POWDERED RESIN ION EXCHANGE MODELING

FOR CONDENSATE POLISHING

By

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The objective of this study is to implement and test mixed bed ion exchange multicomponent model developed at Oklahoma State University for powdered resin ion exchange system for condensate polishing in power industry. The model can predict interfacial concentration and is shown to be provide stable solution. A parametric analysis has been done to study the effect of depth of resin bed and resin bead size on the performance of resin bed.

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Abstract:

Powdered resin ion exchange system can be used widely for condensate polishing in power industry and it can also be useful for various applications in other industries. Optimizing performance of powdered resin system requires a model that can be used to study the effect of different factors. Yi and Foutch (2004) developed a multicomponent model for mixed bed ion exchange system for condensate polishing. The objective of this study was to implement and test multicomponent mixed bed ion exchange model derived by Yi and Foutch [Reactive & Functional Polymers 60 (2004) 121-135] in case of powdered ion exchange resin system for condensate polishing in power industry. The model was implemented for powdered resin ion exchange system and tested for different operating parameters. A parametric analysis has been done to study the effect of depth of resin bed and ion exchange resin bead size on performance of powdered ion exchange system. Several simulations has been done using the model and the results are presented to find the impact of resin bead size and resin bed depth.

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NOMENCLATURE

a_s Specific surface area of resin bead (m^2/m^3), $a_s d_p = 6$ for spherical particles

C_i^f Feed concentration of species i (eq/L)

C_T^f Total ionic concentration in the feed (eq/mL)

C_T Total ionic concentration of the solution (eq/L)

C_i^T Total constituent solution concentration for species 'i' (mol/L)

C_i^b Bulk concentration of ionic species 'i' (eq/L)

C_i^* Interfacial solution concentration of ionic species 'i' (eq/L)

C_i^* Interfacial solution concentration of ionic species 'i' (eq/L)

C_i^m Solution concentration of molecular species 'i' (mol/L)

C_T^* Total interfacial concentration (eq/L)

$d_{p,i}$ Resin bead diameter for constituent 'i' (cm)

D_i Diffusivity of ionic species 'i' (cm^2/s)

D_e Effective diffusivity (cm^2/s)

F Faraday's constant (coulombs/mole)

FAR   Volume fraction of anion resin

FCR   Volume fraction of cation resin

H_d Dimensionless column height

L   Bed height (cm)

N_S Number of theoretical slices

N_i $-z_i / z_Y$, ratio of charge to mean coion valence

P   Calculated parameter in Franzreb's expressions

q_i^T Total constituent resin concentration for species 'i' (mol/L)

q_i^e Equilibrium capacity of species 'i' (mol/L)

q_i^m Molecular species capacity for constituent 'i' (eq/L)

Q_i Total ion exchange resin capacity, 'i' for cations, 'j' for anions (meq/mL)

R   Ideal gas constant (J/mol K)

Re   Particle Reynolds number

r   Film radius (m)

t   Time (s)

u   Velocity (cm/s)

u_s Superficial velocity (cm/s)

x_i Ratio of bulk solution concentration to feed concentration of species 'i' C_i / C_i^f

X_i Bulk solution equivalent fraction of ion 'i' C_i / C_T

X_i^* Interfacial equivalent fraction of ionic species 'i'

X_i^b Bulk equivalent fraction of ionic species 'i'

y_i Ratio of bulk solution capacity to equilibrium capacity of constituent 'i' q_i/q_i^e

Y_i Dimensionless equivalent fraction of ionic species 'i' q_i/Q_i

Y_i^e Equilibrium equivalent fraction of ionic species 'i'

z Bed depth (cm)

z_i Valence of ionic species 'i'

Greek letters

α Scaling constant $\dfrac{C_i^f}{C_r^f}\dfrac{q_r^T}{q_i^T}$

δ Nernst film thickness (cm)

ξ_i Dimensionless distance for constituent 'i'

λ_i Constant for calculating interfacial concentrations

ϕ Electric potential (J/C)

τ_i Dimensionless time for constituent 'i'

τ_r Dimensionless time for reference constituent 'r'

CHAPTER I

INTRODUCTION

Powdered ion exchange resin has a wide variety of applications in industry. The resin pre-coats, as they are known because of a thin layer on porous polypropylene tube supports, were first used in steam-cycle electric-generating power plants. The most common applications are condensate polishing and treatment of low activity radioactive wastes in the nuclear power industry [2], pretreatment of ultrapure water systems, decontamination of cationic and anionic impurities in food industries and purification of antibiotic, vitamins and other fluids in pharmaceutical industries, clarification of toxic organics from potable and industrial waters, decalcification and clarification of sugar juices and sugar syrups and polyhydric alcohols in sugar industries [2]. Optimizing powdered ion exchange performance requires a model for multi-component ion exchange kinetics. Yi and Foutch (2004) developed a multicomponent model for mixed bed ion exchange system for condensate polishing. The objective of this study is to implement and test mixed bed ion exchange model for powdered resin ion exchange system for condensate polishing.

Background of this study

Ultrapure water

Water is typically defined as ultrapure water when the concentration of dissolved impurities is less than 1 part per billion (ppb or µg/L). Water with conductivity less than 0.1 µS/cm can also be defined as ultrapure water. There is extensive usage of ultrapure water in nuclear power

industries, semiconductors and microchip manufacturing industries, Pharmaceuticals and biotechnical industries [6]. The following part describe the use of ultrapure water in power industry.

Usage of ultrapure Water in Power Industry

For sustainable operation of power plants steam cycle water chemistry is very important. Make-up water production, condensate polishing and reactor water clean-up are the major areas of the plants for ultrapure water processing. Each of these applications maintains specific quality of water and uses different technology to achieve the water quality [6].

Nuclear power plants use ultrapure water to minimize erosion and corrosion of materials within the steam power cycle. The temperature, pH and contaminants present in the water are major reasons behind erosion and corrosion of construction materials. The Electrical Power Research Institute (EPRI) recommended the maximum contaminants concentrations for each steam cycle configuration. The water chemistry is determined based on the steam cycle configuration. Two steam cycle configuration are mostly used in nuclear power plants, the Boiling Water Reactor (BWR) and the Pressurized Water Reactor (PWR). Powdered resin are mostly used nuclear power plants with Boiling Water Reactor (BWR) steam cycle configuration. The BWR steam cycle system is described below.

Figure I-1 shows schematic diagram of a BWR nuclear power plant. Water is circulated through the Reactor Core to pick up heat as the water moves past the fuel assemblies. The water is ultimately converted to steam and the steam separators in the upper part of the reactor remove water from steam. After passing through the turbines, the steam condenses in the condenser. The condenser is at a vacuum and cooled by ocean, lake or river water. Then the condensate is passed through condensate polishers to remove the contaminants from the steam cycle.
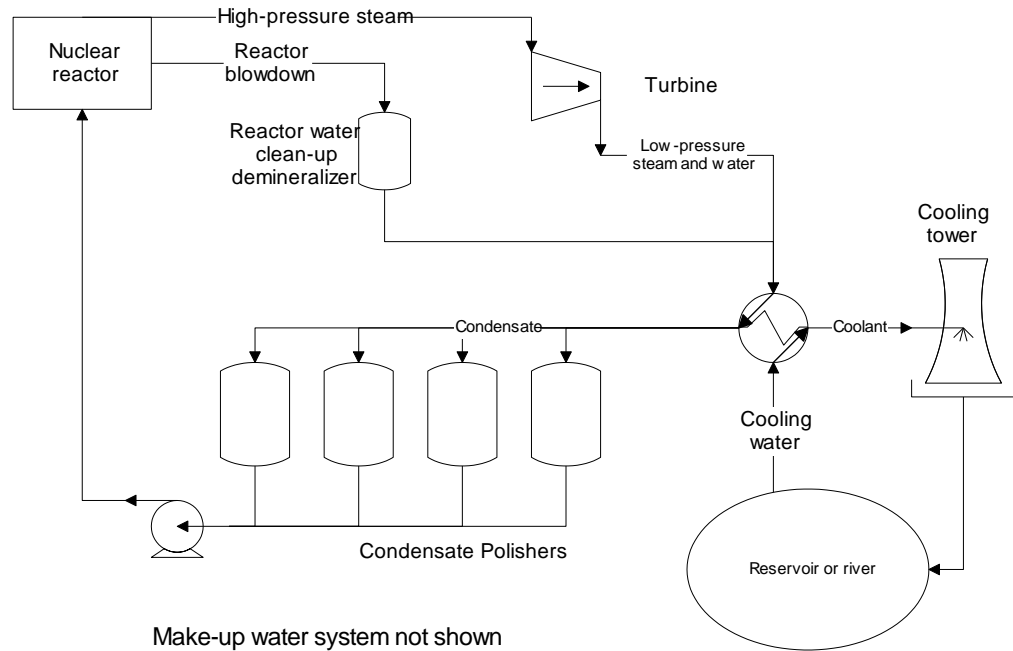
Figure I-1 Skeleton schematic of a BWR nuclear power plant [6].

Condensate polishing

Condensate polishing is a significant part of water treatment for industrial power generating system [8]. In a typical steam condensate loop, steam from the boiler passes through series of turbines and expands in volume while giving up most of its energy. The low pressure steam is condensed in a heat exchanger and this water, or "condensate," is recycled to the boiler and converted back into steam. Recovering and recycling the return condensate reduce the cost of operation significantly. Within this cycle, water is lost during operation due to leaks and boiler blowdown, so a continuous make-up water source is maintained. The boiler make-up water is one factor of feedwater purity and the other is condensed return stream. As a result, condensate purity is a major concern in high pressure utility units. So purification of condensate or assures high quality of feed water stream to the downstream boiler.

The condensate polishing system must deal mainly with impurities that arise inside the system [8]. In cases of condenser tube leaks the condensate polisher also deals with impurities in the raw feed water. The condensate contains solid, gel-like and dissolved impurities. These impurities originate from corrosion of metal surfaces, leaks and repair work errors and from leakage of dissolved contaminants from cooling water when condenser system leaks into the condensate. For these reasons, the applications of condensate polishing is significant within power industry.

Role of Ion exchange resins

Ion exchange resins play a significant role in water purification. The use of ion exchange resins in condensate polishing began with mixed bed ion exchange demineralizer in the 1950's and followed by the introduction of powdered ion exchange precoat filter demineralizers in the 1960's.

Mixed Bed Ion Exchange

Mixed Bed Ion Exchange (MBIE) is a mixture of cationic and anionic resin within a column of 3 to 4 feet depth used to deionize an influent stream. The idea of mixed bed ion exchange was first introduced by Kunin and McGarvey (1951) [14]. The MBIE bed can be designed with various ratios of cation and anion exchange resin, the most typical being 2:1 or 1:1 cation to anion by volume [3]. MBIE column can be operated in different cycle based on the process requirements. It can also be operated in series or in combination with other desalination apparatus to achieve the water purification goal.

Powdered Resin for condensate polishing

Powdered ion exchange resins typically have a particle size of 30-150 microns. Powdered resin usually consists of a strong acid cation resin which may be in either hydrogen or ammonia form and a strong base anion resin in the hydroxide form. The cation or anion resin are available as individual components and the resin must be mixed by the user based on plant operational

criteria. The cation and anion resin can be mixed in various cation to anion ratios as to meet the requirement of the process. The powdered resin is precoated on filter septa, which are approximately 125 cm to 200 cm in length and approximately 2.5 cm to 5 cm in diameter [4]. During system operations two processes occur simultaneously: electrostatic or mechanical depth filtration which removes small particles such as metal oxides and colloidal particles such as silica and ion exchange which removes different ions from the influent.

