resin continually and degrade the kinetic ability. Experimentation with low concentrations of film forming amine (0.5 ppm of FA-1 and fifty bed volumes) did not significantly reduce the MTC. This is because the total mass of film forming amine was low, resulting in little adsorption. The recommended dosage for FA-2 is 15 to 100 ppm. To simulate the range of potential industrial operation, high concentrations of the amines (5 to 1500 ppm) were also used. The objective of this concentration range not only evaluates the possibility of a spike in filming amine exposure to the resin, but also addresses the risk of accumulated exposure at a lower concentration over an extended period. For higher concentration, even 50-bed volumes deposited enough film forming amine on the resin to reduce the MTC significantly.

The beneficial feature of film-forming amines – coating surfaces – is the same reason for experimental challenges. Film-forming amines not only deposit on resins but also coat the experimental supply lines and feed carboy. At low concentration the mass that films can lead to immeasurable quantities in solution. This fact benefits high concentration experiments. FA-1 solutions of 25 and 50 ppm was made and exposed to resin. For other experiments, FA-2 and FA-1 were injected at the entrance of the test column and 50 bed volumes of deionized water were fed to give the total ratio of concentration. The concentration fed initially was that recommended by the manufacturers; no attempt to concentrate the solution was made at any time. Mathematically there is no difference in the MTC calculation whether the value is the result of a decrease in the length of effective exchange zone or by an even distribution throughout the bed. For all the cation resin experiment, 6.5% sulfuric acid was used to regenerate the resin.

In addition to the high and low concentrations discussed previously; for both FA-2 and FA-1, concentrations, as product, as defined by each respective manufacturer were also tested. Table 4-1 shows the comparison of FA-1 and FA-2 impact on ion exchange resin (MTC reduction from unexposed values) over the concentration range tested. For both experiments, FA-1 or FA-2 was injected on the test column loaded with resin. Then fifty bed volumes of deionized water were passed through the column. Then 6.5% sulfuric acid was used to regenerate the resin. MTC measurements were done with unexposed, exposed and regenerated cation resin. The initial impact from exposure of either filming amine is similar. Regeneration showed a more positive impact on FA-2 exposed cation resin, returning the MTC to within 6% of the unexposed values. Recovery of MTC was significantly less after regeneration of FA-1 exposed cation resin. For both filming amines, anion resin MTC loss was similar and regeneration returns MTC to near the unexposed value.

Table Error! No text of specified style in document.**4-1**

Comparison of Impact of FA-2 and FA-1 on MTC of Cation Resin

Concentration (50 BV) of filming amine (as product)	**Exposed resin**		**Regenerated resin**	
	FA-1	**FA-2**	**FA-1**	**FA-2**
50 ppm	19%	23%	13%	7%
250 ppm	24%	26%	13%	6%

CHAPTER V

CLONCLUSIONS AND FUTURE STUDY

Kinetic ability of ion exchange resin was reduced by filming amine exposure to resin for all of the experiments. However this was more severe for cationic resin. Exposing cationic resin to 50 bed volume of different concentrations of filming amine decreased the MTC by 18% to 25% in most cases. In continuous exhaustion, further exposure to filming amine showed further MTC loss. Regeneration increased the MTC but still it was lower than original one. Using strong regenerant was more successful in MTC recovery than standard regeneration. Use of ODA also showed same kind of result. In repetitious experiment, loss of MTC in first cycle was higher. Further exposure in next cycle does not lower the MTC as significantly as previous cycle. MTC was improved in each regeneration but never recovered fully. The cation resin can be considered as irreversibly fouled by filming amine. Loss of MTC results in the poor performance of ion exchange resin. Exposing cation resin with filming amine for a long time without regeneration can prevent the mixed bed polisher from meeting water quality effluent specifications. Anionic resin also showed the reduction of MTC for filming amine exposure. But strong regeneration recovered the MTC about its original value. Both the continuous exhaustion and repetitious exhaustion gave same kind of result.

