

KINETIC STUDY OF ION EXCHANGE COLUMN
OPERATION FOR ULTRAPURE
WATER APPLICATION

By

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PREFACE

The present study will be helpful in application of ion exchange in semiconductor and nuclear industry. Study of Kinetic properties of ion exchange resins is necessary in design, operation and optimization of ion exchange column. Better insight of Mass transfer coefficient will lead to better utilization of column and predict effluent quality. Modeling of rinse process will lead to evaluate the kinetic characteristics of resins

I wish to express my sincere appreciation for my major advisor Dr. Gary L. Foutch for being a great teacher, amazing mentor and a wonderful human being. I learned not only from his technical knowledge and skills but also from his patience, sense of humor, flexibility and attitude. I am also grateful to Dr. Arland H. Johannes and Dr. Karen High for their helpful suggestions and insights while serving on my advisory committee. Particular thanks goes to Dr. Marty High for helping me understand and formulate model for rinsing process. I am also grateful to Dr. Allen Apblett and Dennis Hussy for their work in fouling and radial flow model respectively.

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
Ion Exchange	2
Ion Exchange Resins.....	3
Ion Exchange Application.....	8
Ion Exchange in UPW	8
Ion Exchange Equilibria	9
Ion Exchange Kinetics	14
Mass Transfer Coefficient & its Significance.....	15
II. MASS TRANSFER COEFFICIENT & FOULING MECHANISM	18
Background.....	18
Fouling Mechanism	19
Effects of Fouling on MTC.....	21
III. RADIAL FLOW MASS TRANSFER COEFFICIENT	26
Introduction.....	26
Background.....	27
Radial Flow Model	28
Conclusions.....	37
IV. RINSE MODELING	38
Introduction.....	38
Background.....	39
Rinse Process	40
Model Development.....	42
Single Resin Bead	44
Dynamics of Ion Exchange Column.....	46
Future Work.....	49

Chapter	Page
REFERENCES	51
APPENDIX A – Review of MTC Literature	55
APPENDIX B – Experimental Setup	63
APPENDIX C – Ion Chromatograph.....	67
APPENDIX D – Experimental Results.....	69

LIST OF TABLES

Table	Page
1 List of Equipment	66
2 Experimental Mass Transfer Coefficient Data	69

LIST OF FIGURES

Figure	Page
1. Copolymerization of Styrene and Divinylbenzene	4
2. Production of SAC resins through Sulfonation	5
3. Production of WBA resins through Amination	6
4. Typical Ion Exchange Isotherm	11
5. Predicted Chloride Breakthrough Curve.....	25
6. Inward Flow Radial Flow Mixed Bed	30
7. Concentration Profile inside resin bead at various time	47
8. Resin Surface Concentration variation with time	48
9. Expected Effluent Profile.....	49
10. Typical Binary Ion Exchange System.....	56
11. Flow Diagram for MTC Experimental Setup	63

NOMENCLATURE

a_s	specific surface area of resin bead (m^2/m^3),
d_p	diameter of spherical particles (m)
C_i	fluid phase concentration (mg./L)
C_i^f	fluid phase concentration in feed (mg./L)
C_i^{eff}	fluid phase concentration in effluent (mg./L)
C_i^*	Concentration at the liquid-solid interphase (mg./L)
C_i^b	bulk fluid phase concentration (mg./L)
\bar{D}	Self Diffusion coefficient (m^2/sec)
F	Volumetric flow Rate (m^3/sec)
FR	Volume fraction of sample resin (m^3/m^3 bed)
h	height of radial flow bed (m)
J_A	Diffusive flux of ion A
k_0	Overall mass transfer coefficient (m/sec)
k_f	film mass transfer coefficient (m/sec)
k_p	particle mass transfer coefficient (m/sec)
K_A^B	Selectivity Coefficient
K_P^A	Distribution partition coefficient of ion A

$k_{f,i}$	Average film mass transfer coefficient of ion 'i' (m/sec)
L	Cylindrical bed depth (m)
q_i	resin phase concentration (mg./L)
Q_i	total ion exchange resin capacity, meq/ml
r	radius of column (m)
R	Reaction term
R_i	Inner radius of Column (m)
R_0	Inner radius of Column (m)
t	time (s)
u_r	fluid velocity (m/s)
x_i	dimensionless bulk solution fraction of ion 'i'
y_i	dimensionless resin fraction of ion 'i'
Z	Bed depth (m)
ε	Bed porosity, (m^3/m^3 bed)
ξ	dimensionless distance
τ	dimensionless time
Φ	Constant

CHAPTER I

INTRODUCTION

Water is the most important substance for the existence of human life. Water, because of its amazing properties can be used in a wide variety of unit operations in the process industry; including, washing operations, steam systems, cooling systems, and as solvents. Several specific industrial operations in pharmaceutical industry, nuclear and coal fired power plants, and semiconductor manufacturing requires water of extremely high purity (Ultrapure water). Process water with ionic impurity levels of less than $1\mu\text{g/Kg}$ (ppb) with corresponding low levels of particulate and microbial contaminants is termed as high purity or ultrapure water (Sadler, 1993). The biggest consumers of ultrapure water are the power generation and the electronics industries. Although industrial boiler applications in power generation dwarfs the electronics industry in terms of the volume of ultrapure water produced and used, the ultra-high purity levels required by the electronics industry drive the cutting-edge innovation in water treatment technologies. According to the latest forecast the world market for equipment and services to produce ultrapure water worldwide will rise from US\$3.6 billion this year to US\$4.8 billion in 2010 (Ultrapure Water: World Markets, 2006). Rising water costs, restrictions in water use and increased environmental awareness have driven designers towards more efficient water systems. This data suggest the need for efficient and cost

effective systems for production of ultrapure water. Ion exchange beds are used in final polishing for the production of ultrapure water. Kinetic study of ion exchange resins is important in design, trouble-shooting, and optimization of ion exchange bed operation. Mass-transfer coefficient, a lumped parameter, represents the kinetic ability of ion exchange resins for a particular operation. The objectives of this study are:

- 1). to analyze the effect of fouling on mass-transfer coefficient of resins
- 2). to determine mass transfer coefficient expression for radial flow fixed bed adsorption column and analyze its similarity with axial beds
- 3). to formulate mathematical model for rinse process in ion exchange bed and present ideas to correlate kinetic properties of resins with rinse time and volume
- 4). to review mass transfer coefficient literature

ION EXCHANGE

An ion-exchange reaction is defined as the reversible stoichiometric interchange of ions between a solid phase (the ion-exchanger) and a solution phase; the ion exchanger is usually insoluble in the medium in which the exchange is carried out. Today, ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation, and adsorption. Ion exchange has been used frequently as an economical and convenient separation method for producing ultrapure water. Thus, ion exchange is used to provide large volume of ultrapure water to microelectronics, food, power, pharmaceutical industries. Ion exchange is used in numerous chemical processes which can be subdivided into three

broad categories of substitution, separation and removal of ions. Ion exchange is particularly used in ion separation, heavy-metal recovery, hydrometallurgy, potable water treatment, and catalysis. In addition, ion exchange is also used in various other areas like ion chromatography, pharmaceutical chemistry, medicinal products, hydrometallurgy, blood treatment and many others discussed by Kunin, 2000.

ION EXCHANGE RESINS

Ion exchanger resins are solids and suitably insolubilized high molecular weight cross-linked polyelectrolyte hydrocarbon matrix carrying a positive or a negative electric surplus charge which is exchanged by mobile counter ions of opposite sign in the solution (Dorfner, 1971). The matrix holds these counter ions and is elastic. Therefore, a liquid diffuses into the matrix and ions in the liquid are exchanged with counterions which are attached in the matrix. Exchangeable ions in cation and anion exchange resins are cations and anions respectively. It is the functional group that determines the chemical behavior of resins. Ion exchange beds consist of cation exchange resin or anion exchange resin or a mixture, resulting in removal of ions from the solution. The effluent concentration determines the service cycle operating time of a bed. Further resins are broadly classified as strong or weak acid cation exchange resins or strong or weak base anion exchange resins. This classification depends on the functional group attached to the insoluble polymeric structure. Cation exchange resins contain functional groups such as sulphonic acid ($-SO_3H$), carboxylic acids ($-COOH$), phosphoric acid ($-PO_3H_2$), and arsenic acid ($-AsO_3H_2$) while anion exchange resins contains quaternary ammonium, quaternary phosphonium, or tertiary sulphonium groups as the functional group. The

insoluble polymeric chain is usually made by copolymerizing styrene with divinyl benzene (DVB) as shown (Figure 1)

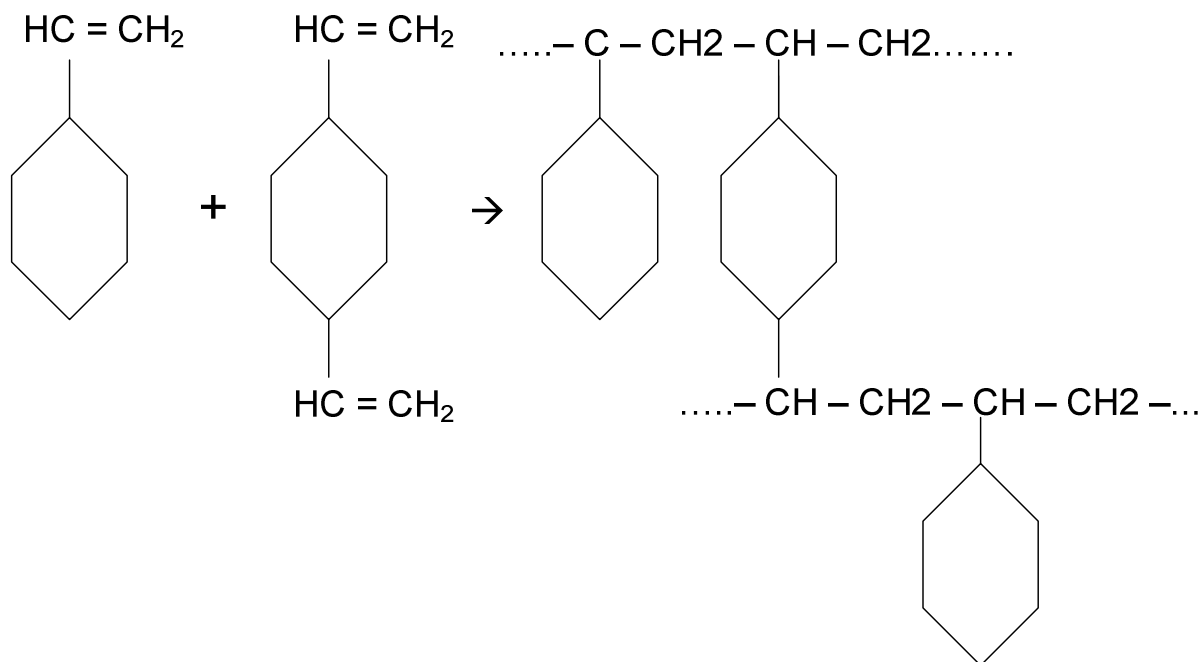


Figure 1. Copolymerization of Styrene and Divinylbenzene (Helfferich, 1962)

The amount of DVB in the reaction mixture controls the degree of spatial inter-linkage of the formed polymeric structure which plays an important role in deciding the properties of the resins formed. Commercial synthetic ion exchange resins of the gel type usually contain 2-12% DVB as cross-linking agent (Dorfner, 1971). The mole percent of DVB used in polymerization reaction is used to classify resin products (Haub, 1984).

Resins are prepared by addition of functional group in the copolymeric chain obtained from styrene and DVB. Cation and Anion exchange resins are prepared by the introduction of acid and base functional group respectively (Haub, 1984). In strong acid cation resin the desired functional group is sulfonic group ($-SO_3^-H^+$), this is achieved by

heating copolymer with sulfonating agents such as concentrated sulfuric acid (Owens, 1985; Haub, 1984).