Powdered ion exchange resins were first utilized as precoats combined with bead form ion exchange resins for condensate polishing in electric power plants. Pre-coat technology was applied in both nuclear and fossil steam-generating plants but evidenced particularly effective in the boiling water reactor (BWR) nuclear plants. Powdered pre-coats generate no liquid waste regenerants. Powdered resin ion exchanger has issues such as short run lengths due to the high level of suspended solids in BWR condensate. This issue led to the development of pre-coats incorporating fiber in addition to the powdered resins [2].

In high pressure utility generating plants, powder ion-exchange resins are being used as a thin precoat, usually about 1cm thick on a precoat filter to treat condensate. Levendusky patented a powdered resin system (named Powdex®) in 1966 [28]. The powdered ion exchange resin was made by grinding ion exchange resin beads or granules into powder. A thin layer of powdered resin significantly improved the rate of ion exchange compared to conventional packed bed of resin. This system has been used as the basis for most practical applications of powdered ion-exchange [2]. The equipment required is a simple pre-coat filter. The amount of resin required is so small that the resin is not regenerated. The exhausted resin bed is removed by backwashing when exhausted, and replaced by a new layer of resin mix [1]. The equipment involved is a mix tank for mixing the resin slurry for pre-coating, a precoat filter and the necessary piping, pumps, valves and instruments. The system requires less floor space also. So the cost is considerably less than a comparable deep-bed polishers.

Basic principles of powdered ion exchange process

Powdered anion exchange resin and powdered cation exchange resin were mixed in water slurry to make the original pre-coats. Both types of resin were ground into the powders (40 – 60% moisture content) using grinding equipment such as hammer mills and the grinding process resulted in a distribution of particle sizes, typically from 1 to 200 μm range. The average size of the particles was 35-70 μm range. As a result, the particle size of powdered ion exchange resins are roughly two orders of magnitude smaller than typical ion exchange resins. Due to this grinding process, there is an increase in the surface area of resin and consequently surface area to weight ratio [2]. As the particle size of ion-exchange resin particles is made smaller, the rate of reaction increases. According to Levendusky, the reaction rate is approximately 100-times greater for powdered resin compared to the standard bead resin [1]. The performance of powdered resin pre-coats depends mostly on particle size of ion exchange resins. Resin particle size influences ion exchange capacity utilization, filtration efficiency and capacity, pre-coat integrity, uniformity and lifetime. Specifically both exchange rate and utilization are inversely proportional to particle diameter. Because of better kinetics, powdered resins typically exhibit equal or higher operating capacities to bead resin counterparts.

Formulation of Pre-coat

The pre-coat formulations used in the Powdex® process were made from just two components: anion resin and cation resin. The powdered resin were added to water and stirred to form a slurry. Innocuous organic material such as dilute polyacrylic acid which reduces clumping can be added to control the bulk volume of the slurry [2]. Since individual components are used to make the pre-coat, the cation to anion ratio can be controlled according to the requirements of the process or applications.

Advantages of using powdered resin

Radioactive exposure of plant personnel is one the major concerns in nuclear power plants. Deep bed ion exchange resin is regenerated with sulfuric or hydrochloric and sodium hydroxide or disposed without regeneration after treatment on a regular basis. The chemicals used for regeneration need to be stored, treated and disposed periodically. Treatment and disposal of deep bed ion exchange resin is potential source of radioactive exposure of plant personnel and one of the potential source of radioactive exposure of plant personnel. As the amount of resin required for powdered ion exchange system is very small and powdered resin polishers do not require regeneration, powdered resin ion exchange bed significantly minimizes radioactive exposure of people in plant.

Powdered resin has performed well in condensate polishing, for both filtration and ion exchange. A powdered resin system has a number of advantages if lower TDS cooling water is being used. One of the major advantages of powdered resin is superior removal of insoluble iron and copper oxides and an adequate deionization capability. Particle size of resin bead plays important role on the diffusion of ion across the film or layer of solution surrounding a resin bead and on the diffusion of ions within a resin bead. The following figure represents the mechanism of ion exchange process .The instantaneous rate of overall ion exchange process can be described by
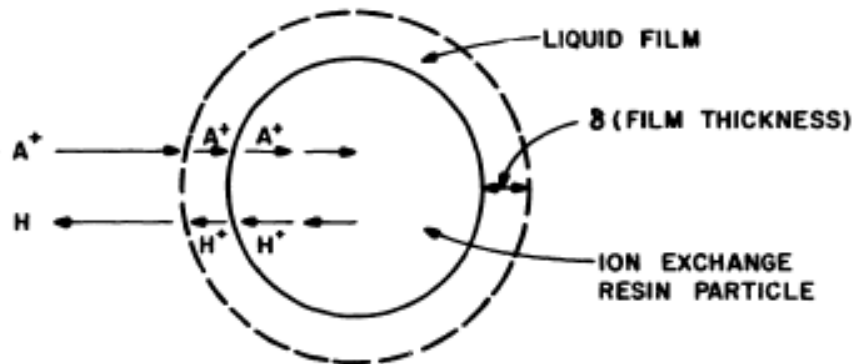
Figure I-2: Mechanism of Ion Exchange Process (Cation Exchange Resin, H^+ Form) [13]

the following equations. Equation (A) is for particle diffusion control [13]:

$$\gamma = \frac{\bar{D}}{0.071r^2}(\bar{C}_A^* - \bar{C}_A) \dots \dots \dots \dots (A)$$

Equation (B) is for film diffusion control [13]:

$$\gamma = \frac{3\bar{D}}{2\delta r}(C_A - C_A^*) \dots \dots \dots \dots (B)$$

Where,

γ	instantaneous rate of the overall ion exchange process
$\bar{D}$	interdiffusion coefficient in the liquid film
δ	thickness of liquid film
r	radius of resin particle
C_A	concentration of A in bulk solution (meq/ml)
$\bar{C}_A^*$	equilibrium concentration in ion exchanger
$\bar{C}_A$	actual concentration in ion exchanger
C_A^*	equilibrium concentration in solution
C_A	actual concentration in solution

So, the ion exchange rate is inversely proportional to the radius of the resin particle. Study showed that powdered resin reacts almost 100 times faster than standard whole bead ion exchange resin [4].

Powdered resin polisher system has very short turnaround period. The time to remove exhausted precoat and lay down a new precoat and return the equipment back into service usually

takes about 1 hour. So powdered resin system can better handle if there any change in the system such as condenser leaks and increased concentration of materials into the condensate.

Resin fouling problem can be avoided in the powdered resin systems since the precoat can be discarded after each service cycle and replaced by new resin. Cation to anion ratios can be changed from one cycle to another to meet the changing conditions of the system while a mixed bed polisher is designed for a specific cation to anion ratio [4]. In case of oil leak into condensate being polished in a deep bed system, the resin is needed to be cleaned with a surfactant or replaced with new resin. Replacing is costly since typically a large volume of resin is required. But powder resin system can be precoated with a precoat rich in cellulose or other fibrous material and oil or other deleterious material can be removed quickly with a much lower cost. The application of deep bed condensate polishers are limited to a temperature of 120° F due to the degradation of anion resin at a temperature greater than 120° F. Degradation of resins with time results in less overall capacity and shorter run lengths. When powder resins run are ended, the resin is discarded and replaced by new resin. This allows the powdered resin system to be operated at temperatures well in excess of 120° F. A study by Simon [4] and presented in a paper by McGarvey reported that Type 1 strong base resin at 140° F lost 1.3% of strong base capacity per month and for each 18° F rise in temperature, the degradation rate is doubled. This means that the half-life of the resin at 194° F is 43 days which also agreed exactly with the previous findings of Baumann. The temperature effects are minimized for powdered resin as the exhausted resin is replaced by new resin approximately every 30 days [4].

Limitations of Powdered resin system

Powdered resin ion exchange systems has some limitations. If high TDS cooling water such as seawater or brackish water is used in the system, a deep bed polisher will be best suitable for condensate polishing [4]. If probability of condenser leakage is high, or condensate polisher is

required to run for long time with small leaks, deep bed ion exchanger would be best suited for the process as deep bed condensate polisher has high ion exchange capacity [3].

Scope and Objectives

The scope and objectives of this work is given below:

1. Implement and test multicomponent mixed bed ion exchange model developed by Yi and Foutch (2004) for powdered resin ion exchange system based on mixed bed ion exchange model [7].
2. Test the model whether it can handle an arbitrary number of ionic species and multivalent dissociative species given the valence, resin loading, selectivities and resin capacity.
3. Predict the effect of resin bed depth and resin bead size on the performance of ion exchange system by a parametric analysis.

In chapter II, a literature review regarding ion exchange model development is presented. In chapter III, the model implementation of powdered resin ion exchange system and the solving strategy is discussed. Chapter IV represents the results and discussion. The conclusions and future study recommendations is included in chapter V.

CHAPTER II

LITERATURE REVIEW

Powdered resin systems have been widely used for the treatment of condensate in the electric power industry. Two theories that can explain multicomponent ion exchange are equilibrium and rate controlled models. Equilibrium theory assumes existence of local equilibrium between the resin and the bulk water phase and considers mass transfer resistance between phases or within the resin beads as negligible. At extremely low concentrations or high flow rates local equilibrium is not accurate. Rate theory is based on the rate of ionic diffusion to the exchange site.

For ultrapure water, rate theory is more appropriate at the low concentrations observed in operating equipment. For this work the model discussed is based on rate theory. The following section discusses some references and gives a brief description regarding the model development efforts of previous students at Oklahoma State University (OSU).

Strong electrolyte ion exchange modeling

Caddell and Moison (1954) conducted a theoretical study on variables affecting the breakthrough of mixed bed ion exchange (MBIE) and developed an empirical relationship between leakage and capacity. Kunin (1960) further conducted an experimental study on the

effects of bed depth, flow rate, influent concentration and temperature on bed performance to understand the kinetics of mixed bed deionization. They found that the rate of ion exchange was controlled by a liquid-film mass transfer mechanism at low concentration. Film mass transfer is one of the major assumptions for the development of a rate expression used within an MBIE model [12].

Schlögl and Helfferich (1957) studied the kinetics of binary ion exchange and applied the Nernst-Planck (N-P) equation to describe the fluxes of ionic species. They concluded that the difference of the diffusivities creates an electric field which has a significant effect on the ion exchange rate [25]. Kataoka et al. (1987) studied the kinetics in a ternary system and developed flux expressions for the ions with equal valences and for ions with different valences separately. The results of their model matched reasonably well with the experimental results but application of the model was limited to systems with not more than three species [17].

Haub and Foutch (1984) were the first to model rate limited mixed bed ion exchange at ultrapure water concentrations. They considered separate material balances for each resin and water dissociation effects to develop a model for hydrogen cycle MBIE at ultra-low concentration. The model was limited to only binary monovalent systems such as Na^+ - Cl^- at 25°C [15].

Divekar et al. (1987) studied temperature effects on physical properties such as diffusivity, viscosity and dissociation constant for certain species and incorporated it with Haub and Foutch's model [20]. Zecchini (1990, 1991) extended this model to simulate a ternary system of monovalent ions with amines [18]. Pondugula (1994) extended the model to bivalent ternary model. The effect of desulfonation of the cation resin on bed performance was also included with this model [21].

Weak electrolyte ion exchange modeling

The concentration distribution of weak electrolytes are pH dependent. Therefore the ion exchange of weak electrolytes depends on the pH of the solution. For this reason, the ion exchange of weak electrolytes differ from strong electrolytes.

Many researchers studied ion exchange with weak electrolytes. Samuelson (1963) concluded that the sorption of weak electrolytes, especially the molecular form was nonionic adsorption [23]. Helfferich (1962) found that the ion exchange resin could absorb more moles of weak electrolytes than the ion exchange capacity of resin, which was observed different in strong electrolyte systems.