The proper application of filming amine should increases the corrosion resistance and improves the heat transfer capacity of boiler and other components in the steam/water cycle. At the same time amine that is not adsorbed in the cycle can have a negative effect on cationic resin. Replacement of cationic resin may be needed more frequent than usual which will increase the operating cost. Again, stronger regenerant concentration is necessary for anionic regeneration which will also increase operating cost. Alternative regeneration method can be explored to recover the capacity of ion exchange resin fully. The extent that filming amine should be used is primarily an economic question. A detailed economic analysis would address the benefit for materials protection versus the cost of more frequent resin replacement.

REFERENCES

Alchin, D. (2008). Ion Exchange Resins. Retrieved January 10, 2013 from nzic.org.nz/ChemProcesses/water/13D.pdf**.**

ASTM International, 'Standard Practice for Evaluating the Kinetic Behavior of Ion Exchange Resins', (West Conshohocken, PA: ASTM International, 2009).

Babler, R., Uhlemann, M., & Mummert, K. (1999). Inhibiting effect of octadecylamine on pitting corrosion behavior of stainless steel type 1.4541 up to 250^{o} C. *Materials and Corrosion*, 50(3), 146-153.

Beck, M., Walker, K.., Workman, B. (2012). American Electric Power Filming Amine Trials. EPRI International Conference on Cycle Chemistry, Seattle, WA.

Bursik, L. (2010). The FA-2 Symposium “Film-Forming Amine in Plant Cycles”. *PowerPlant Chemistry*, 12(7), 396-399

Chernyshev, E. V., Veprov, E. N., Petrov, V. A., Bogdanov, S. L., Levina, T. Y., Petrova, T. I., & Verkhovskii, A. E. (2006). Increasing the Corrosion Resistance of Equipment due to the Use of Film-Formin Amines. *Power Technology and Engineering*, 40(1), 34-37

Cussler, E. L. (1997). Diffusion Mass Transfer in Fluid Systems .Cambridge, UK: Cambridge University Press.

Diaion: Manual of ion exchange resins and synthetic adsorbents, Vol. I and Vol. II, 2nd ed. 1995. Tokyo: Mitsubishi Chemical Corporation

Dow Chemical Company. (2012). Dowex Resin Design Guidelines. Retrieved from http://www.dowwaterandprocess.com/support_training/literature_manuals/ix_techinfo/guide.htm.

Drofner, K. (1971).Ion Exchangers; Properties and Applications. Ann Arbor , Michigan: Ann Arbor science Publishers Inc.

Dwivedi, P.N., Upadhyay, S.N. (1977). Particle-fluid mass transfer in fixed and fluidized beds. *Industrial & Engineering Chemistry Process Design and Development* .16 (2), 157–165.

Gönder, Z. Beril, Yasemin, K., Ilda, V., & Hulusi, B. (2006). Capacity Loss in an Organically Fouled Anion Exchanger. *Desalination,* 189(1). 303-07.

Hater, W., Rudschutzky, N., Olivet, D. The Chemistry and Properties of Organic Boiler Feed Water Additives Based on Film-Forming Amines, and Their Use in Steam Generators. www.bkgwater.com. Retrieved December 10, 2012 from www.bkgwater.com/.../organic-boiler-feedwater-additives-based-on-film.

Harries, R. R., Ray, N. J.(1984) . Anion Exchange in High Flow Rate Mixed Beds. *Effluent Water Treatment Journal*, 24(4), 131-139.

Helfferich, F. G. (1962). Ion Exchange. New York: McGraw Hill Book Company.

Hussey, D. F. and Foutch, G. L.Ion Exchange Kinetics for Ultrapure Water, Sengupta, A. K. and Y. Marcus, editors; Ion Exchange and Solvent Extraction, 16th Edition, March, 2004.

Foutch, G., A. Apblett, M. Hasan, A. Kabir, "Impact of Film-Forming Amines on Condensate Polishing Ion Exchange Resins," EPRI, Palo Alto, CA. Technical Report TR#3002000416, April, 2013

Frayene, C. (2002). Boiler Water Treatment: Principles and Practice. New York: Chemical Publishing Company Inc.