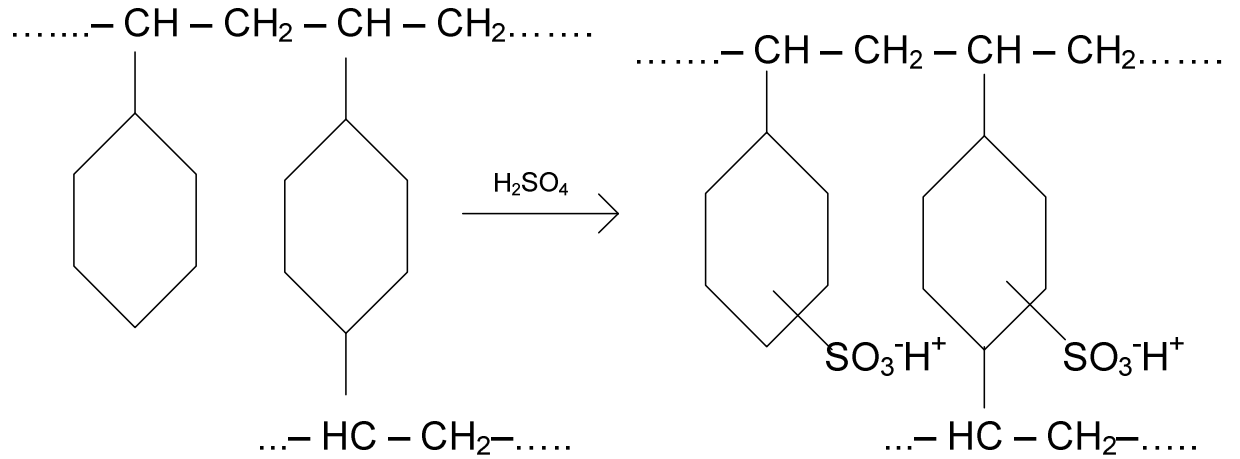


Figure 2. Production of SAC resins through Sulfonation (Helfferich, 1962)

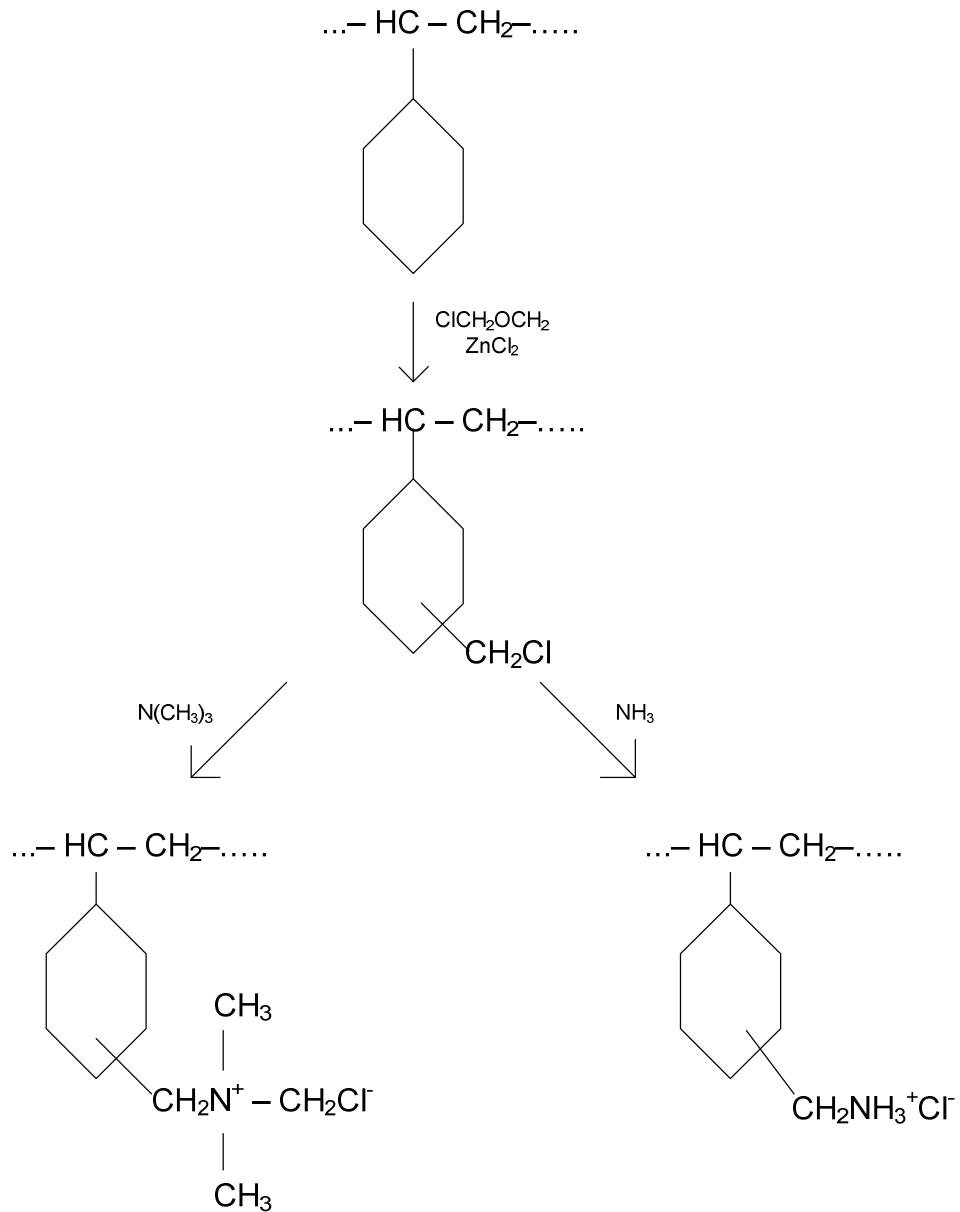


Figure 3. Production of Anion resins through Amination (Helfferich, 1962)

Weak acid cation resins may be prepared by polymerization of DVB with acrylic or methacrylic acid which results in the introduction of carbonic ($-\text{COO}^- \text{H}^+$) group in the copolymer. Strong anionic resins are prepared by introduction of quaternary ammonium ion-exchange functional group ($-\text{CH}_2\text{N}(\text{CH}_3)_2^+ \text{Cl}^-$) which requires more than one step

and is typically involves chloromethylated intermediate followed by amination with trimethylamine shown in Figure 3 (Owens, 1985; Haub, 1984). While for weak anionic resins other amines are used following the chloromethylation step.

Cross linking influences not only the solubility but the mechanical stability, exchange capacity, water uptake and swelling behavior, volume changes in different form of loading, selectivity, as well as oxidation resistance of ion exchange resins. Ion exchange resins with low degree of cross linking are soft and mechanically unstable while highly cross linked products are hard and brittle, and the beads may break easily. The exchange capacity of a dry exchange resins increases with a smaller degree of cross-linking and vice versa, while the exchanger capacity per volume decreases with decreasing cross linking because of more extensive swelling. The selectivity increases with higher degree of cross-linking. Higher Cross-linking also improves chemical and oxidation resistance.

Another important property of ion exchange resins related to degree of cross-linking is porosity. Porosity influences the capacity and selectivity of ion exchange materials. Low porosity ion exchange materials will have relatively low capacity, as high exchange capacities are obtained only because active functional groups located in the interior of the pore also contribute to capacity. Each cation exchange resin has simple cations like H^+ or Na^+ to neutralize the negative charges of the insoluble copolymer, and each anion exchanger has simple anions to balance the positive charge of copolymer structure.

ION EXCHANGE APPLICATION

Numerous applications of ion exchange can be found in industrial operations particularly in removal or recovery of specific ions from the solution. As a result of major advances in the resin development and other improvement in the operation cycle of ion exchange, like counter flow regeneration, improved mixed bed operation, more efficient contacting using countercurrent ion exchange, and other advances in water chemistry involved, ion exchange is applicable as a foremost technique for the production of high quality water for power industry, chemical industry, food and pharmaceutical industry, and ultra pure water for semiconductor industry. Ion exchange is also used in environmental pollution control, particularly in removal of contagious metals, & waste water treatment. Streat (1999) and Kunin (1996) discussed various applications of ion exchange in detail.

ION EXCHANGE IN UPW

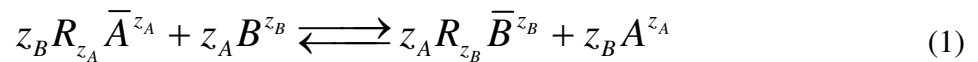
Production of ultrapure water is a multi-step process which includes numerous operations, with each operation removing specific types of contaminant. The various operations involved are filtration, reverse osmosis, ultrafiltration, adsorption, UV treatment and many others (Hussey, 2000). Each operation has a particular role to play by removing specific contaminant. Hussey (2000) discussed various unit operations and the contaminants they remove with their advantages and disadvantages. Ion exchange is useful in removing ionic contaminants. Development in different water treatment procedures have resulted in significant reduction of contaminant but ion exchange has not been replaced by any other process because of the high purity achieved by mixed bed exchange. Due to significant rise in high purity water requirement in semiconductor and

in power industry, ion exchange has become more important in final polishing in ultrapure water production.

The water quality desired in two major consumers (i.e. power and semiconductor industry) of ultrapure water differ distinctly but both need water with extremely low level of ionic impurity. The main concern in power industry is ionic impurity which causes or induces corrosion like sodium, chloride, sulfate ions, silica and iron oxides. While in semiconductor water requirements the main contaminant of concern are microbial and particulates in addition to ionic and organic impurities (Sadler, 1993). Ion exchange is particularly useful in removal of ionic impurities because it has highest removal efficiency and is relatively economical.

ION EXCHANGE EQUILIBRIA

Ion exchange resins after coming in contact with the solution, exchanges counter ions and attain equilibrium. Suppose an ion exchange resin initially in A form is introduced into a solution with counter ions B. Counter ion exchange will take place and ion A in exchanger will be partially replaced by B:



In equilibrium, both the ion exchange resins and the solution will have competing ion species, A and B. The exchange is reversible in nature and the concentration ratio of both ions will not be same in two phases i.e. resin and solution phase (Helferrich, 1962). This is the primary reason for ion exchange to be applicable in water purification as the

reactive sites on polyelectrolytes, zeolites, have a preference for one ion over others. This preference of particular ion over other ion is termed selectivity and is influenced by nature of the counter ion, the fixed charges in the matrix, the degree of ion exchanger saturation, the total solution concentration, and external variables like temperature and pressure (Haub, 1984). The experimentally observed selectivity is given by separation factor, (α_A^B) , which is the quotient of the concentration, molality, or equivalent ion fraction ratios of the exchanging ions in the resin and solution phases and is expressed as:

$$\alpha_A^B = \frac{(m_B)_r^{Z_A} (m_A)_s^{Z_B}}{(m_A)_r^{Z_B} (m_B)_s^{Z_A}} = \frac{(c_B)_r^{Z_A} (c_A)_s^{Z_B}}{(c_A)_r^{Z_B} (c_B)_s^{Z_A}} = \frac{(X_B)_r^{Z_A} (X_A)_s^{Z_B}}{(X_A)_r^{Z_B} (X_B)_s^{Z_A}} \quad (2)$$

where m, c, & X represent molality, molarity and equivalent ionic fraction respectively (Helfferich, 1962; Grimshaw & Harland, 1975).

Ion B is preferred by resin if the value of separation factor is greater than 1. For theoretical studies selectivity is expressed in terms of selectivity coefficient which is expressed in term of activities of components. Ion exchange isotherms characterize the ion exchange equilibrium. An ion exchange isotherm is a graphical representation of ionic composition of ion exchanger as a function of experimental condition. Any specific set of experimental conditions (solution concentration, relative amounts of counter ions, etc.) corresponds to one point on the isotherms. Figure 2 represents a typical isotherm for exchange of ion A in the resin phase for ion B in solution phase.

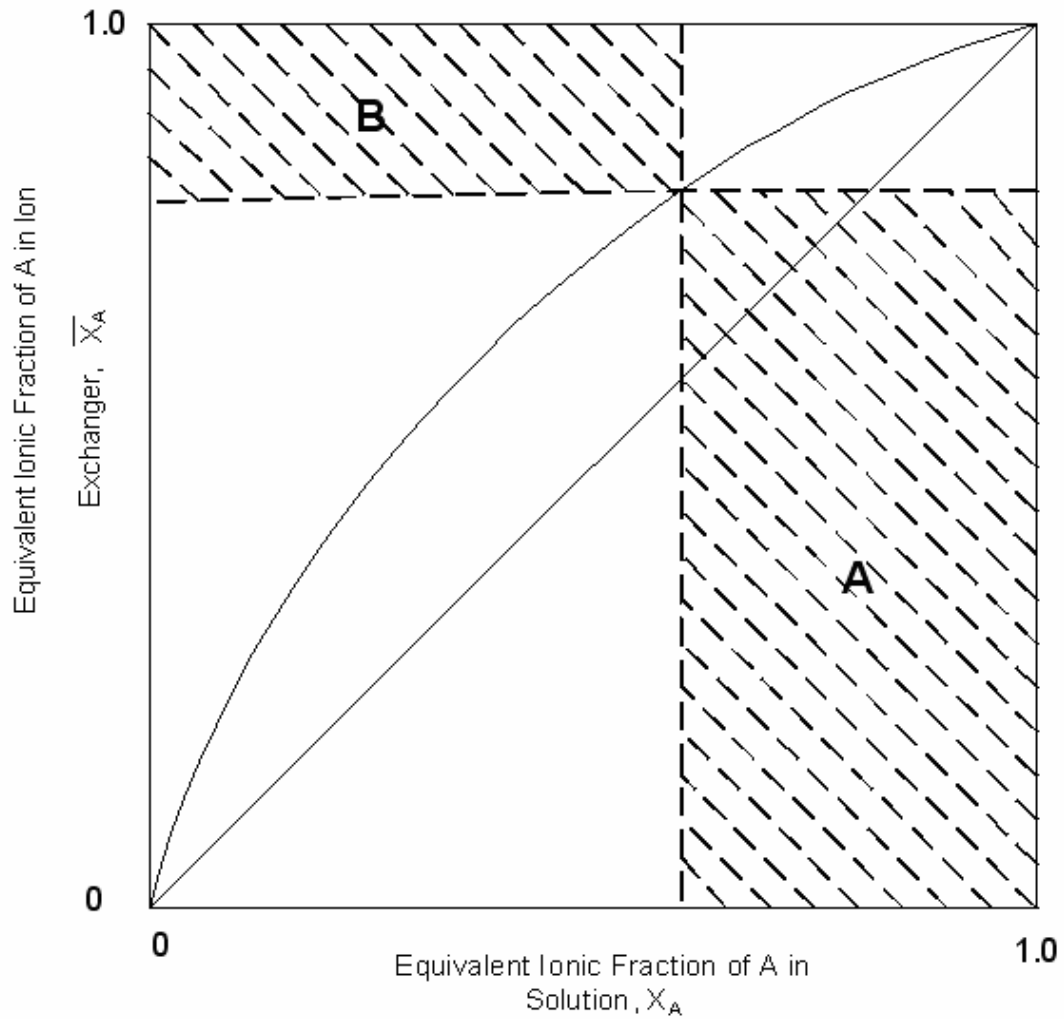
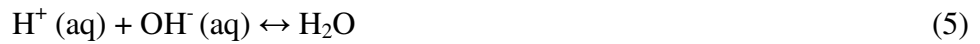
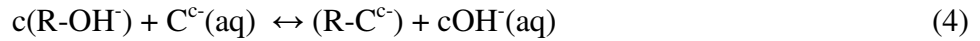
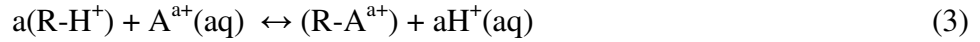


Figure 4. Typical Ion Exchange Isotherm (Helfferich, 1962)

Separation factor can be obtained from the ion exchange isotherm. For a particular resin and solution phase concentration, it is given by the ratio of area B to area A, as shown in Figure 4 (Helfferich, 1962).