Jansen et al. (1996, 1997) studied the influence of pH, solution concentration and dissociation equilibrium on kinetics of weak electrolytes ion exchange. In their study, they found that changes in either pH or solution concentration while the other variable remains constant, changes effluent concentration and pH, respectively. They thought that, sorption of molecular form of electrolytes are the reason behind this phenomena. They concluded that exchange of counterions and sorption on neutral species determine the ion exchange characteristics of weak electrolytes [30].

Bulusu (1994) extended OSU MBIE model which can handle 3 cations and 5 anions with dissociative carbonates. Integration of ionic flux expression developed by Franzreb et al. (1993) with the model enabled the modeling of arbitrary valence systems. Bulusu also added the effect of resin heels with the model [11]. Based on Bulusu's model Sunkavalli (1996) developed a more generalized multicomponent MBIE model which can handle 8 cations and 8 anions and attempted to model carbonate for first time [29].

Hussey (1996) extended the model to calculate interfacial concentrations for ionic species regardless of the form of the resin. He introduced a pseudo-ion concept as reference to make the

calculation of interfacial concentrations stable and assure the solution of the system. The algorithm was incorporated in Sunkavalli's (1996) MBIE model [5].

Lee (1999) extended OSU multicomponent model to include five weak dissociative (single step) bases, five weak dissociative (single step) acids, one two-step dissociative acid and base, one three-step dissociative acid and base and silica.

Jia (2004) extended OSU MBIE model to handle an arbitrary number of species with any valency including dissociative species. He also developed new solving strategy and algorithm to improve the effectiveness and stability of the model. This model can also predict the effects of fouling for both anion and cation resin on the effluent properties and bed performance and effects of cation resin desulfonation on the effluent quality [6].

To summarize the above work, no model to handle powdered resin ion exchange is developed. Therefore a model that can handle powdered ion exchange resin is required to optimize the performance of powdered ion exchange resin system.

In this study, the modeling developed by Jia (2004) for mixed bed ion exchange is considered as basis of powdered ion exchange resin modeling. The bead diameter of ion exchange resin and bed depth are two major factors which make powdered ion exchange system different from mixed bed ion exchange system. The following section describes the theory and development of model algorithm for multicomponent mixed bed ion exchange.

Model assumptions

The following assumptions are considered to develop the model:

- Ion exchange process is controlled by film-diffusion
- Higher valence ions are preferred by ion exchange resins. The ion with higher selectivity is preferred between ions with same valence.

- Ionic forms of species are exchanged with ion exchange resin as counter ions.

- Protonation to resin exchange site and molecular adsorption within resin matrix; these two methods are considered for the transport of nonionic forms of species.

- The protonation of nonionic forms consumes some of the ion exchange capacity of resin.

Model equation

Ion exchange is a diffusion process which involves charged species. Since the Nernst-Planck equation of diffusion incorporates electric potential effects, it is used to calculate ionic diffusion flux. All equations discussed in this section are as presented as derived by Yi (2004).

$$J_i = -D_i \left[\frac{\partial C_i}{\partial r} + \frac{Z_i C_i F}{RT} \frac{\partial \phi}{\partial r} \right]$$

(II.1)[1]

Where the first term represents mass transfer due to concentration gradient and second term represents effect of electric potential gradient [6].

Fick's second law is used to describe mass transfer flux for nonionic or molecular forms of weak electrolytes.

$$J_{Mol} = -D_{Mol} \frac{dC_{Mol}}{dz}$$

(II.2)

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[1] All equations in this chapter are used from reference [6] without any change.

Dissociation equilibrium

Three types of common dissociative species: Type I; Type II; and Type III have been considered in this model. The following generalized equilibrium equations express the dissociative characteristics of the dissociative species involved in the system.

Type I dissociative species

Monovalent amine (e.g. ammonia) and carboxylic acid (e.g. acetic acid) are used as typical examples of Type I cationic and anionic dissociative species. These species have only one-step dissociation equilibrium, that is,

For monovalent amines

$$RNH_2 + H_2O \xleftrightarrow{K_b} RNH_3^+ + OH^-$$ (II.3)
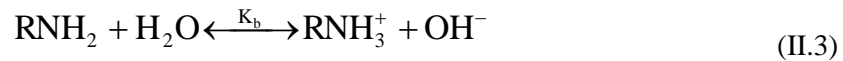
$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$ (II.4)

For organic acids

$$RCOOH \xleftrightarrow{K_a} RCOO^- + H^+$$ (II.5)

$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$$ (II.6)

Equation (II.4) and Equation (II.6) have the same form. Therefore, they can be combined into a generalized equation, that is

$$K = \frac{[TypeI\_Ion][Dum\_Ion]}{[TypeI\_Mole]}$$ (II.7)

Where, Dum_Ion represents either H^+ or OH^- depending on whether the Type I species is acid or base.

Type II dissociative species and Type III dissociative species are discussed in Appendix A.

Interfacial Concentration

Interfacial concentrations for each species are determined by ion exchange equilibria in this model to calculate the ionic fluxes or rate of ion exchange. Specifically, the selectivity expression, which is based on the mass action law, is used to calculate the interfacial concentrations.

Generally, for the exchange of species A with B, the selectivity is defined as

$$K_A^B = \left(\frac{q_B}{C_B^*}\right)^{Z_A} \left(\frac{C_A^*}{q_A}\right)^{Z_B}$$

(II.8)

The above equation can be expressed in terms of equivalent fractions, total resin capacity and total interfacial concentration as

$$K_A^B = \left(\frac{Y_B}{X_B^*}\right)^{Z_A} \left(\frac{X_A^*}{Y_A}\right)^{Z_B} Q^{(Z_A - Z_B)} C_T^{*(Z_B - Z_A)}$$

(II.9)

The generalized form of the above equation for any ion *i* can be expressed as

$$X_i^* = Y_i \left(K_A^i\right)^{-1/Z_A} \left(\frac{X_A^*}{Y_A}\right)^{Z_i/Z_A} \left(\frac{Q}{C_T^*}\right)^{1 - Z_i/Z_A}$$

(II.10)

In general, n such expression can be written for *n* counterions in the bulk liquid replacing ion A in the resin. However, given the resin loading, resin capacity and total interfacial concentration, there are *n*+1 unknown interfacial fractions. Material balance at the solid-film

interface (summation relationship) provide the following equation to completely specify the system.

$$\sum_{i=1}^{n+1} X_i^* = 1.0$$

(II.11)

Since, the ion exchange equilibrium depends on the resin capacity Q and total interfacial concentration C_T^* for an arbitrary valence case (equation II.20), iteration is required to determine the interfacial concentrations. However, an expression for the total interfacial concentration C_T^* is required before determining individual interfacial concentrations.

Flux Expression

In this model, the flux expression of ions is developed based on method proposed by Franzreb et al. (1993) and the derivation is done based on the Nernst-Planck equation. It is assumed that no net coion flux in the film. Therefore, the electric potential term in the Nernst-Planck equation is eliminated. If C_T is the total equivalent concentration, the electric potential term can be written as

$$\frac{d\phi}{dr} = -\frac{RT}{Z_Y F} \frac{1}{C_T} \frac{dC_T}{dr}$$

(II.12)

Where, Z_Y is the mean coion valence, which is defined as:

$$Z_Y = \frac{\sum_{j=1}^{m} Z_j^2 C_j}{\sum_{j=1}^{m} Z_j C_j}$$

(II.13)

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Substituting of equation (II.28) into Eq (II.1) and assuming a pseudo steady state exchange, we have

$$J_i = -D_i \left(\frac{dC_i}{dr} - \frac{C_i Z_i}{C_T Z_Y} \frac{dC_T}{dr} \right)$$

(II.14)

After a series of mathematical manipulations, the final form of the flux expression is:

$$J_i = \frac{D_i}{\delta} \left((1 - \frac{N_i}{P})(C_i^* - C_i^o) + N_i A_i (1 + \frac{1}{P})(C_T^* - C_T^o) \right)$$

(II.15)

Where
$$N_i = -\frac{Z_i}{Z_Y}$$

(II.16)

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^* - X_i^o \right)}{\sum_{i=1}^{n} D_i \left(X_i^* - X_i^o \right)}$$

(II.17)

$$C_T^* = \left(\frac{\sum_{i=1}^{n} (1 + N_i) D_i X_i^o}{\sum_{i=1}^{n} (1 + N_i) D_i X_i^*} \right)^{\frac{1}{P+1}} C_T^o$$

(II.18)

Mixed bed ion exchange column material balance equations

To develop mixed bed ion exchange column material balance, theory analogous to adsorption modeling is used as basis. The fundamental equations of the column material balance for a single cation species and a single anion species in a cylindrical packed bed neglecting radial

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or axial dispersion is mentioned below. The subscripts 'i' and 'j' represent ion/counter-ion systems, for this discussion the subscripts 'i' and 'j' refer to a cation and anion constituent, respectively.

$$\frac{\partial C_i^T}{\partial t} + \frac{u}{\varepsilon} \frac{\partial C_i^T}{\partial z} + (FCR) \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i^T}{\partial t} = 0$$

(II.19)

$$\frac{\partial C_j^T}{\partial t} + \frac{u}{\varepsilon} \frac{\partial C_j^T}{\partial z} + (FAR) \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_j^T}{\partial t} = 0$$

(II.20)

Where, C_i^T and C_j^T are the total constituent solution concentrations, and q_i^T q_j^T are the total constituent resin concentrations. The constants FCR and FAR are the volume fractions of cation resin and anion resin, respectively. FCR and FAR allow the use of the total bed volume to calculate capacity [6].

The implementation of this model in powdered resin system and solution strategy is discussed in chapter III.

CHAPTER III

MODEL IMPLEMENTATION

Introduction

The implementation of MBIE model for powdered resin condensate polishing system is discussed in this chapter. Numerical methods is used to solve the model equations with application of computer program. The solving strategies is also discussed briefly in this chapter. Parametric analysis of powdered resin system is also presented and discussed to determine the effect of resin bead size and depth of resin bed.

Model implementation

Powdered anion exchange resin and cation exchange resin are mixed with water to form powdered resin pre-coat in powdered resin condensate polishing system. Powdered ion exchange process can be considered as a combination of filtering and ion exchange process. Powdered ion exchangers exhibit electrical interaction [8]. So, the system involved diffusion of charge particles. The model equation (equation II.1) based on Nernst-Planck equation is applicable for powdered resin system also where the first part represents the effect of concentration gradient and the second part is the potential gradient effect.

$$J_i = -D_i \left[\frac{\partial C_i}{\partial r} + \frac{Z_i C_i F}{RT} \frac{\partial \phi}{\partial r} \right]$$

Solving strategy

Yi (2004) used two different strategies to solve the model equation numerically [6]. For numerical solution, a dimensionless variable system has been introduces where a system of equations represents changes in dimensionless concentration and capacities with dimensionless time and length. Defining integration limits and increments is the first step for numerical solution. For computational algorithm the number of distance elements is calculated by dividing the dimensionless column height by distance step-size using the following the equation.

$$N_S = \frac{H_d}{\Delta \xi_r} \tag{III.1}$$

Where, the H_d is the dimensionless column height, and it is calculated from,

$$H_d = \frac{k_r (1-\varepsilon) L}{u_s d_{p,r}} \tag{III.2}$$

Usually the maximum dimensionless time parameter is defined by the user. The number of dimensionless time elements is calculated using the following equations.

$$N_T = \frac{\tau_{max}}{\Delta \tau} \tag{III.3}$$

$$\tau_{max} = \frac{k_r C_r^f t_{user}}{d_{p,r} q_r^e} \tag{III.4}$$

The effluent concentrations are determined by solving the system of equations from the column material balance.

The solution strategy derived by Yi (2004) is used for the powdered resin system. The simulator described in Yi and Foutch (2004) is used to generate different effluent concentration data for powdered resin system.