Frisch, Norman W., Kunin, R. (1960).Kinetics of Mixed-Bed Deionization: I. *AIChe Journal*, 6(4), 640-647.

Lee, Gang-Choon, Gary L. Foutch, & Alagappan Arunachalam. (1997) .An Evaluation of Mass-Transfer Coefficients for New and Used Ion-Exchange Resins. *React. Funct. Polym*, 35(1), 55-73.

McNulty, J.T., Eumann, M., Bevan, C.A.; Tan, V.C.T. Anion exchange resin kinetic testing- an indispensable diagnostic tool for condensate polisher troubleshooting. 47th Annual Meeting International Water Conference. Pittsburgh, PA, 1986

Nasef, M. M.,Ujang, Z. (2012). Introduction to ion exchange processes. Inamuddin, Luqman, Mohammad., *Ion Exchange Technology I*(pp. 1-39). doi: 10.1007/978-94-007-1700-8

Pandey, Ashwini K. (2008). 'Kinetic Study of Ion Exchange Column Operation for Ultrapure Water Application. Oklahoma State University.

Raught. Dennis P., Foutch, Gary L., Apblett, Allen. (2005). Ion Exchange Resin Fouling by Organic Amines in Secondary Systems at U.S. Nuclear Power Plants'. *Power Plant Chemistry*, **7**(7).

Stiller, K., Wittig, T., & Urchey, M. (2011). The Analysis of Film-Forming Amines – Methods, Possibilities, Limits and Recommendations. *PowerPlant Chemistry*, 13(10), 4-17.

Topp, H., Hater W., Bache, A, Kolk, C. Z. (2012). Film-Forming Amine in Shell Boilers. *Powerplant Chemistry*. 14(1), 38-48.

Verib, G. J. (2012). Use of Filming Amine in Fossil Fired Utility Boilers. EPRI International Conference on Cycle Chemistry, Seattle, WA.

Voges, N., & Hater, W. (2010). Distribution Ratio and Average Surface Coverage of Film-Forming Amines. *PowerPlant Chemistry*, 12(3), 541-549.

Walker, J. L., Cornelius, T.E., (1975). Filming Amine Emulsions. US Pat. No. 3,860,430.

Assessment of Amines for Fossil Plant Applications. EPRI, Palo Alto, CA: 2010. 1017475.

APPENDICES

ERROR ANALYSIS

Error analysis is the study of uncertainty of result that is caused by error in measurement of input data. Usually all data measurement can be associated with some error or uncertainty. These input errors can propagate to make even more error in the final results. So error analysis gives a picture of the variability of result. Mass transfer coefficient (k, MTC) depends on number of factors which can contribute the variability.

Resin bead diameter(d_p)was supplied by resin manufacturer and treated as constant. Packed bed resin was used for the experiment and voidage (ε) was considered also constant. Error analysis was done for mono bed resin experiment so resin volume fraction (R) was unity. Also column diameter(A) was constant as single column was used. Other input measurements were considered subject to error and standard error of measurement was calculated for these data. Volumetric flow rate was measured several times using a stop watch and cylindrical test tube. Influent and effluent sample were diluted to different ratio and tested in ion chomatograph to get the standard error of measurement. Surface of the resin in the test column was not perfectly flat and bed height data were taken from different side of the column to measure the variability. Then propagation of error analysis was done. From the column material balance (assuming negligible accumulation in the bulk fluid), we find MTC

$$k = \frac{\mathrm{d_p}}{6(1-\varepsilon)R}\frac{V}{Az}\ln\left(\frac{\mathrm{C_i^f}}{\mathrm{C_i^{eff}}}\right) \tag{A-1}$$

$$consider\ \frac{\mathrm{d_p}}{6(1-\varepsilon)R}\frac{1}{A} = M(constant), Which\ leads\ to$$

$$k = M\frac{V}{z}\ln\left(\frac{\mathrm{C_i^f}}{\mathrm{C_i^{eff}}}\right) \tag{A-2}$$