In ultrapure water processing, strong acid cationic polymeric resin exchanges hydrogen ions for other cations, and strong base anionic polymeric resin exchanges hydroxide for other anions. In mixed bed configuration, exchanged hydrogen and hydroxide ion combine to form water. For general case the reactions are



In the above equations, R signifies the resin phase. At equilibrium, the law of mass action can be applied for (3) and (4) to establish an equilibrium selectivity coefficient, K. The selectivity coefficient is a relationship of the component activities, as

$$K_A^B = \frac{(R-B)^z(X)}{(B)^z(R-X)} \quad (6)$$

A simplified approach is frequently used by replacing activities and defining K in terms of concentration in both phases. This gives selectivity coefficient as a function of resin composition and total solution concentration (Reichenberg (1966), Boari et al. (1974)). This resin phase composition can be expressed as equivalent ion concentration, equivalent ion fraction, or mole fraction. Ionic activity, an appropriate thermodynamic parameter, requires activity estimation within the resin from other properties of the resin water system. Barrer and Klinowski (1972 & 1974) addressed this problem by using activity coefficients for species in solution. This result in an apparent equilibrium constant expressed in resin concentrations and solution activities, which work reasonably

well for concentrations less than 2N. The lowest concentration considered was a total normality of 0.002, which is greater in magnitude than the impurity concentration involved in ultrapure water application.

No experimental data for ion exchange selectivity coefficient within the concentration range of interest (0.001-100 ppb) are present. The data available for dilute solution are of two primary categories. The first type was for total solution concentrations down to 0.0001 N. The second type was for specific ionic concentrations approaching ppb range in the presence of higher concentration of salts. For the first type, the work of Liberti and Passino (1985), addresses low solution concentration kinetics for chloride sulfate exchange. The lowest concentration used were 0.006 M. Sheth et al. (1989) describes data for anionic exchange for the removal of metal sulfates. Concentrations used were 25,000, 34,000, and 100,000 ppm. Results obtained by Bergseth (1982) indicate that large difference in selectivity can be anticipated over a range of concentrations. For the second type, Boyd et al., (1947) discussed ion exchange relative to the recovery of trace radioactive species. Data were obtained for micro-component at concentrations as low as 0.1×10^{-5} M, while the macro-component was present at concentrations as low as 0.1 M primarily with one data point at 0.001 M. Gamble et al., (1985) presented data for the ionic equilibria of trace metals on humic compounds in natural water. The ions studied included copper and cadmium at concentrations as low as 1×10^{-6} M in NaCl solutions down to 0.001 N. Limited data of the second type have also been obtained specifically for ultrapure water applications at a nuclear power plant. Sadler et al., (1988) determined a selectivity coefficient for sodium

to morpholine on Amberlite 252 cationic resin. The concentration range for sodium was 0.1 to 3.2 ppb and the morpholine concentration was 6.2 ppm (pH 9.1).

For binary exchange, selectivity coefficient remains nearly constant with change in total solution concentration but separation factor will vary with the solution concentration (Haub, 1984; Tripp & Clifford, 2004). While choosing preferable resin phase for an ion, separation factor is used rather than selectivity coefficient because selectivity coefficient values are not readily comparable and separation factor values of ions are directly comparable (Tripp & Clifford, 2004). For practical purpose selectivity coefficient or separation factor are used for determining interfacial concentration and in getting boundary conditions in ion exchange rate equation (Haub, 1984).

ION EXCHANGE KINETICS

Kinetic study of ion exchange resins is particularly important in designing ion exchange columns and deciding the usability state of resins for a particular operation. The aim of kinetic study of ion exchange process is to determine the exchange mechanism for theoretical purpose and to get mass transfer coefficient for design purposes (Liberti, 1983). The packed-bed kinetics of ion exchange is studied using a mass-transfer coefficient across a liquid-solid interface. Mass-transfer resistance may occur due to external or internal effects, or a combination of both. The three series resistance model e.g. mass transfer resistance through a static liquid film surrounding the resin surface, mass transfer resistance into the resin particle, and the exchange reaction resistance between counterions in the solid and solution phase is universally accepted. Boyd et al. (1947) analyzed the exchange kinetics and applied Ficks' and Nernst-Planck's theory for

ion diffusion. For most of the practical applications ion exchange process is diffusion controlled (Helfferich & Plesset, 1958) although there are few exceptions where reaction at exchange site is controlling mechanism as proposed by Streat (1984). The kinetics of ion exchange bed, at low influent concentrations, is controlled by external mass-transfer resistance (film mass-transfer coefficient), as verified experimentally by Frisch & Kunin and Helfferich. Deterioration of mass-transfer kinetics results in leakage of impurities and poor treated-water quality; hence, the ability to predict mass transfer is critical for the operation of ion exchange beds. The shape of the effluent concentration profile (breakthrough curve) from an ideal bed would be similar to that of the influent concentration profile, with a time lag accounting for the residence time within the bed. However, in a real system, the effluent concentration profile is distorted because of mass transfer resistances, dispersion, and imperfect flow distribution through the bed.

MASS TRANSFER COEFFICIENT SIGNIFICANCE

Ion exchange is a diffusion process. Its mechanism is redistribution of the counter ions by diffusion. An ionic mass transfer coefficient is required for detailed modeling and simulation of industrial ion exchange processes. The mass transfer coefficient is a property that characterizes the kinetic ability of the ion-exchange resin. The Mass transfer coefficient effectively compares the rate at which ions can be removed by the resin to the rate at which water flows through the exchange bed (Foutch & Hussey, 2004). The mass-transfer coefficient, a lumped-parameter, for a system can be calculated using empirical correlations. The mass-transfer coefficient involves the diffusion coefficient and hydrodynamics of the system. Most diffusion processes in dilute solution

can be modeled using Ficks' law, usually combined with a mass balance equation, to calculate the mass flux and mass transfer coefficient across any given interface. Ficks' model describes the transport of molecular species considering only the concentration gradient. The model does not account for other external forces like the thermal gradient, electric-potential gradient, and pressure gradient. In an electrolytic solution, solute-solvent and solute-solute interactions are important. This gives rise to a diffusion coefficient that is a function of both the concentration gradient and electric field potential. The electrostatic effects are primarily responsible for most of the diffusion effects of ions in a low concentrations solution. Ionic mass transport in solution may be modeled using the Nernst-Planck equation that accounts for the chemical and electrical forces that affect ionic flux. The electrical forces include the applied potential on the system and the potential generated because of the difference in ionic diffusivities; the latter occurs only in the case of ion exchange. The potential can be related to the concentration and diffusivity of the numerous species present, and leads to a group of equations characterizing the multicomponent system. Mass-transfer correlations typically require a representative diffusion coefficient to characterize mass transport. Selecting this coefficient is complicated in a multicomponent system. Therefore, multicomponent diffusion behavior of ion-exchange systems has resulted in non-inclusion of mass-transfer data from ion-exchange experiments in finding mass-transfer correlations. Hence, after characterization of the diffusion, an additional objective is to find a correlation to predict the ion exchange-resin mass-transfer coefficient at low solute concentrations. There are lots of empirical correlations available for predicting mass transfer coefficient. Vikram et al. (2003) discussed various correlations given by McCune and Wilhelm, Gaffney and

Drew, Evans and Gerald, Gilliland and Baddour, Selke et al., Bar-Ilan and Resnick, Moison and O'Hern, Carberry, Frisch and Kunin, Williamson et al., Pfeffer, Rao and David, Wilson and Geankoplis, Kunii and Suzuki, Karabelas et al., Kataoka et al., Levins and Glastonbury, Nelson and Galloway, Miyauchi et al., Appel and Newman, Novak, Dwivedi and Upadhyay, Koloini et al., Wakao and Funazkri, Rahman and Streat, Ohashi et al., Kikuchi et al., Zarraa, and Livingstone and Nobel. Apart from this we also have mass transfer equation for kinetic leakage first derived by Frisch and Kunin (1960) and modified appropriately to ion exchanger beds by Harries (1984). A detailed review of Mass transfer coefficient is available in appendix A.

CHAPTER II

MASS TRANSFER COEFFICIENT & FOULING MECHANISM

BACKGROUND

Fouling is caused by irreversible sorption or precipitation of unwanted contaminants on ion exchange resins. Common foulants may include metal oxides, suspended matter, oils, greases, and organic degradation products (fulvic and humic acids). Cation exchange resins are most frequently contaminated by iron compounds while anion resins are fouled by colloidal silica and high molecular weight organic acids. This irreversible process has a degrading effect on the performance of ion exchange resins. Foulants adhere to ion exchanging surface and decrease the exchange capacity by blocking the exchange sites and thus adversely affect operation and product quality. Also the need for rinsing water and the use of regeneration chemicals increase (Ion exchange, Rohm & Hass). Ion exchange resin fouling affects the performance of mixed bed ultrapure water treatment systems. Minor fouling can result in significant reduction in mass transfer properties of the resin. Finding the cause of fouling can be difficult and may not always lead to a clear conclusion. This chapter outlines the range of possible fouling mechanisms seen in resin beds, discusses potential causes for these problems and presents how current analytical methods have the potential to define some of the fouling problems.

FOULING MECHANISM

The mechanisms for resin fouling are many. Griffin (1991) outlined most of the known mechanisms; although, all of their respective effects on the rate of exchange are not fully understood. However, as a first screening these mechanisms can be classified into two major groups: loss of exchange-site capacity or activity, and non-exchange-site fouling that increases the physical resistance to ionic mass transfer from the bulk solution to the exchange site. It is certainly possible that more than one of these effects may be combined for some fouling mechanisms.

Degradation of anionic exchange sites can occur by loss of chemical functionality; by ion exchange with a species of higher selectivity (i.e., sulfonate, carbonate, chelated metals or organic acid anions, among others); or by the conversion of strongly basic sites to weakly basic sites. An example of the first two mechanisms is the migration of a sulfonate from the cationic resin, which then subsequently exchanges with a site on the anionic resin. This transfer results in a loss of functionality from the cationic resin, while the sulfonate has a large selectivity coefficient that effectively eliminates an anionic exchange site. The conversion of strong-base to weak-base sites can be attributed to thermal degradation or oxidation (McGarvey, 1966, Kunin 1972), predominantly near the surface of the particle (Allen et al., 1988).

The major contributor to nonionic fouling of the resin is adsorption. Organics, iron oxides (crud), and particulates are examples of adsorbates. Organic and silicon based lubricating oils can enter the water and contaminate the resins. These can frequently be

traced by chemical analysis of the resins back to specific plant sources. Metals and metal oxides on the resins primarily come from erosion and corrosion products, or from chemical additives used for iron control. Foulants can also be introduced with regeneration chemicals. Another likely source is the resins themselves. Frequently fouling issues are the result of a combination of effects. For example, the combination of metal oxides with dissolved oxygen can cause resin breakdown and produce chemicals that can foul resins. This complex chemistry is a possible mechanism that appears to be enhanced by interaction with ethanolamine (Foutch et al., 2002, Apblett et al., 2003).