Parametric Analysis

The main challenge of this model is to define the step sizes and optimize the calculation time and accuracy of this model. The resin bead size and depth of resin bed are two most important factors. A parametric study has been done to investigate the effect of resin bed depth and resin bead size on the performance of ion exchanger in powdered ion exchange system.

Model parameters

Depth of Resin Bed

For condensate polishing, the powdered resin is used as filter and it is precoated on a filter septa. The typical value of depth of the resin coat is 0.63 cm – 1.27 cm [2]. In this model the parameter of resin bed is considered from 0.75 cm to 1.25 cm.

Resin Bead Size

The typical size of the powdered ion exchange particles is from 1 to 200 µm and the distributions are centered in the range of 35-70 µm range [2]. In this model the range of resin bead size is considered from 35- 75 µm.

The following chapter IV represents the results obtained from the simulation using the model for powdered resin systems. It also includes the results and discussions of parametric analysis of resin bed depth and resin bead size of ion exchanger.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results and analysis of the powdered resin model is discussed. A parametric analysis of effective resin bead size and depth of resin bed using the powdered resin model for condensate polishing has been analyzed and presented.

Model criteria Validation

The column material balance is one of the most important criteria of this model. For every simulation the column material balance results has been monitored. The effluent concentration should gradually reach the influent concentration if the simulation run time is infinite. Results from the model validate the above criteria for almost all simulations. The following Table IV-1 represents the bed geometry and service parameters and Table IV-2 represents the influence concentration and resin loading information for a condensate polishing system in Boiling Water Reactor (BWR) power plant.

Table IV-1 Bed geometry and service parameters for BWR powdered resin system

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.0075
Flow rate (gpm)	40
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Feed pH	9.3
Temperature (^{o}C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Table IV-2 Influent concentration and initial resin loading for BWR power plant

Ion	Influent Concentration (ppb)	Initial resin loading
Na^+	100	0.0001
Cl^-	154	0.0001

The influent concentration and initial resin loading information represented in table IV-2 is used for simulation as typical values in this study. In this case, only one strong cation and one strong anion were considered. But the model can be applied to multiple component system. The BWR power plant data is used to test the model for column material balance.

The following figure IV-1 represents the strong cation breakthrough profile for condensate polishing using powdered resin system based on operating parameters presented in table IV-1 and IV-2.
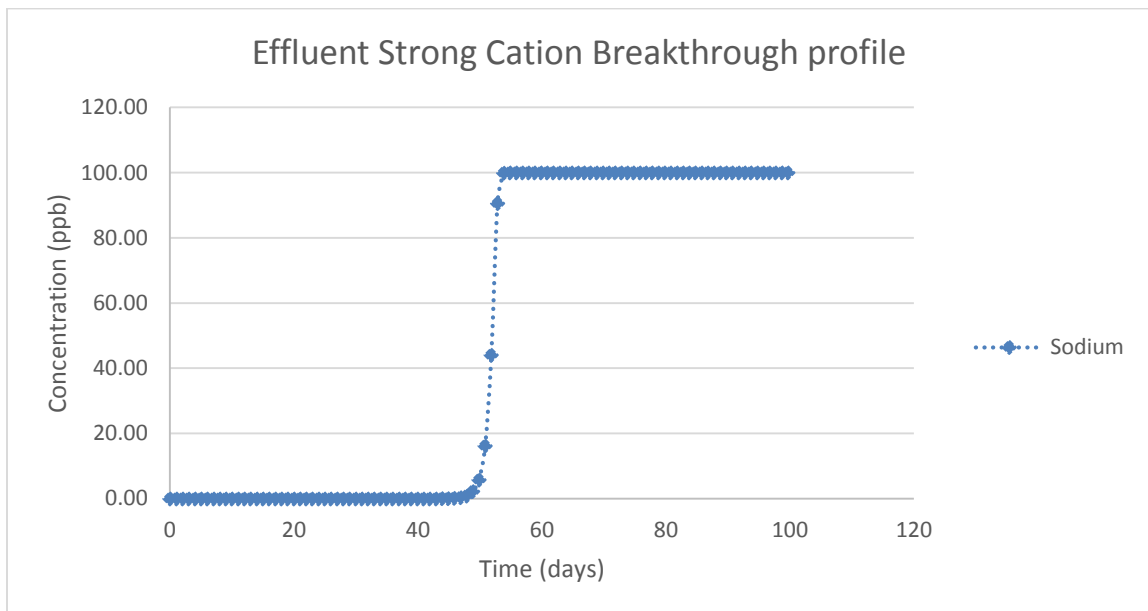

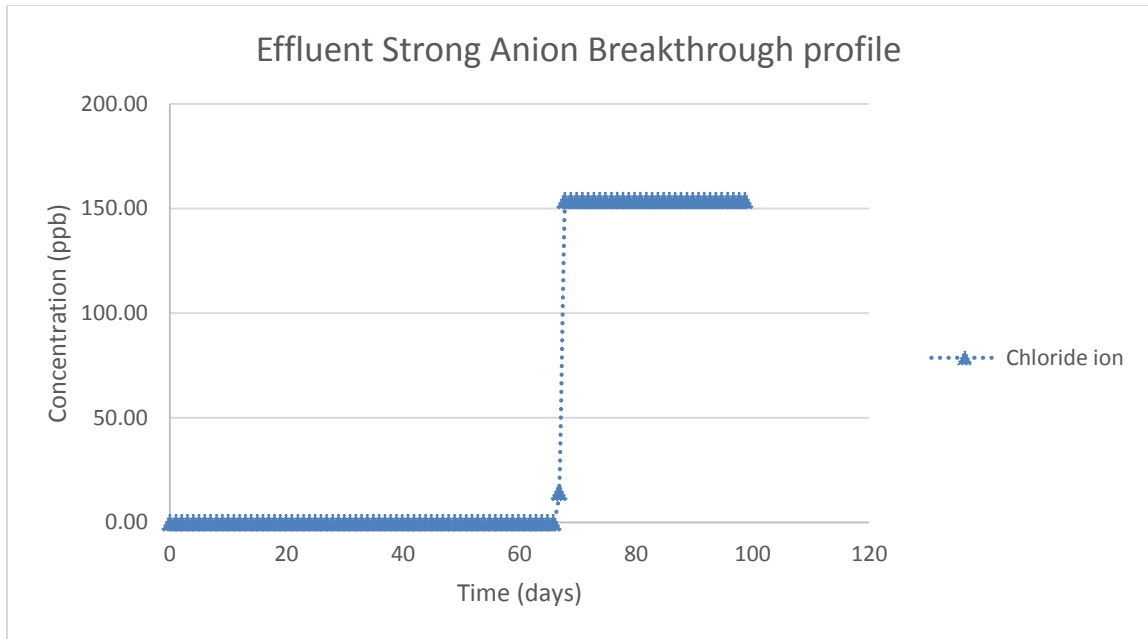Figure IV-1. Effluent strong cation breakthrough for powdered resin system

Figure IV-2. Effluent strong anion breakthrough for powdered resin system

From figure IV-1 shows effluent strong cation breakthrough profile and figure IV-2 represents effluent strong anion breakthrough profile for powdered resin system. Figure IV-1 shows that there is sudden change in the concentration of Na^+ at breakthrough point and it settles at 100 ppb which is concentration of Na^+ in the influents stream. Figure IV-2 shows that concentration of Cl^- settles at 154 ppb after breakthrough which matches with the influent concentration of Cl^- in the influent stream. This results validates that the models prediction of column material balance. Results using different service parameters is represented in appendix B.

Parametric analysis

One of the objectives from this model is to predict the effect of change of resin bead resin bead size and depth of resin bed for powdered resin system. A parametric analysis has been done to determine the effects of resin bead size and depth of resin bed on the performance of the powdered resin condensate polishing system.

Effect of Depth of Resin Bed

Several simulations has been done and analyzed to find out the effect of depth of resin bed on the performance of ion exchange system. Table IV-3 represents the bed geometry and operation parameters of the system.

Table IV-3. Bed geometry and service parameters data-1 for BWR powdered resin system for resin bed size comparison

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.75-1.25
Flow rate (gpm)	50
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Feed pH	9.3
Temperature (^{o}C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Six simulations has been done to compare the effect of the depth of resin bed on performance of condensate polishers using bed geometry and operation parameters mentioned in table IV-3. The simulation results is shown in figure IV-3 and figure IV-4.
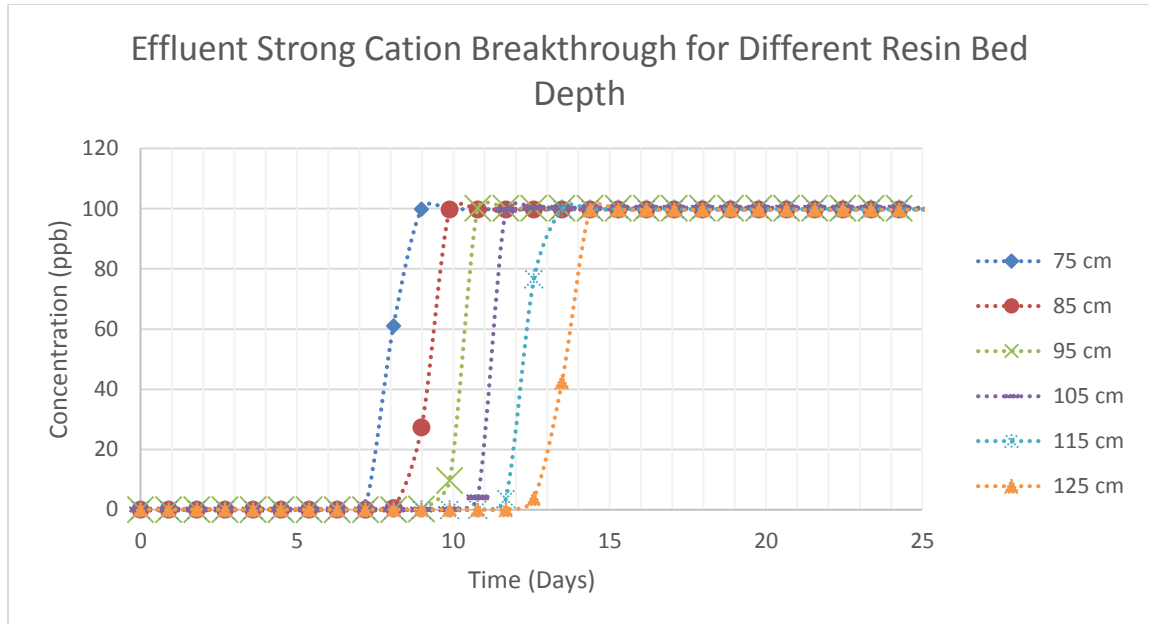

Figure IV-3. Effluent strong cation breakthrough for powdered resin system for different resin bed depth

Figure IV-3 represents the strong cation breakthrough profile for powdered resin ion exchange system with different depth of resin bed. The figures shows that, with increase of depth of resin bed it takes longer time for cation breakthrough. The service period of the ion exchange system increases with increase in the depth of resin bed. Several simulations has been done with variable parameters for 75cm and 125cm resin bed to determine the effects on the capacity. The results of the simulations is represented in following table IV-4.

Table IV-4. Simulation results for 0.75cm and 1.25cm resin bed for different parameters.