We can differentiate the above equation to get the propagated error for MTC,

$$e_k = M\frac{1}{z}\ln\left(\frac{\mathrm{C_i^f}}{\mathrm{C_i^{eff}}}\right)e_v + M\frac{V}{z^2}\ln\left(\frac{\mathrm{C_i^f}}{\mathrm{C_i^{eff}}}\right)e_z + M\frac{V}{z}\left(\frac{1}{\mathrm{C_i^f}}\right)e_{\mathrm{C_i^f}} + M\frac{V}{z}\left(\frac{1}{\mathrm{C_i^{eff}}}\right)e_{\mathrm{C_i^{eff}}} \tag{A-3}$$

e_v, e_z, $e_{\mathrm{C_i^f}}e$, $_{\mathrm{C_i^{eff}}}$ are the standard error of measurement for volumetric flow rate, bed height, influent concentration and effluent concentration respectively. Figure A1 shows the results of the error analysis for new dowex 650 C(H) cation resin MTC experiment.

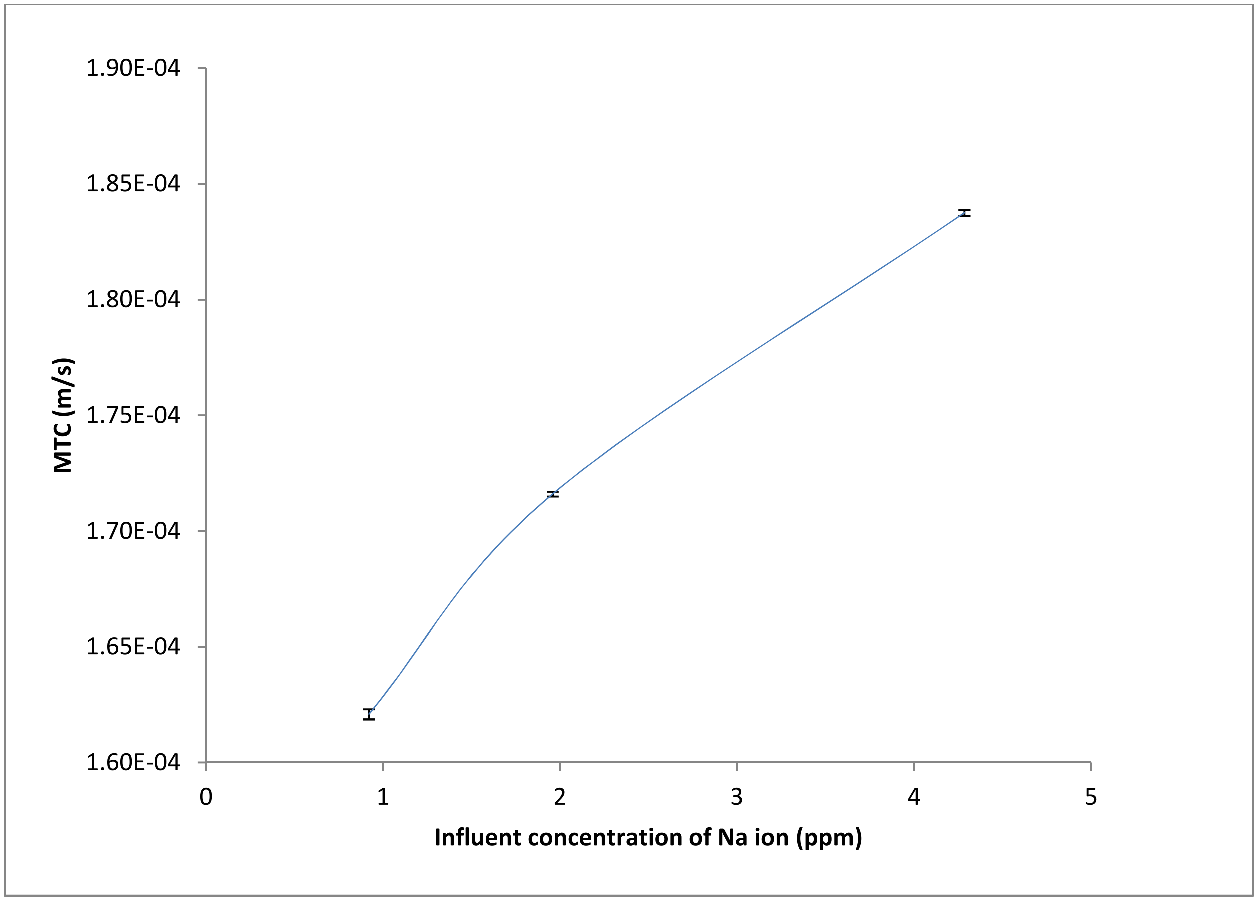

Figure A-1. Error analysis for MTC experiment

Results of error in MTC came really low (about ten power minus seven ranges). Concentration was measured with a new ion chromatograph so standard error of concentration was low (0.001 to 0.004 range). Variability was significant in volumetric flow rate measurement but the input unit in the equation was in cubic meter per second. So the numerical value of volumetric flow was also low. So the main error contributor was the variability of bed height. But considering all the factor, the final error in the MTC was minimal and can be ignored for MTC comparison.

CHANGES IN MTC FOR UNUSED OLD RESIN

MTC for used ion-exchange resins was discussed by Lee *et al.* (1997) who found that fouled resin has 30 to 50% lower coefficients than predicted or measured for unfouled resin. In this study, MTC of unused old resin was measured to determine the degradation or fouling due to storage only. Dowex brand anionic and cationic resin of different ages was used.