Since these fouling agents will differ from system to system, the resins will degrade at different rates as a function of water quality, specific events in the column history, and the regeneration schemes. Regeneration removes some of the adsorbates, but net accumulation can occur with time. Techniques are available to clean the resin in an attempt to return it to its original performance (Griffin, 1991). Allen et al. (1988) believed that organic acids adsorption has little effect on the degradation of exchange properties.

EFFECTS OF FOULING ON MTC

Clean ion exchange resins add little or no resistance to mass transfer removal rates of ionic species. However, as resins age or are damaged fouling may occur that reduces the mass transfer rate and result in less efficient exchange bed operation. For resins discarded after one use these fouling mechanisms are not a major concern. For resins that are regenerated and/or cleaned, and then returned to service, fouling may have a significant impact on exchange performance.

Fouling can be monitored by measuring the mass transfer coefficient (MTC) in a test bed. This is now a fairly common procedure for the nuclear power industry (Harries 1984, ASTM D 6302-98). With a known MTC the bed performance can be estimated using computer simulation (OSUMBIE, 2002). The MTC can also be used as a performance criterion to replace resins should the value fall to a predefined level. More generally, a reduced MTC means there is something wrong with the water chemistry and a search for the most likely cause ensues.

The impact of resin fouling has been discussed in numerous papers. Lee et al. (1997) presented results of resin analysis from two coal fired power plants in Oklahoma. All used resins have lower MTC's than new resins, although some of the reductions were not enough to negatively impact performance. The degree of degradation was not correlated with resin age. The plant with higher organics in the cooling water (downstream of two Tulsa refineries) had more resin fouling than the plant using lake water for cooling.

In general, however, loss of capacity does not correlate with reduced resin performance. Most resins through normal use lose a few percent of effective capacity without having much impact on ultrapure water treatment. A 10% reduction in effective capacity would likely not be noticeable in operation. On the other hand, a 10% reduction in MTC would be noticeable in normal operation with reduced run times until a particular effluent concentration.

Given the myriad of potential mechanisms and the variation in resin degradation rates as a function of operating conditions, how can we hope to determine the cause of a particular fouling problem and recommend a solution? First, degradation can be characterized using the overall mass transfer coefficient (MTC) test (e.g. ATSM D 6302-98). This test does two primary functions; a qualitative indication that a problem exists and the ability to quantify the effect of reduced MTC on performance (e.g. expected run time until a specific effluent concentration is achieved).

Using the residual capacity and the overall MTC allows us to evaluate degradation. As an example, Foutch et al. (1992) presented a simulation for hydrogen cycle operation with no additives. The operating conditions are as follows: superficial velocity of 85 meters per hour, column depth of 0.9 meters, cation-to-anion resin ratio of 1:1, operating temperature of 25°C, and a feed concentration of 5.0×10^{-5} milliequivalents per milliliter (meq/mL) of NaCl (sodium chloride). The resins used have the following properties: cationic diameter of 0.8 millimeter (mm) anionic diameter of 0.6 mm, void fraction of 0.34, cationic capacity of 2.18 meq/mL, anionic capacity of 1.10 meq/mL,

chloride/hydroxide selectivity of 22, and sodium/hydrogen selectivity of 1.13. (an unusually low cation selectivity for this specific trial; normally 1.4 to 1.5 is more typical for sodium/hydrogen selectivity)

The effect of decreasing the available anionic resin capacity was nearly proportional to the decreased capacity. This certainly affects the run time until a specific concentration limit is reached. Due to the high chloride-hydroxide selectivity, however, essentially no difference is observed in initial equilibrium leakage from the resin at this flow rate. Higher superficial velocities would show some difference in the initial effluent-to-feed concentration ratio. Sodium breakthrough is also affected by anionic capacity because of the coupled charge balances between the anionic and cationic resin. Lower anionic capacity results in less hydroxide liberation; which in turn gives lower pH and moves the neutralization reaction away from the cationic resin into the film surrounding the anionic resin; which in turn lessens sodium removal efficiency. After anionic exhaustion, the column is no longer functioning as a mixed bed; and cationic exchange continues with a very rapid decrease in pH. This is not surprising, since the total cationic capacity is double to triple the anionic capacity.

In either case with changes in capacity it takes a significant reduction to impact performance. Losses of a few percentages are not expected to have major impact, if any, on equilibrium leakage. The focus must be on the resin MTC for major performance impact with minor changes in system chemistry.

Foutch et al. (1992) showed that with anionic resin fouling chloride leakage from the bed is significantly greater (Figure 5). The level portion of the plot at 1.00×10^{-7} eq/L is due to equilibrium leakage as a result of the residual loading of chloride on the anion exchange resin. If the initial loading was zero the sloped curves would continue to well below the detection limit. The no fouling case gives the longest time until initial breakthrough at 2800 minutes. When 20% fouling (a 20% reduction in the chloride MTC) is included with no decrease in capacity the initial break point is 2000 minutes, or 28.6% reduction in time. With 40% fouling the initial break occurs at 1200 minutes, less than half of the new resin break time. By the time 60% fouling occurs the resin can no longer achieve equilibrium leakage even at the very first minute of operation. The impact on sulfate is typically greater than for chloride because of the divalent versus monovalent characteristics of the exchanging ion.

In practice, an operator could generate the performance curves similar to those in Figure 5 for their specific plant conditions. They could then select the length of time required at operation with equilibrium leakage. Finally, the maximum fouling and minimum MTC can be defined based on those expectations. Sampling of ion exchange resin at regular intervals can confirm whether the resin should be cleaned, discarded or performance expectations modified.

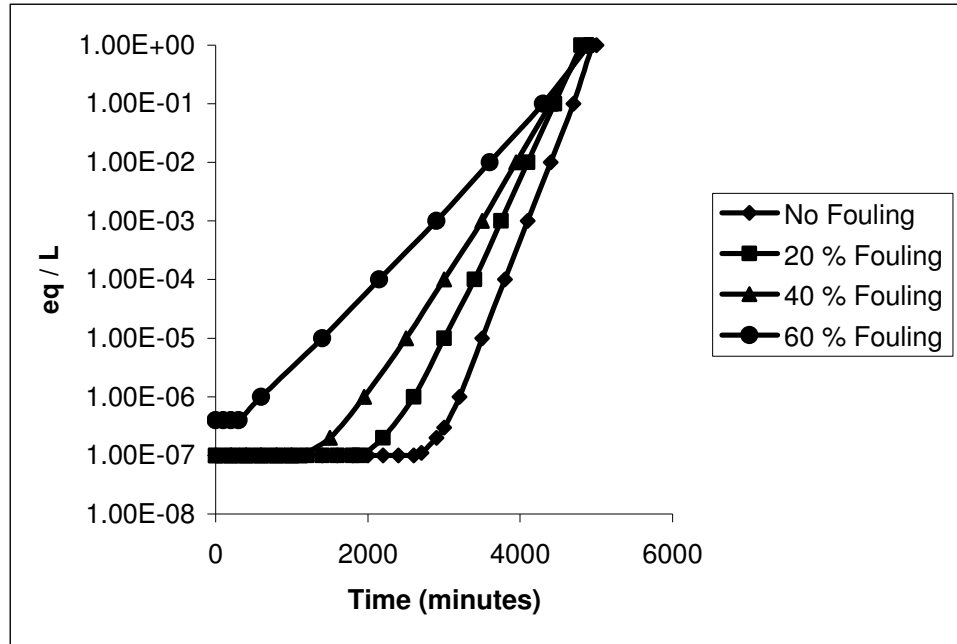


Figure 5. Predicted Chloride Breakthrough (adopted from Foutch et al., 1992)

Regeneration efficiency is negatively impacted by fouling because rinsedown is more difficult. If it's more difficult to get ions into fouled resins it's also more difficult to get them back out. The ability to see the actual fouling based on on-line data is difficult since changes typically occur gradually and because operation is at or below the analytical detection limits of online equipment. As a result, occasional MTC tests are needed to assess the state of the resin over time.

CHAPTER III

RADIAL FLOW MASS TRANSFER COEFFICIENT

INTRODUCTION

Ion exchange is a process that redistributes counter ions between solution and solid phases by diffusion. An ionic mass transfer coefficient (MTC) – a property that characterizes the kinetic ability of the ion-exchange resin – is required for modeling and simulation of industrial ion exchange processes. The MTC effectively compares the removal rate of ions from the flowing stream by the resin to the water flow rate through the exchange bed; and is included in a derivation of the kinetic rate expression. At low concentrations, kinetics is controlled by external, film mass-transfer resistance (Frisch and Kunin, 1960; Helfferich, 1962). An estimate of a clean system MTC is available from numerous dimensional analysis expressions (Chowdiah et al., 2003). As resins become old, or are damaged, the MTC lowers due to chemical or physical resistances – typically referred to as fouling.

Deterioration of kinetics results in ionic leakage from the bed and poor water quality. An accurate MTC will allow for performance estimation of ion exchange beds. In an ideal bed the breakthrough curve is S-shaped with a long baseline and relatively rapid rise to the feed concentration (exhaustion). However, as a bed fouls, the initial concentration break occurs earlier, with significantly less water treated to a specific end point.

The MTC is a combination of the hydrodynamics and all diffusion resistances, and has units of velocity. Physically, the MTC represents the average velocity of an ion across the stagnant film. The MTC is obtained experimentally with a simple column test, although the method does not distinguish fouling mechanisms and is effectively a lumped-parameter. When resins are at their best quality the MTC equals that predicted by hydrodynamics alone; typically greater than 2.0×10^{-4} m/s for moderate flow systems and 3.0×10^{-4} m/s for high flow systems. Although specific plant performance criteria should be established for acceptable MTC's, severely fouled resins may have MTC's an order of magnitude or more lower.

Several resin properties may change with age or damage. For ultrapure water applications, MTC changes significantly as compared to other properties like water retention and total exchange capacity. Commonly, as resins foul, the mass transfer can drop by an order of magnitude whereas the exchange capacity might decrease only by 1-2%. Because the reduction in MTC correlates with the extent of resin deterioration and age, the overall MTC is used to characterize the resin kinetic properties.

BACKGROUND

Harries and Ray (1984) developed a simplified film mass transfer coefficient model to rate the performance of a cylindrical mixed bed. The model assumes zero interfacial concentrations and no interactions resulting from dissociation equilibrium. The model characterizes the removal efficiency of an ionic species with respect to bed geometry and service parameters. The relationship is presented in a modified form without proof.

$$\ln\left(\frac{C_i^{\text{eff}}}{C_i^f}\right) = -\frac{6k_{f,i}(1-\varepsilon)(FR)}{d_{p,i}} \frac{\pi r^2 L}{F} \quad (7)$$

where

F = the volumetric flow rate

$k_{f,i}$ = the average film mass transfer coefficient of ion 'i.'

L = the cylindrical bed depth

The model is useful for evaluating the kinetic performance of ion exchange resin, Lee (1994), Arunachalam (1996) and others have successfully shown the reduced mass transfer coefficients of fouled resin by using the influent and effluent concentrations of simple bench-scale column experiments.

RADIAL FLOW MODEL

Most industrial ion exchange beds are cylindrical columns with one dimensional axial flow. These systems have been modeled to obtain an overall MTC, and the results have been presented by several researchers (Harries and Ray (1984), Harries (1986, 87) , Haub & Foutch (1986a, 1986b) with applications discussed by many others. In the 1980's radial-flow ion exchange technology was developed in Europe but it came to US in 1997 when a patent was granted on Method for removing contaminants from water using ion exchange media packed in a radial flow column (Schneider et. al., 1997). Tsuar and Shallcross (1997) have shown that radial ion exchange is more efficient than conventional flow under identical operating conditions for simulated geometries. The model developed by Lou (1997) indicated that radial flow geometry offers sharper

profiles, which is favorable for separation and makes best use of resin capacity. Though this technology is limited commercially, it offers potential advantages over axial flow because the velocity varies with bed depth. One of the key assumptions in developing an axial flow MTC is that the fluid velocity is constant. As a result, the standard MTC method does not apply for axial flow and a new derivation is presented here.

A factor limiting the bed depth in axial flow is the mechanical strength of ion exchange resin beads. The beads at the bottom must withstand the weight of the bed. In an annular ion exchange bed, the path length is between the inner and outer diameters of the bed and not by the height. Therefore, it is possible to increase the flow path length through the ion exchange material by increasing the bed diameter (Duong et. al., 2005).

For systems with high concentration of suspended solids – like nuclear reactor water clean up (RWCU) – one dimensional axial flow beds may rapidly build up suspended solid, causing an increased pressure drop during the operation. This high pressure drop may result in bed replacement before the available exchange capacity has been exhausted (Fejes et al., 1989) or else require high pumping cost. Figure 6 shows the schematic of an inward flow radial column. The water enters the outer perimeter and flows through with increasing velocity to the center of the vessel where it leaves through the bottom.

The variable flow velocity complicates mathematically modeling the radial flow mixed bed. Lou (1997) developed a numerical model based upon the principles used in this work for a sodium chloride influent. The model was a coupled, high-order system of

differential equations; it included radial dispersion and used Patankar's control volume method for the solution of the terms. The model produced apparently reasonable results that were useful to rate the performance of a radial flow bed; however, it was never implemented as readily usable software.