Depth of Resin Bed (cm)	Resin bead size (micron)			
	75	35	75	
	cation-anion ratio			
	0.37:0.63	0.37:0.63	0.5:0.5	
	Breakthrough Time (Day)			
0.75	5	6	8	Cation
1.25	8	10	13	
1.67	**1.60**	**1.67**	**1.63**	
% Error	4.00	0.00	2.50	
0.75	5	4	5	Anion
1.25	9	7	8	
1.67	**1.80**	**1.75**	**1.60**	
% Error	8.00	5.00	4.00	

From the data in table IV-4, it is found that, the capacity of the resin bed is proportional to the depth of the resin bed within 10 percentage of error. So this model can be a useful tool to get some idea about resin bed depth using the simulation results based on the requirements of the system in the industry.
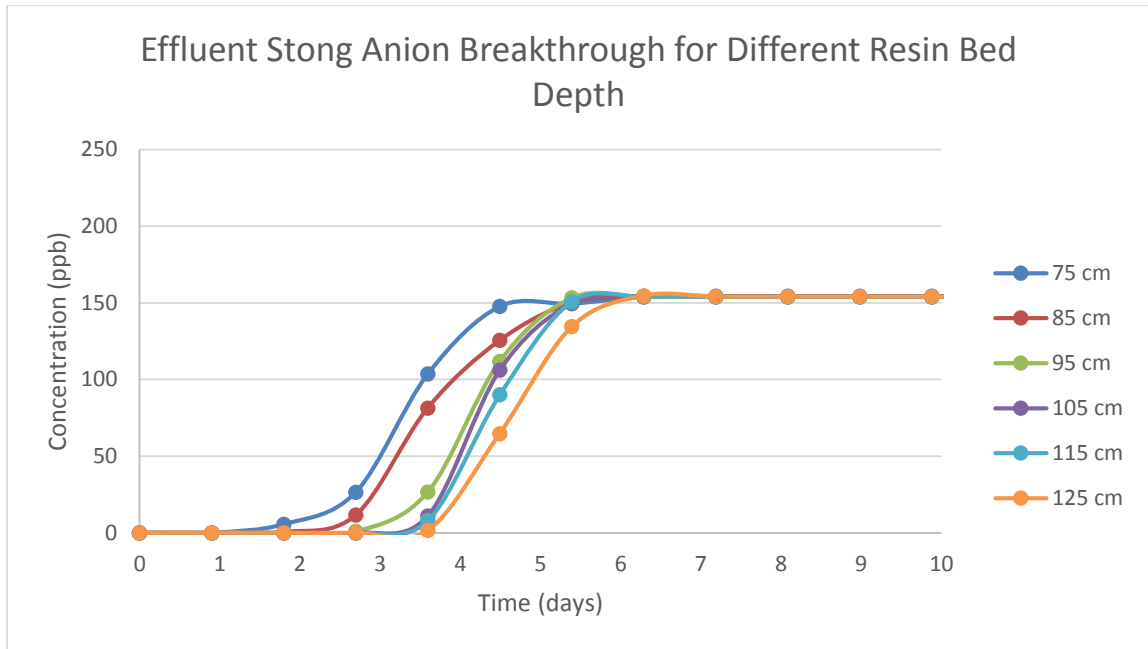
Figure IV-4. Effluent strong anion breakthrough for powdered resin system for different depth of resin bed.

. Figure IV-4 represents the effluent strong anion breakthrough with same operating parameters and it is found that for anion, it also take longer time for breakthrough.

Another two simulations is done with the parameters presented in table IV-5.

Table IV-5. Bed geometry and service parameters data-2 for BWR powdered resin system for resin bed size comparison

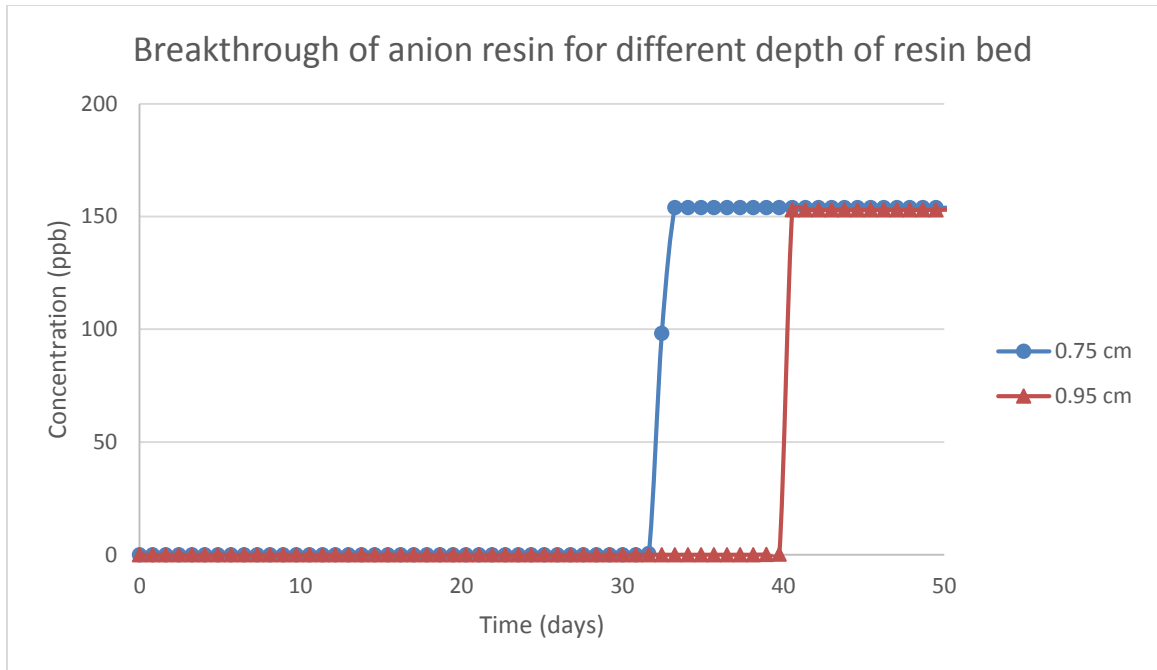| Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.75, 0.95
Flow rate (gpm)	4
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Feed pH	9.3
Temperature (^{o}C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0035
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0035
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure IV-5. Effluent strong anion breakthrough for powdered resin system

The results of this simulation is presented in figure IV-5. So, increase in resin bed depth increases the time for both anion and cation to breakthrough. So, based on the parameters and requirements of the system the resin bed depth can be predicted using this model. More simulation results is shown in APPENDIX B.

Effect of resin bead size

Parametric analysis has been done to see the effect of resin bead size on performance of condensate polisher. Table IV-6 represent the operation parameters and resin bed geometry of the ion exchange system. Two simulation has been done with two different resin bead size. The bead size of anion and cation ion exchange resin is considered same in one particular simulation.

Table IV-6 Bed geometry and service parameters data-1 for BWR powdered resin system for resin bead size comparison.

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	1
Flow rate (gpm)	50
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Feed pH	9.3
Temperature ($^{\circ}$C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0035, 0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0035, 0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure IV-7 shows the results of the two simulations. All the service parameters are remain constant except the bead size of the ion exchange resin. The history of strong cation breakthrough is represented in figure IV-6. As the size of the resin bead size decrease, the surface area of the powdered resin increases and it gives higher surface area to weight ratio. Specifically, both exchange rate and utilization of ion exchange capacity are inversely proportional to the diameter of

the resin particle. The model also predict increase in ion exchange capacity as it took longer time

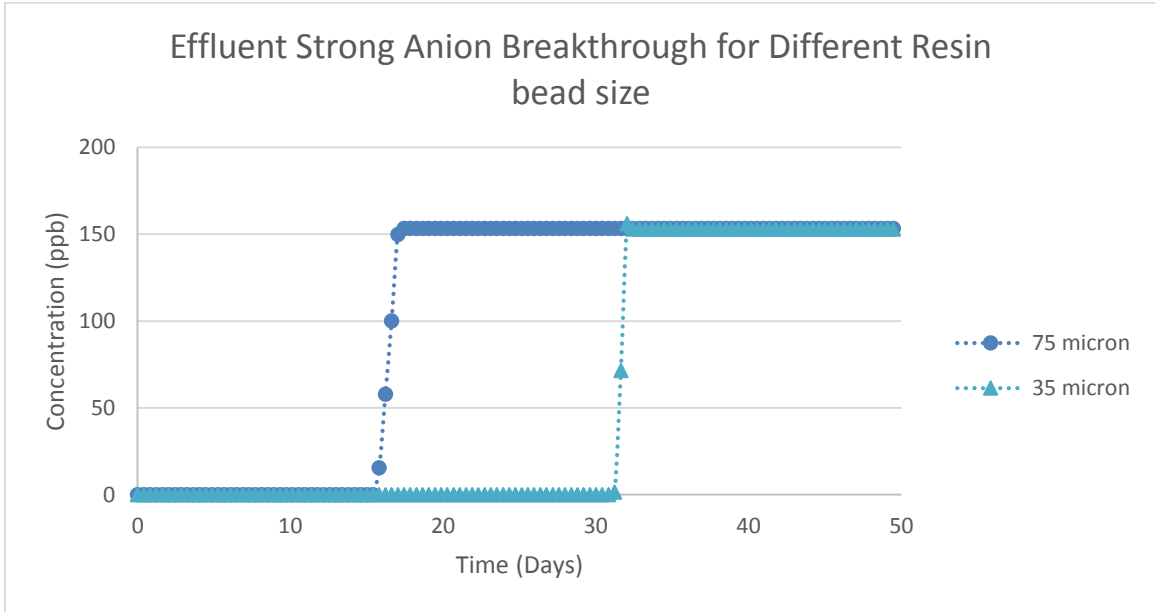for anion ion exchange resin to breakthrough with smaller size of resin.

Figure IV-6. Effluent strong anion breakthrough for powdered resin system for different resin bead

size

A number of simulations has been done to investigate the effect of resin bead size

for which the operating parameters are given in the following table IV-7. The bead size of

both anion exchange resin and cation exchange resin varied from 0.45 μm to 0.65 μm.

Table IV-7: Bed geometry and service parameters data-2 for BWR powdered resin system

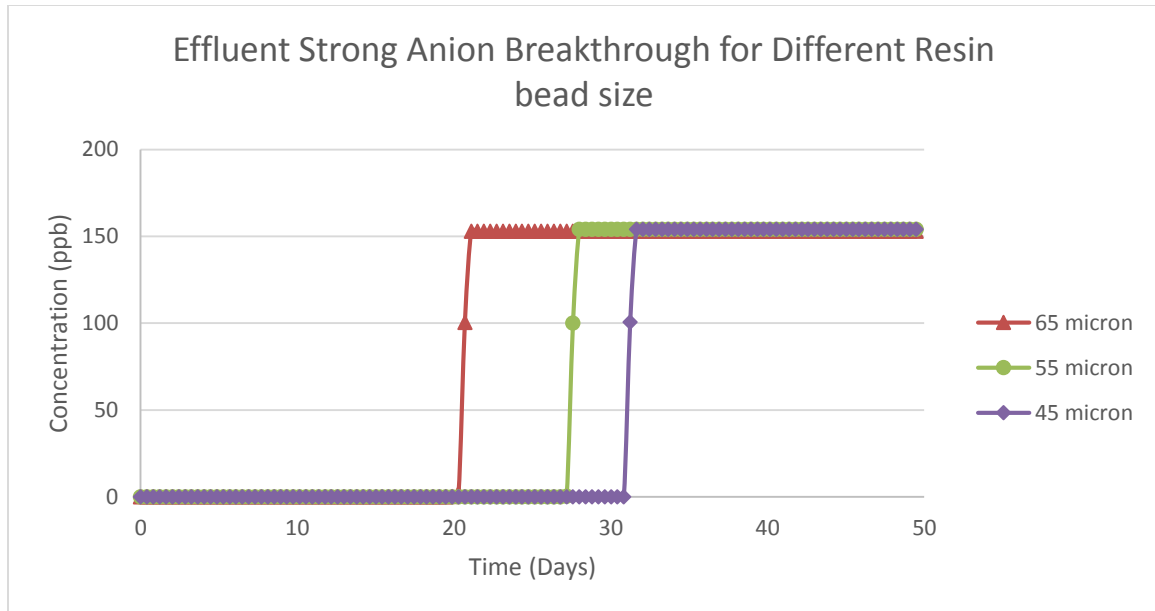| Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	1
Flow rate (gpm)	40
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Feed pH	9.3
Temperature (^{o}C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0045, 0.0055, 0.0065
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0045, 0.0055, 0.0065
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure IV-7. Effluent strong anion breakthrough for powdered resin system to compare effect of different resin bead size

Figure IV-7 represents the profile of strong anion breakthrough for different resin bead size. The graph also predict increase in ion exchange capacity for smaller resin bead and the time for breakthrough is longer than comparatively larger resin bead.