Figures 2 and 3 show Na^+ and Cl^- MTC data for various influent concentrations and ages of resin. MTCs are essentially constant over the feed water concentration range within experimental error. These results are similar to data from Harries and Ray that showed slightly lower MTCs at lower chloride feed concentrations in experiments with fouled resins. Resins that were stored in dry conditions showed more significant MTC decrease with age. Wet resins showed a lower rate of MTC decrease than dry resins. Comparative MTC data for new resins are from Lee *et al.* (1997). They showed the new resin MTCs in the range of 2.2E-04 to 2.4E-04 m s^{-1} under similar operating conditions.

For cationic resin with sulfonate functionality, both three-year old wet and five-year old dry show 22% MTC decrease. Reduction is more severe for anionic resins – as expected for the more unstable amine functionality. For instance, MTC for three year old dry anion resin was 45% lower than new resin. Five year old wet anion resin showed 35% reduction. For 10 year old dry samples of both anionic and cationic resins, MTCs were more than 50% lower than new resins. We are aware that there are slight variability in flow rates, influent concentration and bed depth from batch to batch that may account for some of the differences on MTC but these effects were not considered.

Nearly horizontal lines on Figures 2 and 3 reinforce the hypothesis that MTC is independent of ionic influent concentration, as expected. As such, MTC is clearly a property of the resin and not a function of the experimental method used to obtain its numerical value.