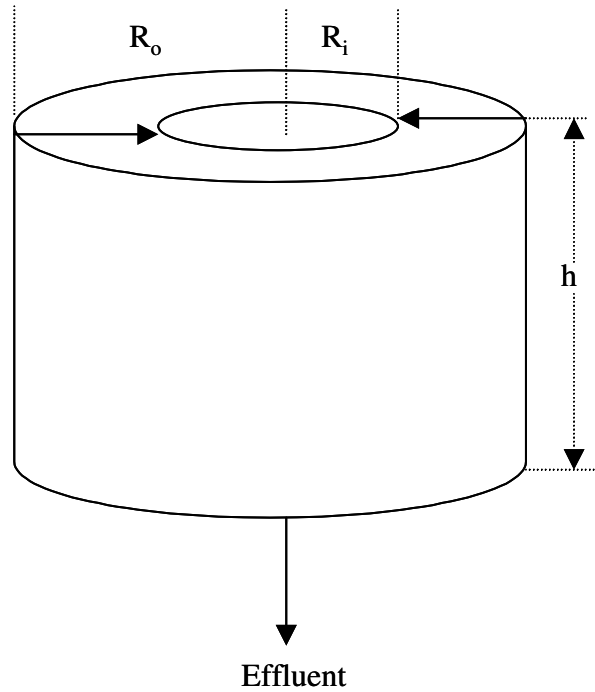


Figure 6. Inward flow radial flow mixed bed

Hussey (2000) proposes an analogous film mass transfer coefficient model for radial flow based upon the assumptions applied in the Harries model. The derivation present here is adopted from Hussey (2000).

Equation (8) is the reduced continuity equation for a radial-flow packed bed assuming longitudinal and angular derivatives are equal to zero.

$$\frac{\partial C_i}{\partial t} + \frac{u_r}{\varepsilon} \frac{\partial C_i}{\partial r} - R = 0 \quad (8)$$

R is the reaction term and is equated to the change in resin phase concentration using a linear driving force model.

$$-R = \frac{1-\varepsilon}{\varepsilon} \frac{dq_i}{dt} = k_{f,i} a_s (C_i^* - C_i^b) \quad (9)$$

Equation (9) is substituted in to Equation (8) to yield the following continuity equation.

$$\frac{\partial C_i}{\partial t} + \frac{u_r}{\varepsilon} \frac{\partial C_i}{\partial r} + (FR) \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q_i}{\partial t} = 0 \quad (10)$$

The equation as written is non-linear because the fluid velocity, u_r , is a function of the radius. However, the fluid velocity can be related to the radius with the following expression developed in Bird et al., (2002).

$$ru_r = \phi \quad (11)$$

where ϕ is a constant. For the radial-flow system,

$$\phi = \frac{F}{2\pi h} \quad (12)$$

Substituting Equation (11) into Equation (10) yields,

$$\frac{\partial C_i}{\partial t} + \frac{\phi}{\varepsilon r} \frac{\partial C_i}{\partial r} + (FR) \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t} = 0 \quad (13)$$

Defining the solution fraction and resin fraction dimensionless variables with respect to the individual species feed concentrations and total capacity,

$$x_i = \frac{C_i}{C_i^f} \quad (14)$$

$$y_i = \frac{q_i}{Q} \quad (15)$$

and dividing Equation (13) by $\frac{C_i^f Q}{Q}$ gives the following continuity equation with dimensionless solution and resin fractions, and dimensional time and radius.

$$\frac{\partial x_i}{\partial t} + \frac{\phi}{\varepsilon r} \frac{\partial x_i}{\partial r} + (FR) \frac{1-\varepsilon}{\varepsilon} \frac{Q}{C_i^f} \frac{\partial y_i}{\partial t} = 0 \quad (16)$$

Equation (16) is a partial differential equation that has the solution fraction varying with time and the radius, and the resin fraction varying with time. The solution fraction shares a common boundary condition in time and space, the feed concentration C_i^f . This implies the combination of variables may be applied; however, the 'r' term is still in the denominator of the radial variation of solution fraction.

The choice of dimensionless variables is critical. The dimensionless variables chosen for this work were found by substituting the velocity definition, Equation (11), into the dimensionless time and distance and used for cylindrical flow.

$$\tau = \frac{k_{f,i} C_i^f}{d_p Q} \left(t - \frac{r^2 \varepsilon}{2\phi} \right) \quad (17)$$

$$\xi = \frac{k_{f,i} (1-\varepsilon) r^2}{2\phi d_p} \quad (18)$$

The constant '2' is not in the velocity definition; however, it was needed to facilitate the reduction of the continuity equation to an ordinary differential equation.

The derivatives of the dimensionless variables are scale the dimensional time and distance to dimensionless time and distance.

$$\frac{\partial \tau}{\partial t} = \frac{k_{f,i} C_i^f}{d_p Q} \quad (19)$$

$$\frac{\partial \xi}{\partial t} = 0 \quad (20)$$

$$\frac{\partial \tau}{\partial r} = \frac{-k_{f,i} C_i^f \varepsilon r}{d_p Q \phi} \quad (21)$$

$$\frac{\partial \xi}{\partial r} = \frac{k_{f,i} (1-\varepsilon) r}{\phi d_p} \quad (22)$$

Applying the chain rule to change the integration axes from dimensional time and distance to dimensionless time and distance.

$$\frac{\partial x_i}{\partial t} = \frac{\partial x_i}{\partial \xi} \frac{\partial \xi}{\partial t} + \frac{\partial x_i}{\partial \tau} \frac{\partial \tau}{\partial t} \quad (23)$$

$$\frac{\partial x_i}{\partial z} = \frac{\partial x_i}{\partial \xi} \frac{\partial \xi}{\partial z} + \frac{\partial x_i}{\partial \tau} \frac{\partial \tau}{\partial z} \quad (24)$$

$$\frac{\partial y_i}{\partial t} = \frac{\partial y_i}{\partial \xi} \frac{\partial \xi}{\partial t} + \frac{\partial y_i}{\partial \tau} \frac{\partial \tau}{\partial t} \quad (25)$$

Substituting the derivatives into Equation (16) and expanding yields;

$$\left[\frac{\partial x_i}{\partial \xi} (0) + \frac{\partial x_i}{\partial \tau} \left(\frac{k_{f,i} C_i^f}{d_p Q} \right) \right] + \frac{\phi}{\varepsilon r} \left[\frac{\partial x_i}{\partial \xi} \frac{k_{f,i} (1-\varepsilon) r}{\phi d_p} - \frac{\partial x_i}{\partial \tau} \frac{k_{f,i} C_i^f r \varepsilon}{d_p Q \phi} \right] + \quad (26)$$

$$(\text{FR}) \frac{1-\varepsilon}{\varepsilon} \frac{Q}{C_i^f} \left[\frac{\partial y_i}{\partial \tau} (0) + \frac{\partial y_i}{\partial \tau} \frac{k_{f,i} C_i^f}{d_p Q} \right] = 0$$

Equation (26) collapses to the following partial differential equation.

$$\frac{\partial x_i}{\partial \xi} = -(\text{FR}) \frac{\partial y_i}{\partial \tau} \quad (27)$$

Assuming the interfacial concentration is zero, the right hand side of Equation (27) can be related to the particle rate.

$$\frac{dy_i}{dt} = \frac{k_{f,i}a_s}{Q} C_i^f \quad (28)$$

Changing the integration axis to dimensionless time yields,

$$\frac{\partial y_i}{\partial \tau} = \frac{\partial y_i}{\partial t} \frac{\partial t}{\partial \tau} = \frac{k_{f,i}a_s C_i^f}{Q} \left(\frac{d_p Q}{k_{f,i} C_i^f} \right) \quad (29)$$

which reduces to the following function of x_i .

$$\frac{\partial y_i}{\partial \tau} = d_p a_s x_i \quad (30)$$

Equation (30) is substituted into Equation (27) to give an ordinary differential equation that can be integrated by the separation of variables.

$$\frac{\partial x_i}{\partial \xi} = -(FR) d_p a_s x_i \quad (31)$$

The boundary conditions are

$$C_i = C_i^f @ r = R_o$$

$$C_i = C_i^{eff} @ r = R_i$$

Separating the variables yields,

$$\frac{\partial x_i}{x_i} = -(FR) d_p a_s \partial \xi \quad (32)$$

Integrating,

$$\ln(x_i) \Big|_1^{x_i^{eff}} = -(FR) d_p a_s \Big|_{\xi_i}^{\xi_0} \quad (33)$$

$$\ln\left(\frac{C_{eff}}{C_f}\right) - \ln(1) = (FR) d_p a_s (\xi_0 - \xi_i) \quad (34)$$

Inserting the dimensionless definitions to transform Equation (34) back to dimensional distance,

$$\xi_0 = \frac{k_{f,i}(1-\varepsilon)R_o^2}{2\phi d_p} \quad (35)$$

$$\xi_1 = \frac{k_{f,i}(1-\varepsilon)R_i^2}{2\phi d_p} \quad (36)$$

and reducing yields the following equation.

$$\ln\left(\frac{C_{eff}}{C_f}\right) = (FR) \frac{k_{f,i}(1-\varepsilon)a_s}{2\phi} (R_o^2 - R_i^2) \quad (37)$$

Finally substituting the definition of the specific surface area, a_s , and ϕ yields the following expression in the final form

$$\ln\left(\frac{C_{eff}}{C_{inf}}\right) = (FR) \frac{-6k_{f,i}(1-\varepsilon)}{d_p} \frac{\pi(R_o^2 - R_i^2)h}{F} \quad (38)$$

Comparing Equations (38) and (7),

$$\ln\left(\frac{C_i^{eff}}{C_i^f}\right) = (FR) \frac{-6k_{f,i}(1-\varepsilon)}{d_p} \frac{\pi R^2 L}{F} \quad (7)$$

it is easy to see the only difference is the volume of the container; $\pi R^2 L$ for the cylindrical flow bed, $\pi(R_o^2 - R_i^2)h$ for the radial flow bed. Hence, there is no difference between the equations besides the volume of the bed. The mass transfer coefficient values calculated from each expression are identical for equal volume and flow rate systems.

The terms in Equations (7) and (38) has physical significance; V/F is the superficial residence time of an element of fluid in the empty bed while the remainder of the right

hand side represents the rate (with the units of inverse time) which ions are transferred into a specific volume of resin. It applies to both outward and inward flow radial beds.

Equation (38) is useful for evaluating the performance of a radial flow mixed bed ion exchange column (or any radial flow fixed bed adsorption columns with a constant density fluid), but the derivation has greater significance than the estimation of an experimental mass transfer coefficient.

Equation (27) is exactly the same form as the well-known cylindrical fixed bed adsorption equation that can be solved with many numerical methods (e.g. Euler's method or Gear's Backward difference method); the only difference is the definition of the dimensionless time and distance variables. This is advantageous because continuity equations in cylindrical coordinates often result with analytical solutions that require Bessel functions, and a simple relationship to the mass transfer rate would be more difficult to obtain. However, with this derivation, numerical software models of the cylindrical case can be readily adapted to radial flow cases with only minimal changes in the algorithm. This would be relatively simple to implement; one caveat is that the mass transfer coefficients would need to be calculated as a function of radial distance to account for the varying fluid velocity.

CONCLUSIONS

The following conclusions are drawn from this chapter:

- A mass transfer coefficient expression has been derived for radial flow fixed bed adsorption columns.
- The radial flow fixed bed adsorption column continuity equation has been transformed to a form that is similar to cylindrical continuity equations.

Future work includes applying these expressions to numerical simulators of radial flow fixed bed adsorption columns.

CHAPTER IV

RINSE MODELING

INTRODUCTION

Depending on the capacity and properties of resin material and the water purity desired, various streams are passed through column for definite time. In order to optimize the use of ion exchange material and to achieve the required quality and quantity of water, we need to accurately describe the various processes involved during the ion exchange operation i.e. service or exhaustion cycle, regeneration cycle as well as rinsing cycle. The modeling of rinse operation can be used to assess the kinetic state of resins based on the rinsing time. Rinse time and rinse volume depends on the rate at which the ions diffuse into the bulk fluid from the resin exchange sites. And this diffusion rate is dependent on the mass transfer coefficient. This way the rinse time is inherently dependent on the kinetic properties of resins and it can be used to extract mass transfer coefficient of resins. So correlating rinse time with the kinetic properties will be beneficial as rinse time can be easily obtained without stopping the normal bed operation in an industrial setting. Exhaustion and regeneration has been modeled by many over the last few decades but a very limited attempt has been made in study of rinsing cycle. Gromoglasov et al. (1986) presented a mathematical model for process of rinsing ion exchange resins considering concave adsorption isotherm of electrolytes on resins. This chapter presents problem

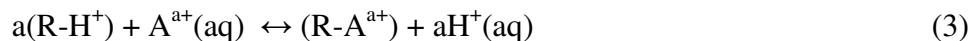
statement for the development of model for rinsing process and its application in evaluating kinetic properties of resins and future work that can be done.