Simulation results for multiple anion and cation system

The model can handle system containing multiple anion and cation in any ion exchange system. The following Table IV-8 represents bed geometry and service parameters of condensate polishing system containing multiple anion and cation in the influent stream. Table IV-9 provides the feed water concentrations of different constituents of the system.

Table IV-8 Bed geometry and service parameters of BWR powdered resin system containing multiple anion and cation

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.75
Flow rate (gpm)	2580
Volume fraction of cation resin	0.575
Volume fraction of anion resin	0.425
Void fraction	0.35
Feed pH	9.3
Temperature (^{o}C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Table IV 9: Feed water constituents concentrations for multiple cation and anion

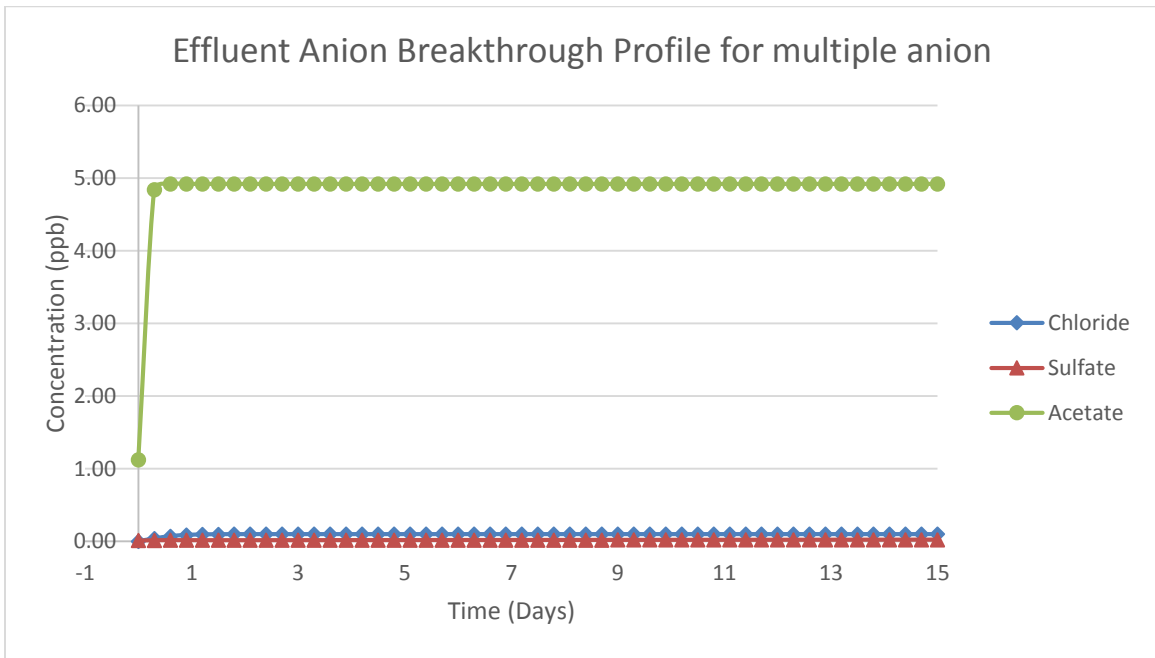| Ion	Influent Concentration (ppb)
Na$^+$	0.05
NH3	100
ETA	1700
Cl$^-$	0.1
Sulfate	0.1
Acetate	5

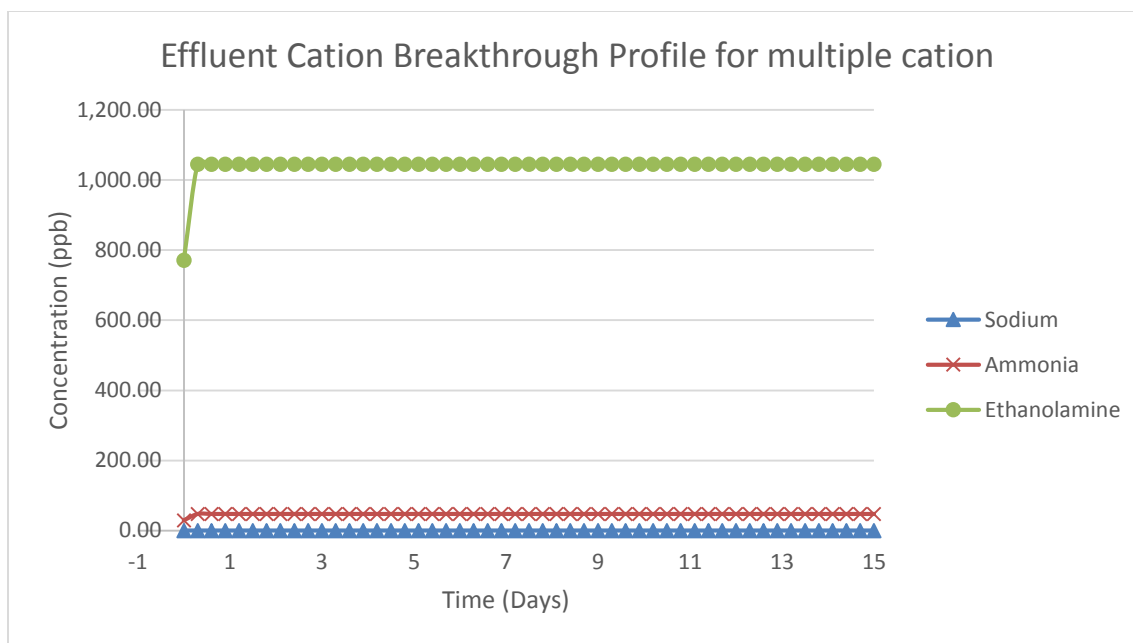Figure IV-8. Effluent anion breakthrough profile for multiple anion system

Figure IV-9. Effluent cation breakthrough profile for multiple anion system

Figure IV-8 and figure IV-9 represents the effluent anion and cation breakthrough profile respectively for multiple anion and cation system. The process contains two strong anion and one weak electrolyte species and two strong cation and one weak electrolyte. So, the model can handle multiple species with different valence and selectivities.

Effects of different parameters on resin performance

Sensitivity of resin capacity to change in different parameters is important to predict the performance of powdered ion exchange system. Bed depth, resin bead diameter, flowrate of influent stream, and cation to anion resin ratio were varied to run simulations and study the effects on performance of ion exchange capacity. The following Table IV-10 represents the service parameters. One variable was changed at a time by keeping other variable as constant. Breakthrough time is considered as performance index. Figure IV-10 and Table IV-11 represents the breakthrough time for different parameters using powdered ion exchange model. The flowrate of was 40 gpm for the result shows in figure IV-10 and Table IV-11.

Table IV-10 Bed geometry and service parameters of BWR powdered resin system to determine effects of change in multiple parameters

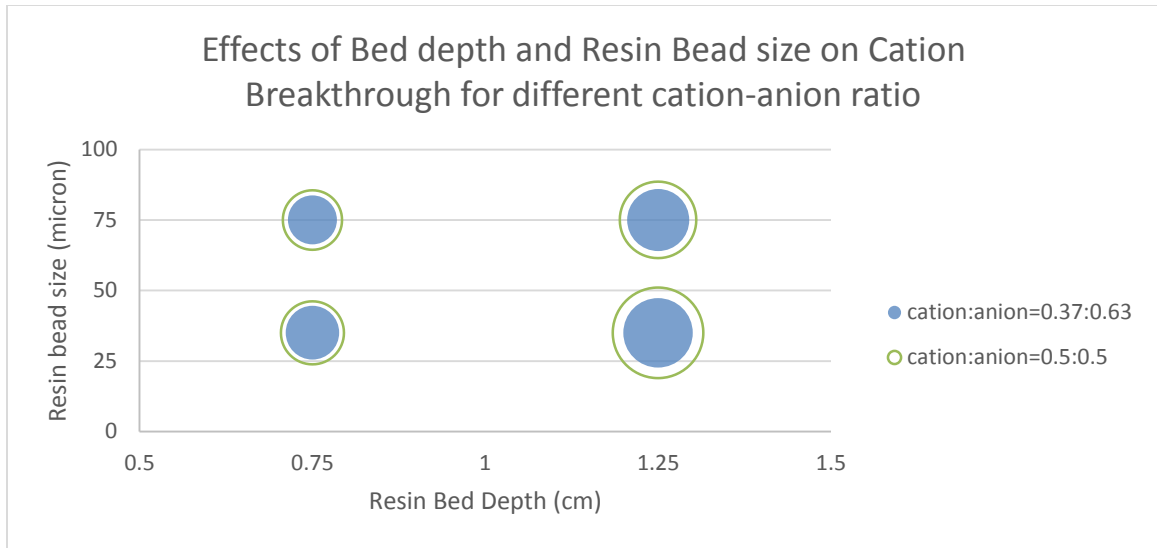| Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.75, 1.25
Flow rate (gpm)	40, 20
Volume fraction of cation resin	0.37, 0.5
Volume fraction of anion resin	0.63, 0.5
Void fraction	0.35
Feed pH	9.3
Temperature (°C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0035, 0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0035, 0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure IV-10: Powdered resin ion exchange system performance for different parameters.

In figure IV-10 the size of the circle represents the breakthrough time for cation ion. It represents that the capacity of ion exchange increase with decrease in resin bead size and increases with resin bed depth. The blue solid circle represents cation breakthrough time for cation to anion ratio 0.37 to 0.63 and the open green circle represents breakthrough time for cation to anion ratio as 0.5 to 0.5.

Table IV-11: Effects of Bed depth and Resin Bead size on Cation Breakthrough for different cation-anion ratio

Resin Bead size(micron)	Resin Bed depth (cm)	Time (Day)	cation-anion ratio
75	0.75	5	0.37:0.63
75	1.25	8	
35	0.75	6	
35	1.25	10	
75	0.75	8	0.5:0.5
75	1.25	13	
35	0.75	9	
35	1.25	18	

Table IV-2 represents the cation and anion loadings and the influent concentration. From the graph and the value from table IV-11, it can be said that, the effect of resin bed depth is more significant than resin bead size. The cation to anion ratio of the resin can be selected based on the requirement of the system. Factor analysis can be done to find the load of different parameters change using the simulations results to predict the performance of the ion exchange system. Several simulation results are mentioned in appendix B.