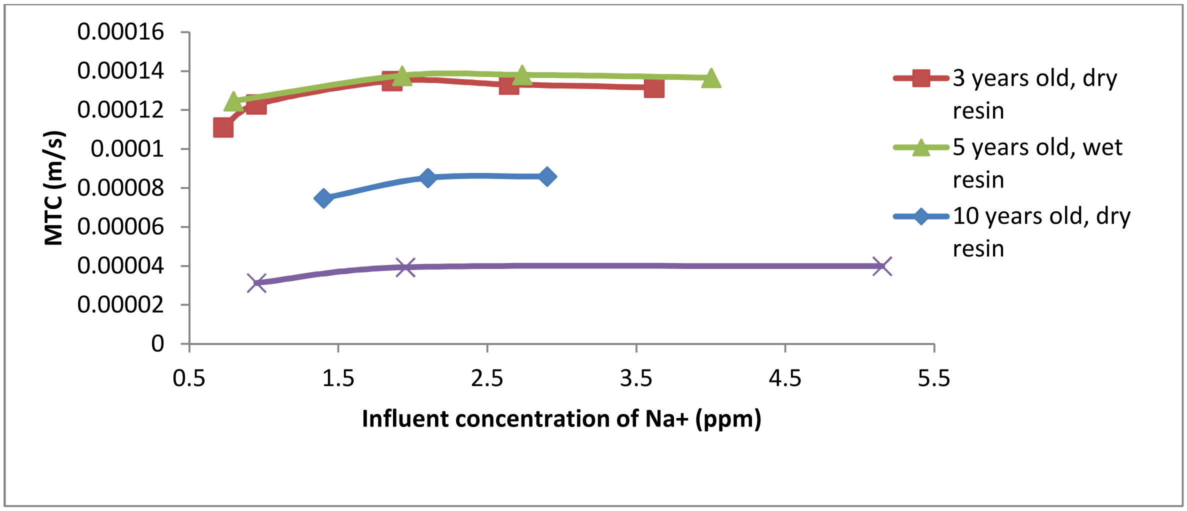

Figure A-2. Sodium MTC for old cationic resins at various influent concentrations

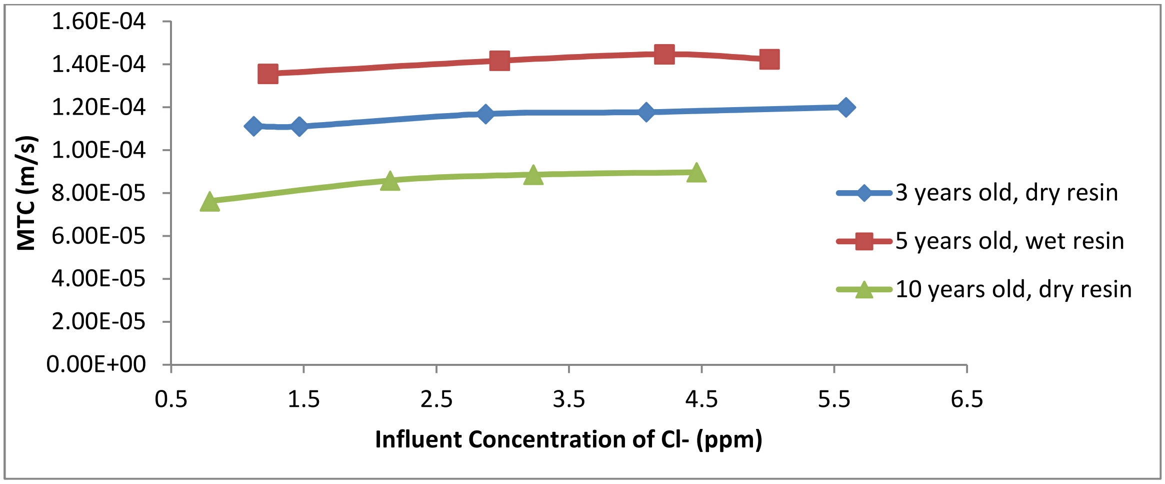

Figure A-3. Chloride MTC for old anionic resins at various influent concentrations

Figure 4 shows the change of average MTC of dry cationic resins of different age. Steady decrease of MTC continues as age of the resin increases. At this rate, resin MTC can fall below 0.0001 m s^{-1} in approximately five years and become unusable. Figure 6 shows the average MTC of dry anionic resins of different age. MTC loss was higher in the first three years for anionic resin than cationic resin. Therefore, anionic resin may become unusable quicker than cationic resin. Trend of MTC loss in both cases is close to linear. So, for both cases, linear equations were obtained to relate age and MTC for dry resin.