BACKGROUND

Industrial ion exchange column usually consists of a resin bed (mono or mixed bed) which is retained in the column with different streams flowing through the system for specific time. The three main operations that take place in ion exchange column are

1. Service cycle– In this step normal bed operation takes place i.e. exchange of ions take place. Ionic solution is passed through the bed in regenerated form and resins get exhausted
2. Regeneration – Resins in the bed is regenerated by passing regenerant solution (usually mineral acids or base). In this step exhausted resins get converted in the original form.
3. Rinse – Pure water is passed through the bed to remove excess regenerant present in interstitial space.

Initially the resin is in fully regenerated form when the feed solution containing ions to be removed is passed through it. In this step, ions in the feed solution are exchanged with the ions in resins which may be represented by following as given in chapter 1:



After the resin has been exhausted it is required to regenerate the resins for reuse, commonly used regenerant's are dilute sulfuric acid or sodium hydroxide solutions. Regenerant solution is passed through the bed and its converts the resin into original form by exchanging ions. In regeneration step the reactions taking place are reverse of the exhaustion step. After regeneration resins are required to be rinsed with pure water. Usually the process of rinsing resins begins directly after passing the regenerating agent through the bed. During rinsing of ion exchange resins both products of regeneration and the regenerant itself are removed. Usually large amount of rinse water is required to prepare the resin for reuse after regeneration. Normally resins are rinsed for a particular time to reach resin condition proper for next cycle of operation.

RINSE PROCESS

Rinsing of ion exchange resins in industrial operation is followed by regeneration. And the purpose of rinsing is to remove the product of regeneration as well as regenerant itself present in the resin pores and void volume of bed. This process is essentially a mass transfer process and diffusion of ions takes place from the exchange sites in the resins to the surface of the resin bead and finally to the bulk liquid flowing in the column. The driving force for rinsing is concentration difference between the bulk liquid and resin particles. Usually in beginning rinse water flow rate is low until resin bed is free of regenerant, this is known as displacement or slow rinse. Slow rinse is followed by higher flow rate of rinse water to remove last trace of regenerant and this is known as rapid rinse. Next cycle starts when the exit concentration of rinse water falls down to an appropriate value (Ion Exchange, Rohm & Haas).

Volume of Rinse Water

The rinse water requirement varies significantly with factors like level of regenerant, structure and condition of resins and also on the resin quality desired in next cycle. Rinse volume also varies with the type of resins used and general rinse volume requirement for different type of resins can be found in literature (Owens, 1985).

Volume of rinse water is critically dependent on the resin condition. If the resin is old and degraded it will leach out various ions for long time and hence increase the rinse volume. In kinetic terms, for fouled or aged resins the mass transfer resistance is higher because of large particle resistance and hence the overall MTC is lower. So the rate of exchange will be slower increasing the rinse volume requirement. Anionic resins may need large amount of rinse volume because of potential problems of fouling and oxidation. Oxidation of weak base anionic resin results in formation of weak acidic group on the resin which increases the rinse volume requirement. Similarly fouled anionic resins require large amount of rinse water (Owens, 1985). As the resin degrades its mass transfer value goes down which leads to slow diffusion of ion within the interstices pores of the resin. Slow diffusion of ions in the resin leads to larger rinse volume and time. So rinsing time and rinse volume can be used as a qualitative parameter to judge the condition of ion exchange resin for further use.

Mechanism

Mechanism involved in rinsing is essentially combination of diffusion of ions within the ion exchanger and in the adherent liquid film. The two resistances involved are called

particle diffusion and film diffusion. The mechanism differs on some extent with the mechanism involved in exchange of ions during exhaustion of resins. During uptake of ions from feed water to resin, the diffusion is particularly film controlled for dilute solutions. During normal ion exchange operation, kinetics is studied using overall mass transfer coefficient which is a bulk parameter that includes film, interfacial and particle effects as discussed by Lee et al. (1997) but normally for UPW production the film effects are dominant. While in rinsing the overall rate of removal of ions from resins is combination of both film and particle diffusion and one can not be neglected in comparison to other. The effluent coming out during the rinsing operation inherently depends on column conditions, resin loading, flow hydrodynamics and kinetic properties of ion exchange resins.

MODEL DEVELOPMENT

The motive to develop the model is to simulate the bed conditions during rinsing and correlate kinetic condition of resins with the rinsing time. The rate laws and column models for ion exchange has been extensively discussed by many in literature. To represent the rinse process mathematically reasonable assumptions are made based on the system process condition. Diffusion resistance, both in the liquid film and the resin phase, is important during the rinsing.

Following assumptions which are commonly applied in modeling of ion exchange column operations are been employed here:

- linear driving force In liquid film

- quasi-stationary or pseudo steady state film diffusion
- unity activity coefficients
- constant individual diffusion coefficients of the ions and the neutral molecule
- electrical neutrality
- homogeneous ion exchange particles
- negligible swelling changes of the ion exchange resin
- plug flow, no dispersion in both radial and axial directions
- isothermal, isobaric operation
- spherical ion exchange resin bead

The modeling of ion exchange column can be considered as a combination of two mechanisms. Firstly the ions inside the resin particle diffuse to the boundary of resin bead and secondly the ions on the surface of resin bead crossing the film and coming into the bulk phase. These conditions can be represented by three coupled partial differential equations, which present complex mathematical system. Solving these equations and determining boundary conditions for the solution is not easy. In the coming sections the equations involved will be developed for the rinsing process.

SINGLE RESIN BEAD

During the rinsing process the ions are diffusing into the resin to the surface. The flux of diffusing ion A can be given by:

$$J_A = -\bar{D}\text{grad}(q) \quad (39)$$

where \bar{D} is self diffusion coefficient of ion A. The given flux of ion A is related to time rate of change of concentration as

$$\frac{\partial q}{\partial t} = -\text{div}(J_A) \quad (40)$$

Combining above two equations (39) and (40) will yield

$$\frac{\partial q}{\partial t} = -\text{div}(-\bar{D}\text{grad}(q)) \quad (41)$$

using definitions of divergence and gradient equation (41) can be represented as

$$\frac{\partial q}{\partial t} = \frac{\bar{D}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) = \bar{D} \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (42)$$

This equation must be solved under appropriate initial and boundary conditions for the rinse process, to determine concentration of diffusing ions on the surface.

The possible initial and boundary conditions of equation (42) are:

$$\text{I.C} \quad q = q_0 \quad \text{at} \quad 0 \leq r \leq R \quad t = 0$$

$$\text{B.C} \quad \frac{\partial q}{\partial t} = 0, \quad \text{at} \quad r = 0 \quad t \geq 0$$

$$\text{B.C} \quad q = K_p^A C_i \quad \text{at} \quad r = R \quad t > 0$$

Where K_p^A is distribution partition coefficient of ion A and C_i is the concentration of ion A in the bulk phase but for ultrapure water application & to pacify mathematical complexities we can take $C_i = 0$ when considering single bead. This assumption is practically justified as diffusion rate is very slow in the particle and approximate value of driving force (concentration gradient) will not make much difference. Therefore second boundary condition can be rewritten as:

$$\text{B.C} \quad q = 0 \quad \text{at} \quad r = R \quad t > 0$$

DYNAMICS OF ION EXCHANGE COLUMN

The effluent concentration as a function of time is obtained by studying column dynamics. Helfferich (1962) discussed that numerous equations of column performance can be obtained depending on the individual set of negligible terms and simplifications applied. For a particular case, valid assumptions and simplifications are made to obtain column performance equation. The effluent concentration profile is largely influenced by the kinetic parameters in addition to the flow hydrodynamics in the column. In general no axial or radial dispersion is assumed in the column which leads to the following continuity equation for each species:

$$\frac{\partial C_i}{\partial t} + \frac{u}{\varepsilon} \frac{\partial C_i}{\partial z} + FR \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_R}{\partial t} = 0 \quad (43)$$

in the above equation first term represents fluid phase accumulation, second term represents convective transport of ions in axial direction, & the third term accounts for solid phase sorption. FR is the volumetric fraction of cationic or anionic resin in a mixed bed. The resin phase sorption term can be given by:

$$\frac{\partial q_R}{\partial t} = -K_{f,i} a_s (q_R - C_i) \quad (44)$$

where q_R is concentration at resin surface and depends upon the rate of diffusion inside the resin. Putting (44) in the (43) will give

$$\frac{\partial C_i}{\partial t} + \frac{u}{\varepsilon} \frac{\partial C_i}{\partial z} - FR \frac{1-\varepsilon}{\varepsilon} K_{f,i} a_s (q_R - C_i) = 0 \quad (45)$$

where q_R can be obtained by solving diffusion equation in single bead i.e. equation (42).

and equation (45) is subjected to following conditions:

$$\text{B.C} \quad C_i = 0 \quad \text{at} \quad t = t \quad z = 0$$

$$\text{I.C} \quad C_i = 0 \quad \text{at} \quad t = 0 \quad z = z$$

Diffusion equation inside single resin bead can be solved using grids and applying forward and backward difference methods. For obtaining a approximate solution bulk concentration has been assumed to be zero. This assumption is fairly reasonable as diffusion inside the bead is very slow and will be negligibly affected by small variation in the bulk concentration.