Stability of the model

Stability is one of the major factors for the effectiveness of the model. The step size of distance and time plays important role to solve the model equations. The model provide stable results and smooth graph for small step size. The step size for both parameters: distance and time was set as 0.01 for all the simulations in this study. It is observed that, if the step size is smaller then, after breakthrough the model does not provide stable and smooth concentration profile. The model provides more accurate results with decrease in the step sizes. The better and stable simulation results can be achieved by decreasing both the distance and time step sizes. The mass balance of anion resin is found more sensitive to the distance step size of the model. The mass balance percentage error also increased with larger step size. On the other hand, large step size will decrease the simulation runtime. So balance must be done between runtime and accuracy of simulation result. The following figure IV-11 represents material balance error percentage for different distance and time step sizes.
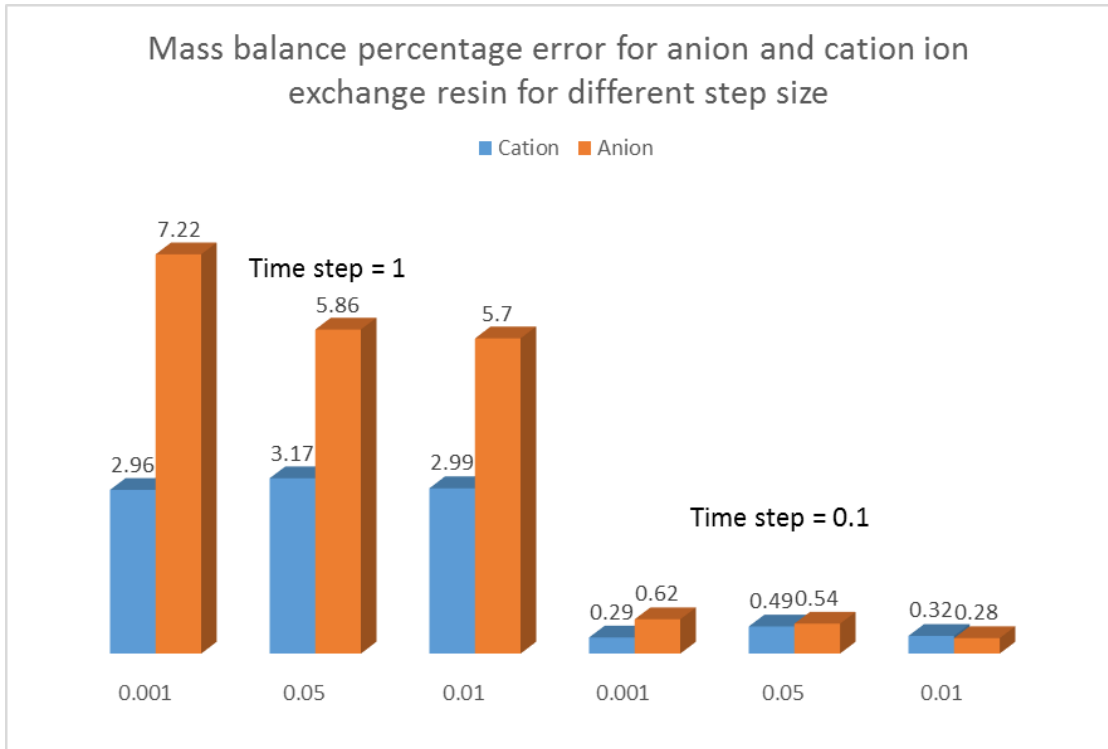
Figure IV-11: Material balance error percentage for cation and anion mass

balance for different step size

The step size for this study was 0.01 for both time and distance step and runtime was for 100 days. The simulations runtime can vary based on service parameters, number of ions in the system, and also computation capability of machine. The calculation time is one of the major issues for industrial applications. The following table represents some run time data for simulations in this study.

Table IV-12: Simulation runtime with step size

Step Size	Runtime (hr)
Distance = 0.01, Time = 0.01	4.00
Distance = 0.01, Time = 0.1	1
Distance = 0.05, Time = 0.1	0.67

The results from the powdered resin can be applicable not only in power industry but also in different other industry. The total amount of water treated by the resin system can also be calculated from the model. The depth of resin bed and resin bead size can be optimized using the model data. To predict the service cycle and handle any sudden change in the system can also be optimized using the model.

CHAPTER V

CONCLUSIONS AND FUTURE STUDY

Conclusions

The generalized mixed bed ion exchange model has been applied in powdered ion exchange resin system for condensate polishing in power industry. The depth of resin bed and bead size of the both anion and cation ion exchangers is considered as limiting parameters. The range 0.75 cm to 1.25 cm of resin bed depth was used in this model. Also the resin bead size of both anion and cation ion exchange resin was varied from 35 micron to 75 micron. From the simulation results, it was found that, with distance step size less than 0.01 and time step size less than 0.01, the model provides smooth curve for breakthrough of anion and cation ion exchange resin. The effluent concentration gradually approaches the influent concentrations in infinite run time. The simulation results provide indication that, the model can be applied to powdered resin system. Simulations with multiple components also completed without fail. The simulations run successfully for different service parameters.

A parametric analysis has been done to investigate the effect of depth of resin bed and resin bead size. From simulation results, it was found that with increase in resin bed depth, it took longer time to breakthrough for ion exchange resin. The capacity of resin bed was found to be proportional

to the depth of resin bed with some error. Small bead size of ion exchange resin takes longer time for breakthrough compared with large ion exchange resin bead.

The model may be applied to determine optimum resin bed depth and resin bead size. Using sensitivity analysis, the model can be useful tool to predict the effects of different parameters on the performance of the ion exchange system.

This study shows the preliminary but promising results for powdered ion exchange system. There are also some limitations with this model. After breakthrough, the model does not provide smooth and stable graph. With proper time and distance steps the result can be improved. There is also scope to improve the solving method that will reduce the simulation time. The models needs to be applied with radioactive isotopes with the service parameters used in nuclear power plant.

Future study

There is still a lot of scope to improve the model and the model can be applied in different industries along with power plants. The computational time is one of the major issues with this model. Further work is required to decrease the computational time for simulation. With simulations, the comparison between mixed bed ion exchange and powdered ion exchange system can be compared before building the projects. The model can be improved to optimize resin bed depth, resin bead size and mixing ratio of anion and cation ion exchange resin for different service parameters.

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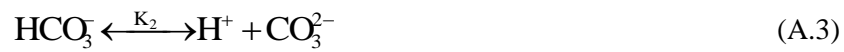[13] Lin K.H. Use of ion exchange for the treatment of liquids in Nuclear power plants, December 1973.

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APPENDIX A

Type II dissociative species

Diprotic acid □ carbonate are example of Type II dissociative species respectively. This species dissociate in two steps. The dissociation equilibrium of carbonates can be expressed as

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad\qquad (A.1)$$

$$H_2CO_3 \xleftrightarrow{\quad K_1 \quad} H^+ + HCO_3^- \qquad\qquad (A.2)$$

$$HCO_3^- \xleftrightarrow{\quad K_2 \quad} H^+ + CO_3^{2-} \qquad\qquad (A.3)$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad\qquad (A.4)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad\qquad (A.5)$$

Hence, the following equations represent the generalized dissociation equilibrium for Type II dissociative species

$$K_1 = \frac{[TypeII\_MonoIon][Dum\_Ion]}{[TypeII\_Mole]} \qquad\qquad (A.6)$$

$$K_2 = \frac{[TypeII\_DiIon][Dum\_Ion]}{[TypeII\_MonoIon]} \qquad\qquad (A.7)$$

implementing equation (A.6) and equation (A.7) in the computer code, the model can

handle any weak electrolytes having the same dissociation equilibrium [6].

Type III dissociative species

The characteristics of three-step dissociation of Type III species can be described in similar ways

as Type II and Type I species.

The generalized dissociation equilibrium equations of Type III species are as follows:

$$K_1 = \frac{[Dum\_Ion][TypeIII\_MonoIon]}{[TypeIII\_Mole]} \qquad (A.8)$$

$$K_2 = \frac{[Dum\_Ion][TypeIII\_DiIon]}{[TypeIII\_MonoIon]} \qquad (A.9)$$

$$K_3 = \frac{[Dum\_Ion][TypeIII\_TriIon]}{[TypeIII\_DiIon]} \qquad (A.10)$$

Any Type III dissociative electrolytes can be handled by implementing equation (A.8) through
(A.11) into the charge balance equation of the model.

APPENDIX B

Table B.1. Service and operating parameters for powdered resin ion exchange system

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	1.5
Flow rate (gpm)	4
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Temperature (ºC)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure B.1: Effluent strong cation breakthrough profile

Table B-2 Bed geometry and service parameters for BWR powdered resin system to compare

different resin bed

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	1.05, 1.15, 1.25
Flow rate (gpm)	4
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Temperature (°C)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure B.2: Effluent strong anion breakthrough profile to compare the effect of different depth of resin bed.

Table B-3 Bed geometry and service parameters for BWR powdered resin system to compare different resin bead size

Parameter	Value
Bed Diameter (m)	1.5
Bed Depth (cm)	0.75
Flow rate (gpm)	40
Volume fraction of cation resin	0.4
Volume fraction of anion resin	0.6
Void fraction	0.35
Temperature (ºC)	40
Cation Resin (Dowex Monosphere 650C)	
Bead diameter (cm)	0.0075, 0.0045
Capacity (meq/ml)	1.9
Form	Hydrogen
Anion Resin (Dowex Monosphere 550A)	
Bead diameter (cm)	0.0075, 0.0045
Capacity (meq/ml)	1.1
Form	Hydroxyl
Fouling effects	Yes
Desulfation	No
Resin heel effects	No

Figure B.3: Effluent strong anion breakthrough profile to compare the effect of different depth of resin bead size.
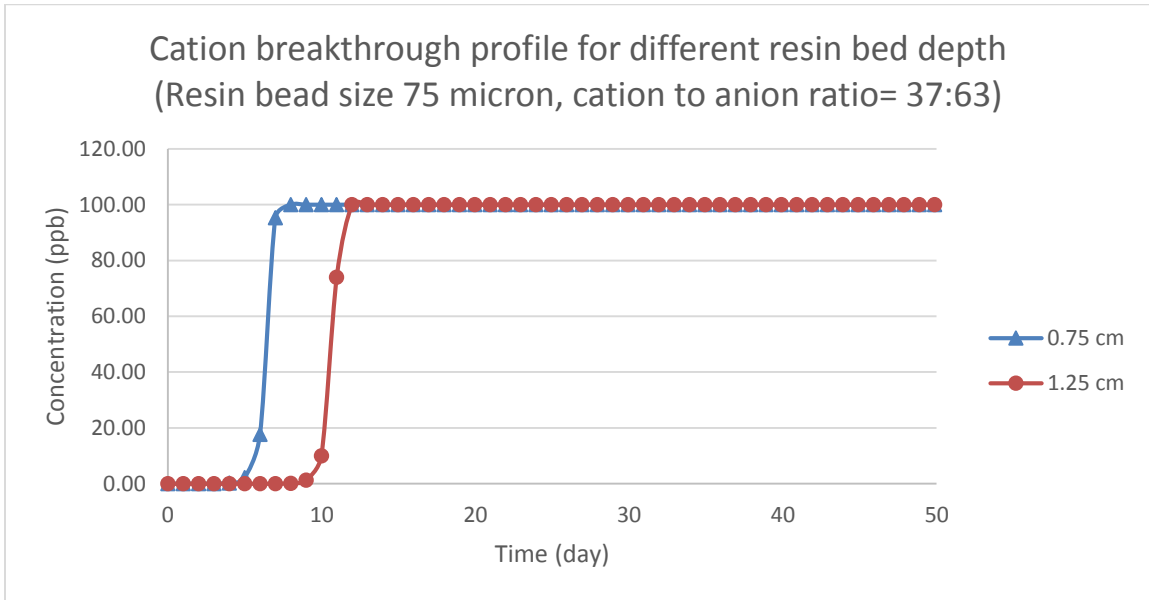