Figure A-4. Average MTC for old cationic dry resins of different age

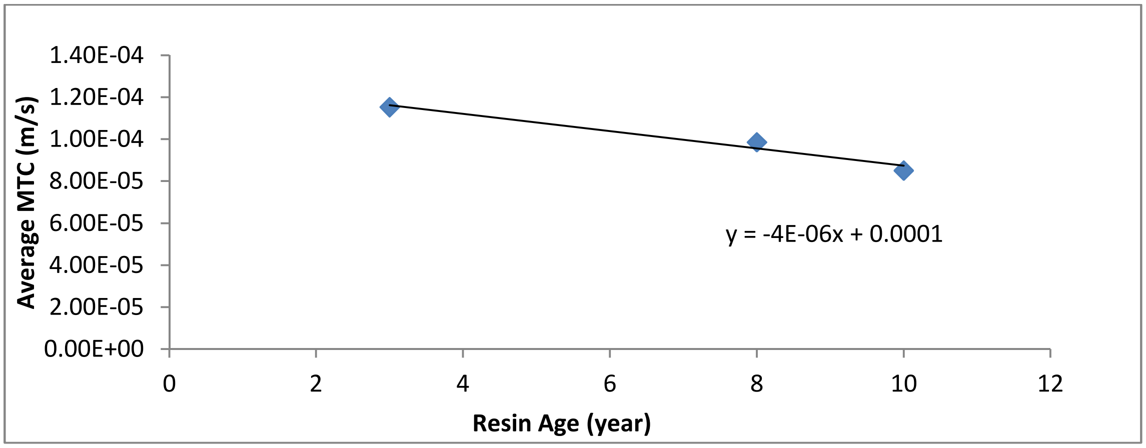

Figure A-5. Average MTC for old anionic dry resins of different age

Resins stored dry showed significantly lower MTC than resins stored wet. In figure 6, dry and wet five-year old resin MTC comparisons are shown. Due to a lack of availably of five year old dry resin, MTC values were estimated by the age-MTC correlation. Dry cationic resin showed less than 50% MTC of that of wet cationic resin while dry anionic resin showed 56% of MTC value of wet anionic resin.

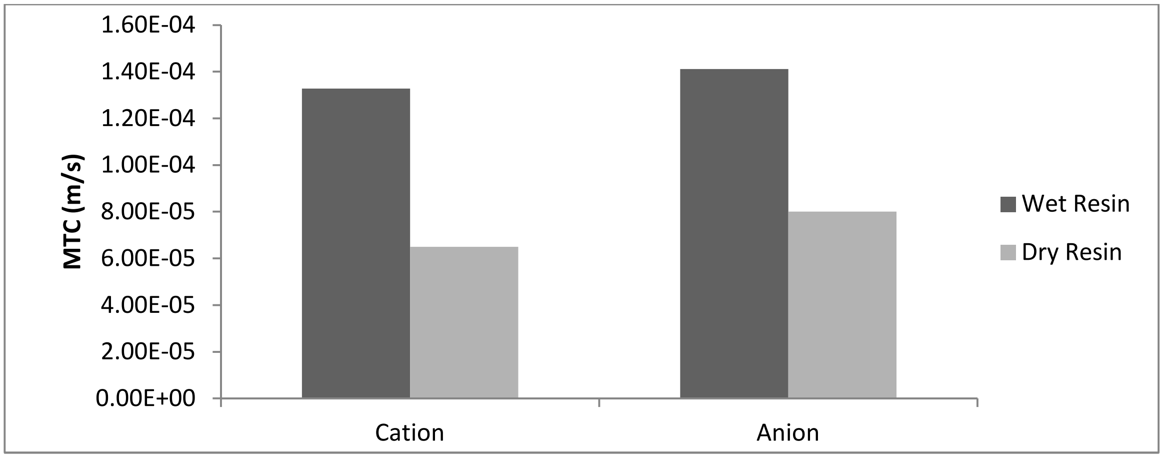

Figure A-6. Effect of storage condition of resins on MTC (both 5 years old)

We believe MTC is an excellent indicator for the acceptability of ion exchange resin. From the literature MTC has no strong correlation with external factors, influent concentration, flow rate, bed height. The results show the steady decrease of ion exchange resin MTCs indicating deteriorating resin quality, even when unused. Thus for maximum effectiveness, resin should be used within a reasonable time. Indefinite storage cannot be assumed. Also, results show resin stored wet have better MTC than resin stored dry.