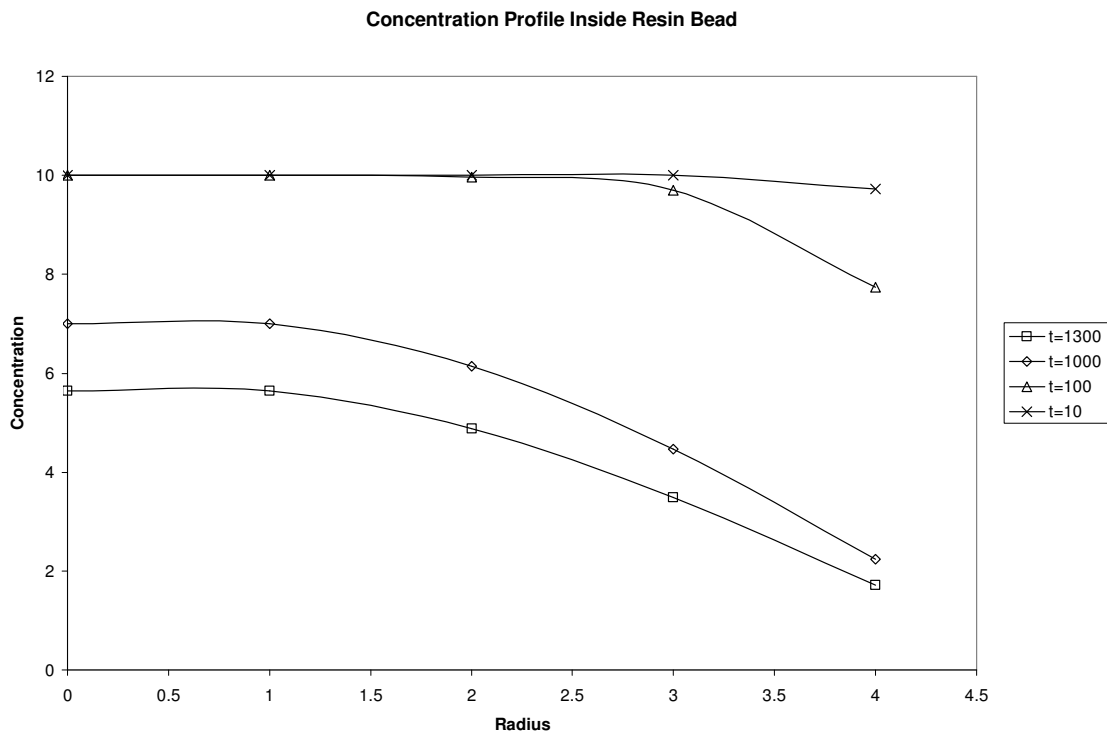


Figure 7 .Concentration profile inside resin bead at various time

The resin surface concentration

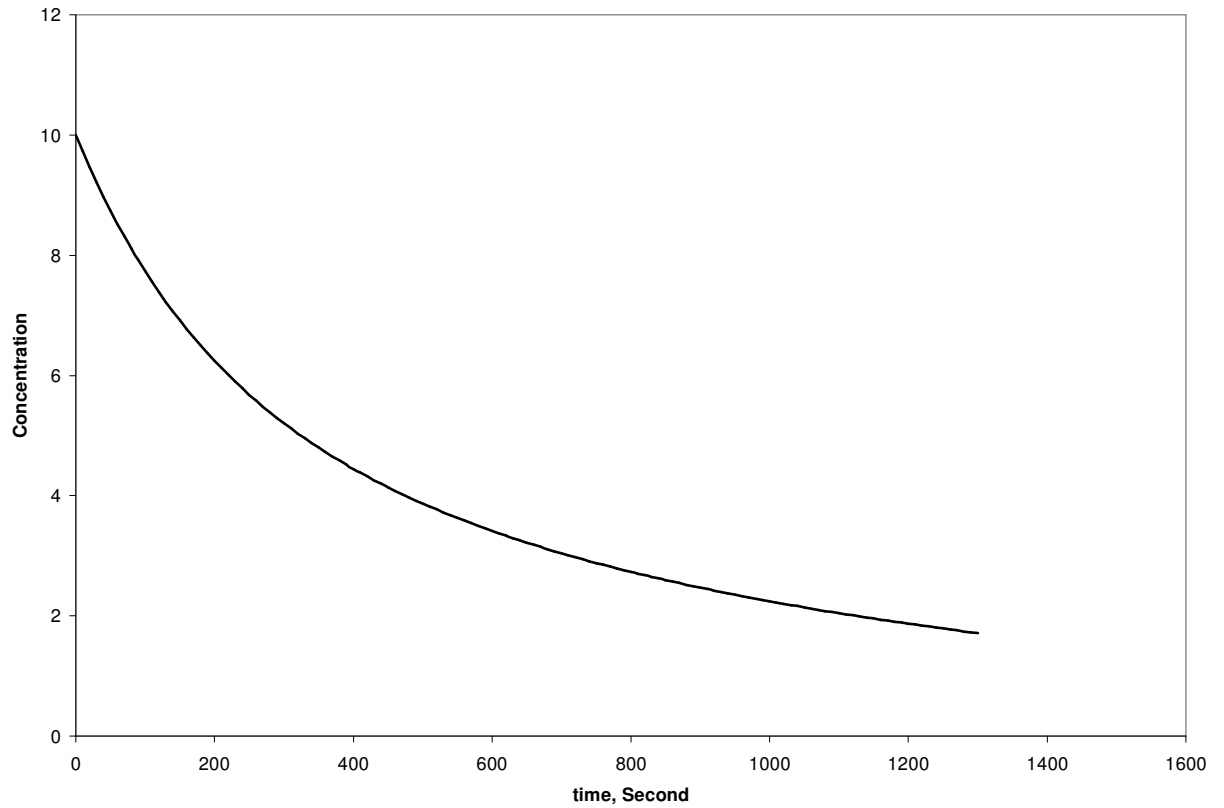


Figure 8. Resin surface concentration variation with time

Although this gives a approximate resin surface concentration because we have neglected the bulk phase concentration which will affect diffusion inside the resin bead. After obtaining the resin concentration profile and resin surface concentration at different time we can solve column material balance equation to obtain effluent concentration profile. The expected effluent profile is shown in Figure 9.

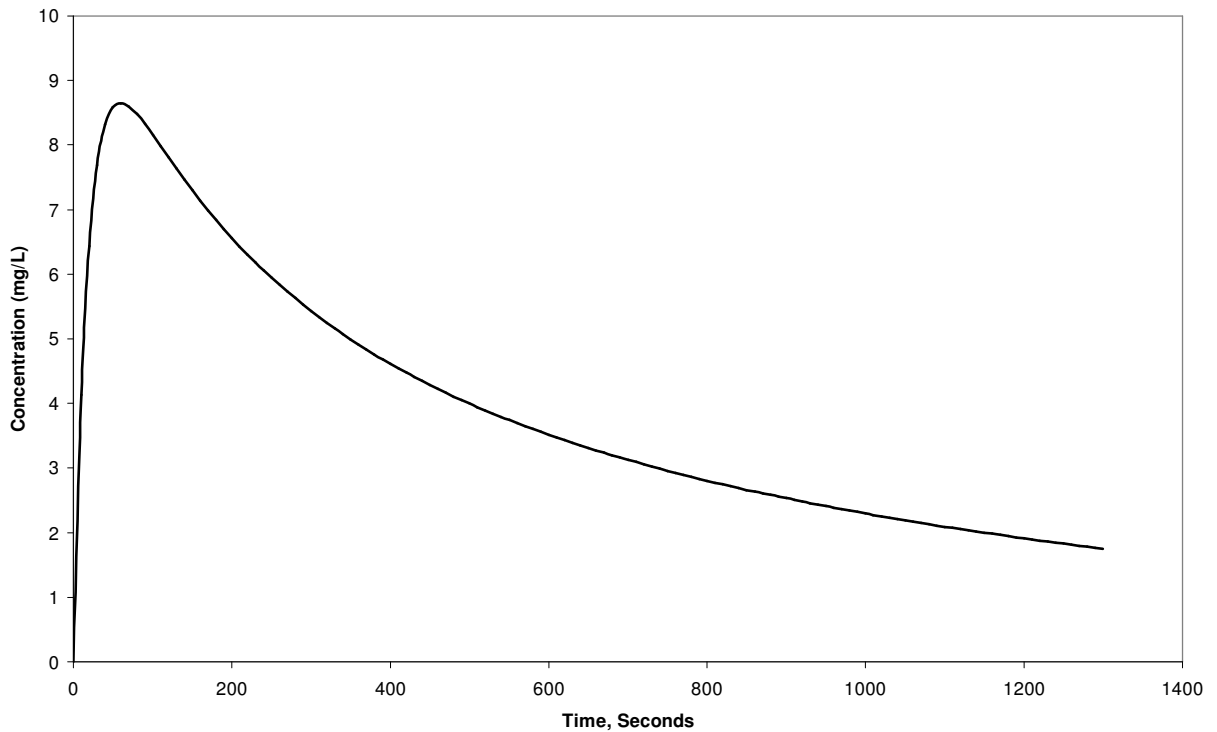


Figure 9. Expected Effluent Profile

We have employed crank Nicholson method to obtain the solution of the equation but not able to find stable solution for the acceptable range of values of MTC i.e. for the values of $K = 2e-4$ to $3.5e-5$. This instability is because of the order of magnitude difference between radial and axial steps since the resin bead radius is very small compared to the axial bed depth.

FUTURE WORK

Future work includes finding stable solution for the set of developed equations. The model will be validated with the experimental data and kinetic properties can be obtained using rinse time. The MTC obtained using model and experiments will be compared to analyze the capability of model for industrial application. Model assumptions will be

verified if model results didn't match with the experimental results. This technique to get kinetic state of resins using rinse time can be industrially useful.

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APPENDIX A
REVIEW OF MASS TRANSFER COEFFICIENT LITERATURE

INTRODUCTION

Ion exchange is used in numerous industrial applications particularly in production of ultrapure water. Ultrapure water is extensively used in many industrial application which includes micro-chip industry (rinse water), nuclear power plants (make-up water, condensate polishing, reactor water clean-up), pharmaceutical industry and in other process industry operations (Foutch et. al., 2004). Ion exchange phenomena take place between a stationary and mobile phase. Stationary phase typically comprised of porous particles with functional groups (Carta, 2005) while mobile phase is generally solution containing ions. These porous particles are called resins which are polymeric structures with ionic functional groups. This exchange of ions from solution to resin phase is dependent on both factors affecting equilibrium as well as the rate of exchange. The equilibrium between the resin and mobile phase is characterized by properties such as selectivity and adsorption coefficient. While rate is studied using the mass transfer coefficient. The purpose of this section is to review the kinetics of the ion exchange process.

ION EXCHANGE KINETICS

Ion exchange is essentially a distribution of ions by diffusion process with rate of diffusion limited by mass transfer resistance in particle or in the solution phase (Helfferich, 1983). The mechanism controlling the rate of exchange are: mass transfer through the liquid film surrounding the resin, diffusion resistance in the porous resin particle, and the exchange reaction between the counter ions in the solid and solution phase (Boyd et al. 1947). Among these the slowest process will be the rate determining process. When the resistances are comparable the rate will be combination of all the resistances.

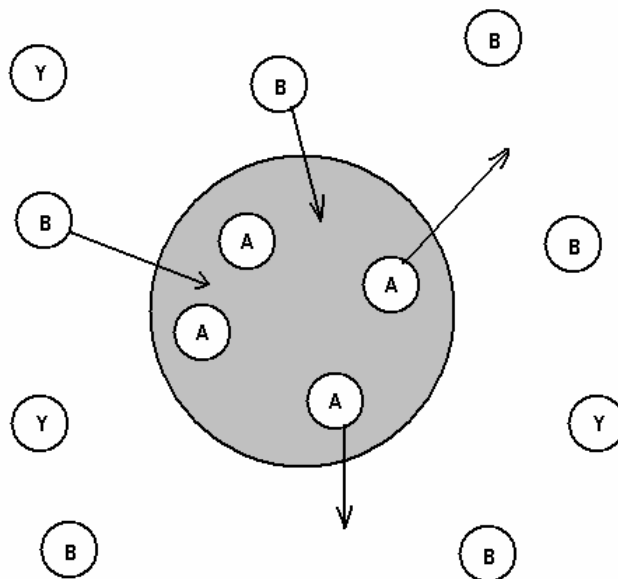


Figure 10. Typical Binary ion exchange system

Many including Bieber et al., Streat, Helferrich & Plesset, Petruzzelli et al. have studied and analyzed the rate determining steps in numerous ion exchange applications. For

applications dealing with dilute solutions, especially for ultrapure water application, ion exchange is purely film diffusion control (Helferrich and Plesset, 1958). Particle diffusion control is particularly observed in applications with highly concentrated solutions, large resin diameters, highly cross linked resins and in highly agitated solution phase. Film diffusion is observed when conditions of a high concentration of fixed ionic groups, low resin cross-linking, dilute solutions and low agitation are prevalent (Helferrich, 1962; Gopala Rao and Gupta, 1982). As the agitation in mobile phase increases the film thickness decreases and thus the path length for diffusion decreases and hence the resistance is less. Similarly as the degree of cross linking increases the path of diffusion becomes more torturous which increases the resistance. Helferrich (1962) gave theoretical criteria to quantitatively establish the effect of various factors in film and particle diffusion. The criterion for determining rate determining step is :

$$\frac{X\bar{D}\delta}{CDr_0}(5 + 2\alpha_B^A) \ll 1 \quad \text{Particle diffusion control} \quad \text{A.1}$$

$$\frac{X\bar{D}\delta}{CDr_0}(5 + 2\alpha_B^A) \gg 1 \quad \text{Film diffusion control}$$

where X is concentration of fixed ionic group; C is concentration of solution, \bar{D} is interdiffusion coefficient in ion exchanger; D is interdiffusion coefficient in film; r_0 is bead radius; δ is film thickness; and α_B^A is separation factor (Helferrich, 1962).

The diffusion process in general is described in terms of Fick's law

$$J_i = -D \text{grad} C_i \quad \text{A.2}$$

Where J_i is the molar flux (mol/(area)(time)), C_i is the concentration of constituent i, and D is the diffusivity or diffusion coefficient of diffusing constituent (Helferrich, 1962;

Trybel, 1981). Negative sign in equation A.2 emphasizes the fact that diffusion occurs in the direction of decreasing concentration. Although ion exchange is diffusion process it can not be explained only on the basis of Fick's law because of electric field effects. So in order to consider the electric effect in addition to ordinary diffusion in fluxes of ions Nernst –Planck equation is used. Electro-neutrality is preserved in both resin and the film during the ion exchange. The difference in mobilities of diffusing ions generates electric potential which influences the rate of slow and fast counter-ions and preserves electro-neutrality. Nernst-Planck equation is given as:

MASS TRANSFER COEFFICIENT

The packed-bed kinetics of ion exchange is studied using a mass-transfer coefficient across a liquid-solid interface. Analytically it represents rate constant for an interfacial physical reaction (Cussler, 1997). A mass transfer coefficient characterizes the kinetic ability of resins for ion exchange. Mass transfer coefficient effectively gives the ratio of rate at which ions are exchanged to the rate at which solution flows through the exchange bed (Foutch et. al., 2004). Mass transfer coefficient can be used to determine the effective rate of exchange and in evaluating the effectiveness of resin.

$$\frac{dc_i}{dt} = K \Delta c_i \quad \text{A.3}$$

As resins age or fouls it offers more mass transfer resistance to diffusing ions which implements for same concentration difference less ions are diffusing, implementing lower MTC value. As MTC decreases the rate of exchange becomes slower. Because of resin fouling and aging the exchange capacity might decrease only by 1-2% but it decreases the MTC by an order of magnitude making it ineffective for particular use (Foutch et. al.,

2004). Mass transfer coefficients can be obtained by simple laboratory experiments within $\pm 10\%$ range (ASTM D 6302). The MTC usually obtained in the experiments is a lump parameter, and represents the overall mass transfer coefficient. It is widely used because of its simplicity. It gives a lumped parameter considering film, interfacial and particle effects and there is no sound approach to analyze which resistance is predominant. But the overall MTC obtained by this simple experiment is a very useful parameter in determining the ionic breakthrough in column operation (Lee et al. 1997).

As resin ages or degrades the overall MTC value decreases and the particle or diffusion resistance can no longer be neglected. And the process must be modeled considering all of the resistance in order to accurately predict the effluent concentration (Lee et al. 1997). The difference in MTC values of new and old resin qualitatively indicates the degree of degradation of resins. Foutch et al. (1992) discussed the effect of resin degradation on MTC and on the overall performance of mixed-bed ion exchange.