Figure B.4: Effluent strong cation breakthrough profile (Resin bead size 75 micron, cation to anion ratio= 37:63)
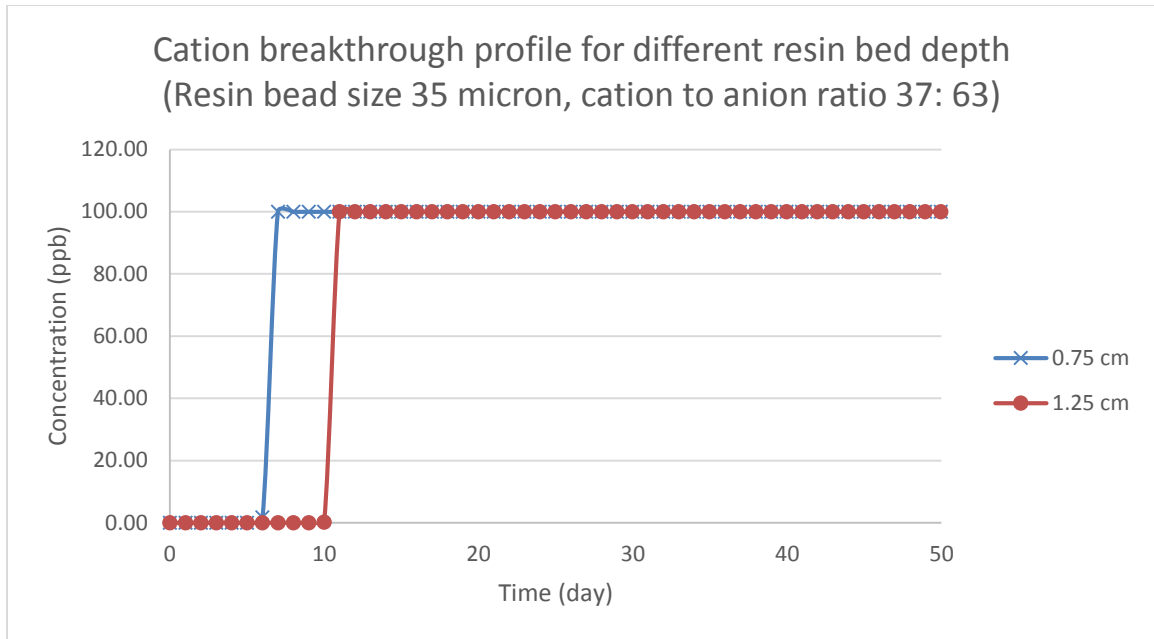
Figure B.5: Effluent strong cation breakthrough profile (Resin bead size 35 micron, cation to anion
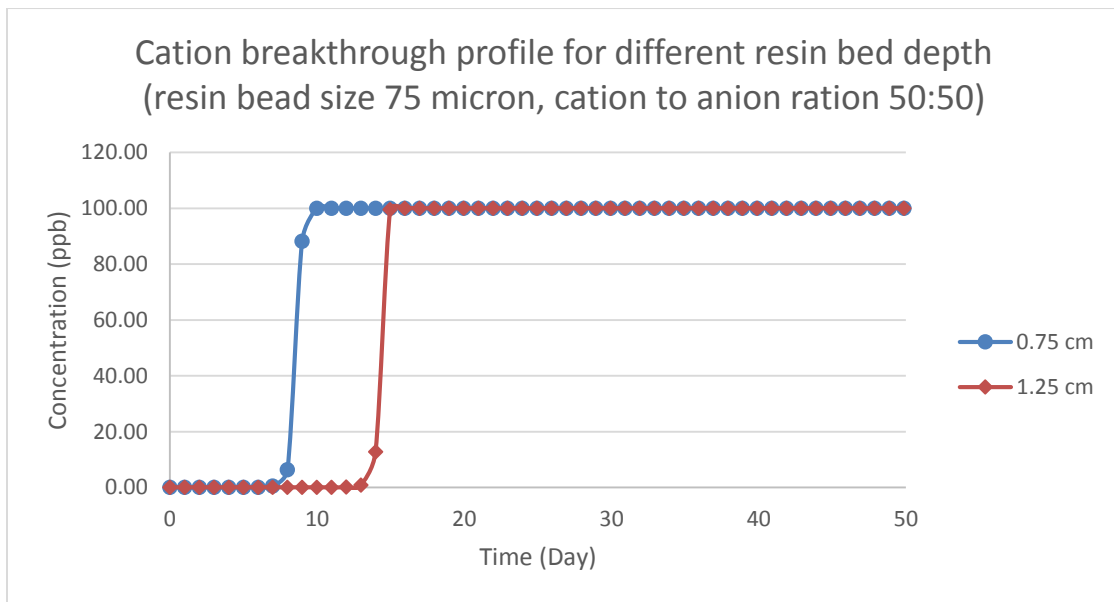
ratio= 37:63)

Figure B.6: Effluent strong cation breakthrough profile (Resin bead size 75 micron, cation to anion
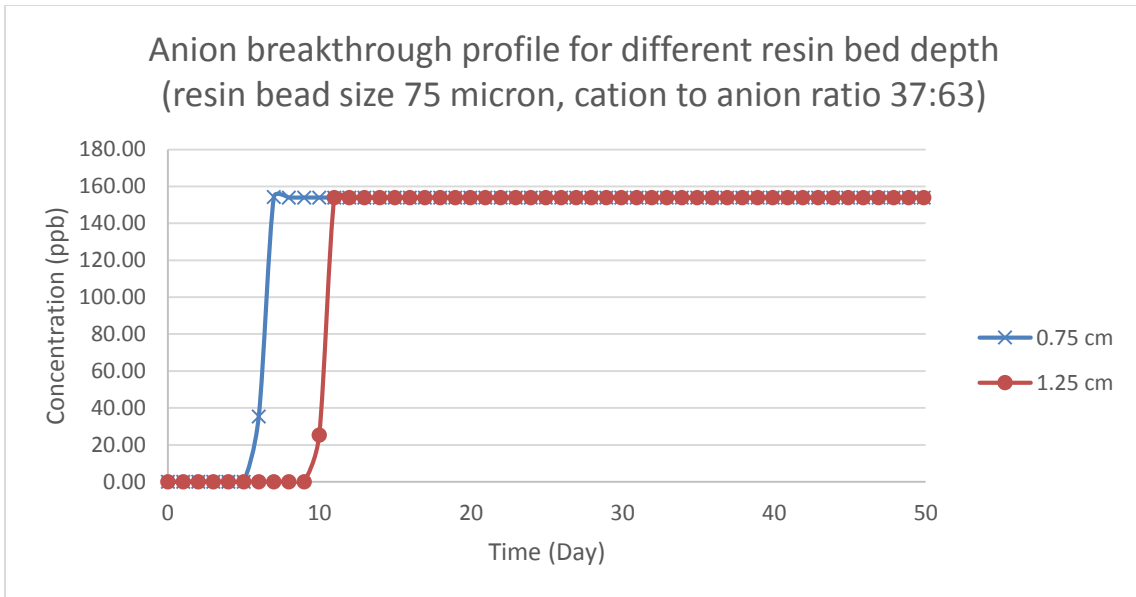
ratio= 50:50)

Figure B.7: Effluent strong anion breakthrough profile (Resin bead size 75 micron, cation to anion ratio= 37:63)
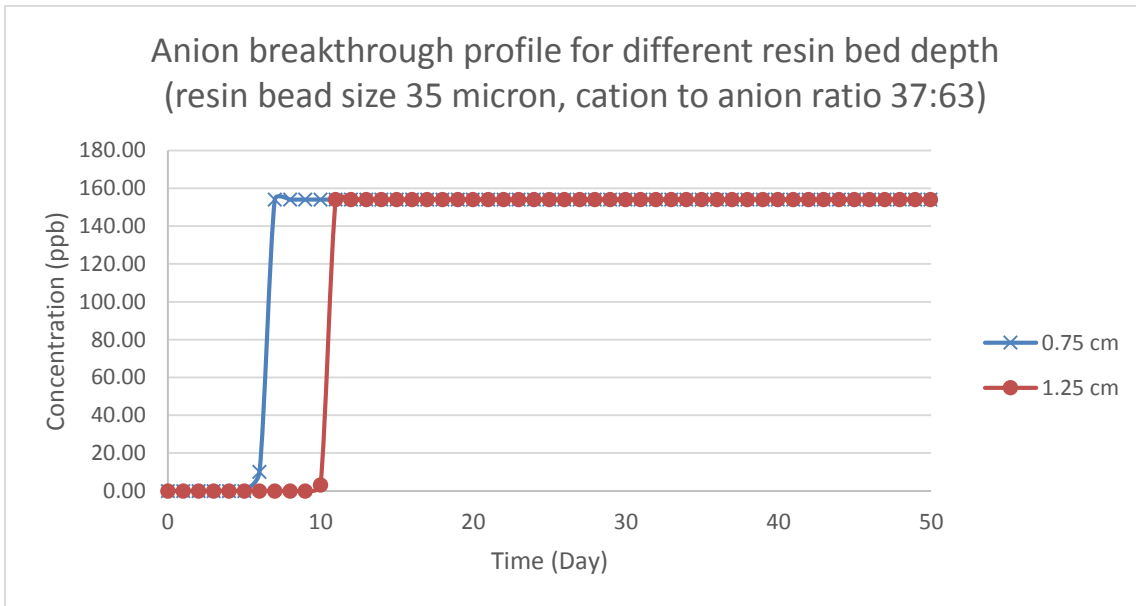

Figure B.8: Effluent strong cation breakthrough profile (Resin bead size 35 micron, cation to anion ratio= 37:63)
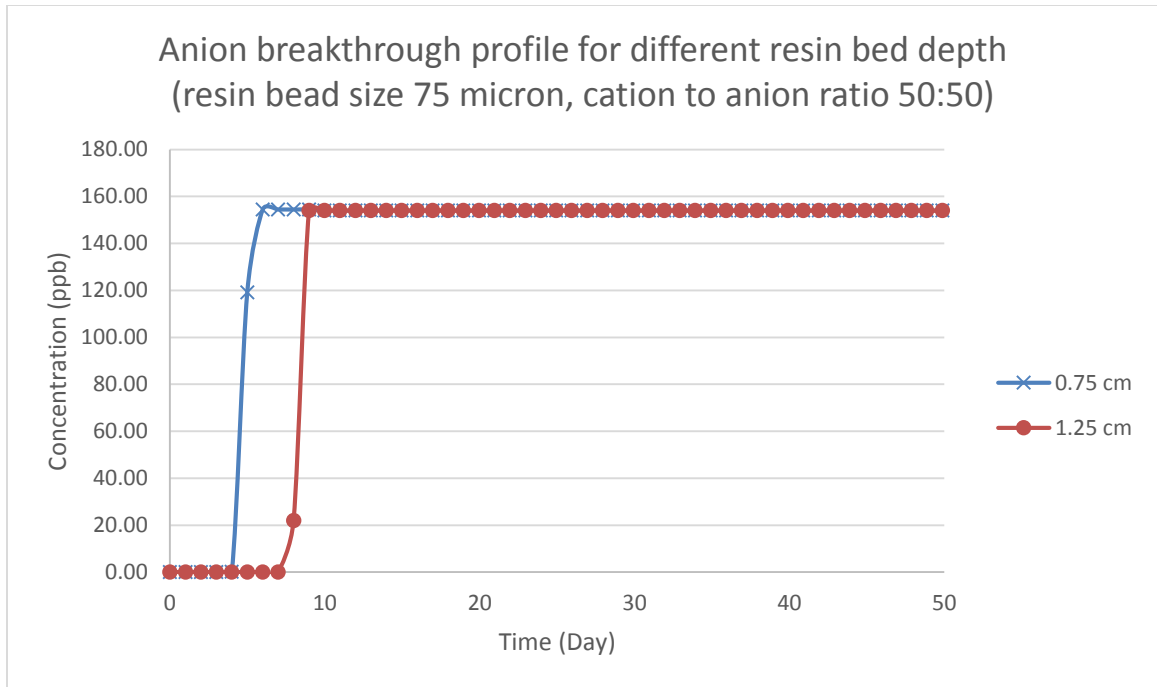
Figure B.9: Effluent strong cation breakthrough profile (Resin bead size 75 micron, cation to anion ratio= 50:50)

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