SAMPLE RESULT

Mass Transfer Coefficient depends on different variables. Major variables were bed height and influent concentration. Flow rate of 1 liter per minute was used for most of the experiment. Packed bed voidage of 0.35 was used in the calculation. Following table gives sample experimental results

Table A-1

New cation resin (Dowex MS 650 C H) in mono bed

Flow rate	1 liter/ minute
Influent Concentration	0.92 ppm sodium
Effluent Concentration	0.0456 ppm sodium
Volume fraction	1
Bed height	4 inch
Particle Diameter	0.00065 meter
Mass Transfer Coefficient	0.000162087 meter/ second

Table A-2

25 ppm of FA-2 exposed cation resin in mono bed

Flow rate	1 liter/ minute
Influent Concentration	0.1092 ppm sodium
Effluent Concentration	0.0864 ppm sodium
Volume fraction	1
Bed height	4 inch
Particle Diameter	0.00065 meter
Mass Transfer Coefficient	0.000136856 meter/ second

Table A-3

25 ppm of FA-2 exposed and regenerated cation resin in mono bed

Flow rate	1 liter/ minute
Influent Concentration	0.9644 ppm sodium

Effluent Concentration	0.0521 ppm sodium
Volume fraction	1
Bed height	4 inch
Particle Diameter	0.00065 meter
Mass Transfer Coefficient	0.000157441 meter/ second

Table A-4

25 ppm of FA-1 exposed anion resin (Dowex 550 A OH) in mono bed

Flow rate	0.9 liter/ minute
Influent Concentration	1.0612 ppm sulfate
Effluent Concentration	0.02709 ppm of sulfate
Volume fraction	1
Bed height	14.5 inch
Particle Diameter	0.00059 meter
Mass Transfer Coefficient	0.000044612 meter/ second

Table A-5

25 ppm of FA-1 exposed and regenerated anion resin (Dowex 550 A OH) in mono bed

Flow rate	0.9 liter/ minute
Influent Concentration	1.2084 ppm sulfate
Effluent Concentration	0.00768 ppm of sulfate
Volume fraction	1
Bed height	14.5 inch
Particle Diameter	0.00059 meter
Mass Transfer Coefficient	0.0000615148 meter/ second

PROPRIETARY FILMING AMINES

FA-1

FA-1 is used for high pressure scale passivation and corrosion inhibition. It works as a filmer to protect both ferrous and admiralty metals throughout the steam water cycle. According to the company, this product significantly eliminates flow assisted corrosion to successfully attain operational control. No detail information on the formulation or physical properties was supplied from the manufacturer.

FA-2

FA-2 is a filming amine product to be used in boiler and closed loop water treatment. It makes a monomolecular film on metal surface which acts as a barrier between metal and water media. It also disperses the scale forming salts and control pH by means of neutralizing agent.

Table A-6

General description of FA-2

Chemical formula	Cyclohexylamine (z)-N-9-Octadecenypropane-1,3-diamine
Appearance	Yellowish Liquid
Density (68^{o}F)	0.98 ± 0.03 g/cm^3
pH (1% solution)	12.00 ± 0.5
Freezing point	-15 ± 1 ^{o}C
Solubility in water	Dilution is not recommended
Dosage	Depends on concentration ratio, hardness, total alkalinity, chloride content, temperature, holding time index and suspended solids.
Application	At feed tank or feed water pipe

VITA

Maruful Hasan

Candidate for the Degree of

Master of Science

Thesis: IMPACT OF FILMING AMINE ON ION EXCHANGE RESIN FOR ULTRAPURE WATER APPLICATION

Major Field: Chemical Engineering

Biographical:

Education:

Completed the requirements for the Master of Science in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma in December, 2013.

Completed the requirements for the Bachelor of Science in Chemical Engineering at Bangladesh University of Engineering and Technology, Dhaka, Bangladesh in 2007.

Experience:

Research Assistant at Oklahoma State University from August 2011 to December 2013
Teaching Assistant at Oklahoma State University from August 2011 to December 2011
Research Fellow, IRPT Dhaka, Bangladesh from April 2009 to March 2011
Assistant Manager, Sam Heung Environmental Industry, Bangladesh from September 2007 to March 2009

Professional Memberships:

CheGSA, OSU automation society