EXPERIMENTAL MTC CORRELATION

The model to obtain experimental MTC has been well discussed by many including Harries, Foutch and others. The expression for MTC is derived using continuity equation in column. For a certain ion continuity equation is

$$\frac{\partial C_i}{\partial t} + \frac{u_r}{\varepsilon} \frac{\partial C_i}{\partial r} + (FR) \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q_i}{\partial t} = 0 \quad \text{A.4}$$

In this equation the first term represents ion accumulation in the bulk solution, the second term is for movement of ions due to bulk fluid flow, and the third term is for ionic sorption on the resin beads. Assuming negligible accumulation in the bulk fluid we can

drop the first term. This assumption holds good for shallow beds (Foutch et. al., 2004).

We get

$$\frac{u}{\varepsilon} \frac{\partial C_i}{\partial z} + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial q_i}{\partial t} = 0 \quad \text{A.5}$$

The rate of sorption by the resin bead through the film is given by:

$$\frac{\partial q_i}{\partial t} = K_{f,i} a_s (C_i - C_i^*) \quad \text{A.6}$$

Where C_i^* is the interfacial concentration and for ultrapure water purpose, where resin loading is small, it can be assumed zero in all calculations (Frisch and Kunin, 1966; Rahman and Streat, 1981). Solving equation A.6 with following boundary conditions:

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

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

Eq. (second last) after integration yields mass transfer equation for ion I,

$$\ln \left(\frac{C_i^{eff}}{C_i^f} \right) = (FR) \frac{-k_{f,i} a_s (1-\varepsilon) z}{u} \quad \text{A.7}$$

Now using $a_s d_p = 6$ for spherical resin bead and volumetric flow rate as $F = Au$, where

A is the cross sectional area of bed. Therefore the final mass transfer equation for ion i is (Harries & Ray, 1984)

$$\ln \left(\frac{C_i^{eff}}{C_i^f} \right) = (FR) \frac{-6k_{f,i} (1-\varepsilon) \pi R^2 Z}{d_p F} \quad \text{A.8}$$

This above equation obtained by Harries et al. is the basis of MTC experiment (ASTM D-6302). D_p is the harmonic mean size of resin beads and usually provided by the manufacturer or can be obtained by sieve analysis of the resin.

This derivation is adopted from Foutch et. al., 2004. All the experimental procedure commonly used in practice use shallow bed (20-50 cm) approximation but the industrial ion exchange column varies over a range of 1.0 – 2.0 m. Foutch et. al. (2004) reviewed various experimental methods used for kinetic evaluation of ion exchange resins. In packed bed operation, film mass transfer coefficients can be obtained using theoretical correlations. Vikram et al. (2003) reviewed various theoretical correlations for film MTC present in literature.

The experimental MTC obtained here represents the overall mass transfer coefficient and considers both particle and film resistance. If new resins are used the value obtained will be essentially the film mass transfer coefficient but for old resin it will also include the particle resistance. So qualitatively the difference in the MTC values of new and old resin will represent the degree of fouling or degradation. Lee et al. (1997) discussed theoretical relations to extract particle MTC from overall MTC. For old or fouled resin the total mass transfer resistance is the sum of individual resistance offered by the film as well as by the particle. As discussed by Cussler the overall MTC can be given as:

(Total mass transfer resistance) = (resistance in film) + (resistance in particle)

which can be written as (Lee et. al., 1997)

$$\frac{1}{k_0} = \frac{1}{k_f} + \frac{K}{k_p} \quad \text{A.9}$$

where K is distribution factor. In this expression k_0 can be obtained by performing MTC experiment for used resin and k_f can be approximately equal to the MTC value for new resin. Lee et al.(1997) suggested that these two value can be used to get particle mass

transfer coefficient value which in turn will provide a quantitative measure to the resin fouling or degradation.

References for Appendix A

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APPENDIX B
EXPERIMENTAL SETUP

The experimental system used was based on ASTM procedure (D-6302). The theory behind the experiment is based on the derivation of Harries (1984) and evaluates overall MTC of resins. The system used in this study is composed of an experimental column, conductivity meter, pump, and ion chromatograph to measure effluent concentration from the test column. Figure 8 shows the experimental system used.

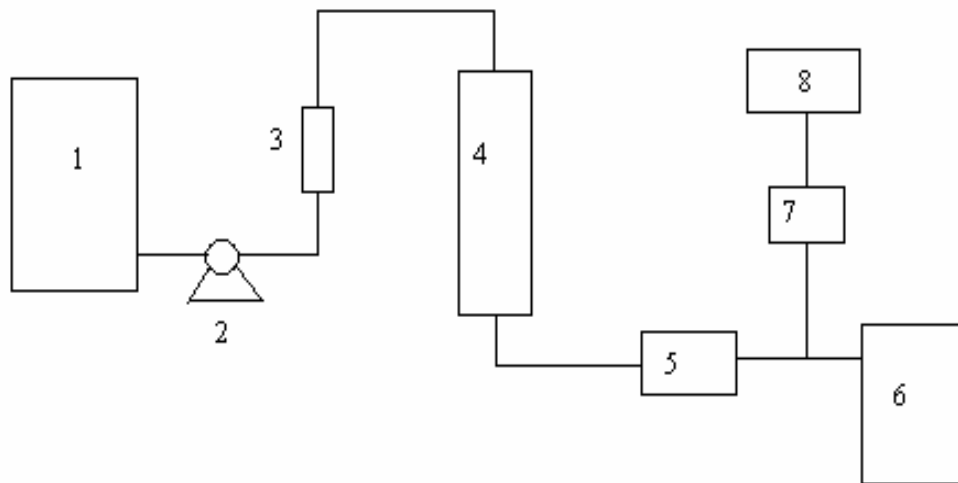


Figure 11. Flow Diagram for MTC Experimental Setup

- 1: Feed carboy
- 2: Pump
- 3: Rota meter
- 4: Test Column

5: Conductivity meter

6: Waste carboy

7: IC

8: PC

Ultrapure water of conductivity in range of 17.9-18.2 $\mu\text{S}/\text{cm}$ was collected in properly rinsed and dry drums from ATRC RO unit. This pure water was used for solution preparation, regenerating solution preparation, rinsing and other purposes. Resin sample was regenerated and rinsed for sufficient time to reach effluent conductivity of 18 $\mu\text{S}/\text{cm}$. Solution containing ions (sodium & sulfate) was passed through the resin column and effluent conductivity was observed. Samples of effluent were collected when sudden rise in the conductivity was observed. Collected samples were analyzed using ion chromatograph to obtain the ionic concentrations.

Test Column

The column used in the experiment was a Pyrex glass transparent column. A fine sieve was fixed at the bottom of the column to hold the resins while operation. The size of column was one inch inside diameter \times 6 inch length \times 0.11 inch wall thickness. Resin samples was filled properly in the column and before starting experiment column was filled with deionized water in order to prevent resin floating and insure uniform flow through the bed. Column was tapped sufficiently to remove any air bubble trapped in the resin bed.

Ion Exchange Resin

The resins used to perform MTC experiments were Dowex resins, Monosphere 650C-H, Monosphere 550A-OH and also on used Dungeness resin samples obtained from British Energy. The used resin samples obtained were Purolite A500 strong base anion exchange resin (Dungeness anion fraction), Purolite C150 strong acid cation exchange resin (Dungeness R21 cation resin) and Purolite SGC100 strong acid cation exchange resin (Dungeness cation fraction resin). All the resin samples used are made by copolymerization of styrene and DVB. In this study new Monosphere 650C-H and Monosphere 550A-OH resins were used while 3-6 year old Monosphere 650C-H, Monosphere 550A-OH resin samples were used. Before performing MTC experiment resins samples were regenerated with NaOH or H_2SO_4 solution.

LIST OF EQUIPMENT

Equipment	Unit	Capacity	Manufacturer
Carboy	2	50 liter	Nagle Comp.
	2	30 liter	
Sampling bottles	25	100 ml	
Pump	1	5 gal/min	Iwaki Co.Ltd.
Temperature probe	1		Thornton Associates Inc.
Resistivity Meter	1		Barnstead
Stop watch	1		
Ion Chromatograph	1		Metrohm Peak Inc.
Personal computer	1		Dell

Table 1. List of Equipment

The experiments performed in this study restricts to mono bed operations. Before carrying out the main experiment: deionized water was obtained, feed solution was prepared, and resins were regenerated and rinsed. The ASTM procedure D-6302 describes the resin regeneration, rinsing, and experimental procedures for the main experiments. ASTM experimental procedures were adopted because of their extensive use and simplicity.

APPENDIX C

ION CHROMATOGRAPH

The effluents from the experimental test columns were analyzed by a Metrohm 790 personal ion chromatograph (IC). This section describes the IC, the preparation of chemicals used for IC operation, and the operating procedure for IC. The 790 personal IC used is quick and easy to use. The software of 790 personal IC is easy to operate because of good user interface. The conductivity detector of the 790 Personal IC has a working range of 1000 $\mu\text{S}/\text{cm}$. SO ionic concentration from the high ppb up to percentage range can be analyzed. The determination limits are approximately 0.1 mg/L (\approx 100 ppb) for anions and cations. However lower concentration may be obtained with less accuracy by obtaining calibration curve for low concentration.

Preparation of Solution

The purpose of eluant solution in ion chromatograph is to act as carrier of ionic sample through the column. In Metrohm 790 personal IC a mixture of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate was used as anion eluant and the mixture of 2.0 mM nitric acid and 0.75 mM dipicolinic acid as cation eluant for detection of monovalent ions. The flow rates of anion and cation eluants were 0.7 and 1.0 ml/min respectively. The concentrated (10X) cation and anion eluant stock solutions were prepared. For cation eluant stock solution 1.25 gm 2,6-Pyridinedicarboxylic acid and 1.19 ml 70% nitric acid

was dissolved in 1 liter of ultrapure water. And for anion eluant stock 3.39 gm of sodium carbonate and 0.84 gm of sodium bicarbonate was dissolved in ultrapure water.

Only Anion IC was installed with suppressor unit and 100 mM sulfuric acid solution was used as the regenerant. 10X regenerant stock solution was prepared by taking 54.63 ml of 98% sulfuric acid and making 1 liter of solution. The IC unit also required Ultrapure water for rinsing. The procedure in the operation manual of 790 Metrohm personal IC was followed to get the ionic concentration.

APPENDIX D

EXPERIMENTAL RESULTS

The following table present experimentally calculated mass transfer coefficient of various ion exchange resin samples using ASTM standard method. Various experimental variables are also listed. All the experiments were performed for mono beds. Sulfate and sodium ions were used in feed solution for anion and cation exchange resins respectively.

Experimental Parameters

Flow rate = 1 lt /min

$\varepsilon = 0.35$

TABLE 2

Experimental Mass Transfer Coefficient Data

Dungeness Cation Fraction :

Variables	Values
Bed Height	10.6 cm
Area	0.000893773 m ²
Particle Size	0.7 mm (0.6-0.8 mm)
C _{in}	0.151 mg/lt
C _{out}	42µg/lt
MTC	0.0000369 m/s

Dungeness Anion Fraction :

Variables	Values
Bed Height	11.8 cm
Area	0.000893773 m ²
Particle Size	0.7 mm (0.6-0.85 mm)
C _{in}	405 µg/lt
C _{out}	99 µg/lt
MTC	0.0000396 m/s

Dungeness R21 Cation resin :

Variables	Values
Bed Height	10.4 cm
Area	0.000893773 m ²
Particle Size	0.7 mm (0.6-0.85 mm)
C _{in}	80 µg/lt
C _{out}	151 µg/lt
MTC	0.0000204 m/s

550 MS A OH Anion resin (old):

Variables	Values
Bed Height	11.0 cm
Area	0.000511 m ²
Particle Size	0.59 mm
C _{in}	1.50 mg/lt
C _{out}	27 µg/lt
MTC	0.0001806 m/s

550 MS A OH Anion resin (new):

Variables	Values
Bed Height	11.0 cm
Area	0.000511 m ²
Particle Size	0.59 mm
C _{in}	1.5 mg/lt
C _{out}	17 µg/lt
MTC	0.0002014 m/s

650C-H Cation resin (old)

Variables	Values
Bed Height	10.6 cm
Area	0.000511 m ²
Particle Size	0.7 mm (0.6-0.8 mm)
C _{in}	0.98 mg/lt
C _{out}	70 µg/lt
MTC	0.0001457 m/s

650C-H Cation resin (new)

Variables	Values
Bed Height	10.6 cm
Area	0.000511 m ²
Particle Size	0.7 mm (0.6-0.8 mm)
C _{in}	0.91 mg/lt
C _{out}	48 µg/lt
MTC	0.0001625 m/s

VITA

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Scope and Method of Study: Study of Kinetic properties of ion exchange resins is necessary in design, operation and optimization of ion exchange column. Better insight of Mass transfer coefficient will lead to better utilization of column and predict effluent quality. Modeling of rinse process will lead to evaluate the kinetic characteristics of resins

Findings and Conclusions: Mass transfer coefficient is an important parameter in evaluating the bed operation. Ion exchange resin fouling was evaluated using MTC values. Radial Flow bed is modeled and analyzed. Rinse process model is presented in the form of problem statement. Solution of which will be of importance in evaluating kinetic properties during rinsing.

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