A MODERATOR ION EXCHANGE MODEL TO PREDICT CARBON-14 BEHAVIOUR DURING OPERATIONS

D.K. Ryland, L. Rodrigo and D.H. Barber
Atomic Energy of Canada Limited, Chalk River Ontario, Canada

Abstract

Carbon-14 emissions from CANDU 6 stations are reduced through the removal of inorganic carbon ions by the ion exchange (IX) columns in the moderator purification system. A model has been developed to simulate the ion exchange behaviour of anions and cations present in the moderator. The model can be used to generate breakthrough curves for IX columns.

Results from the program were compared to breakthrough curves generated by a small-scale experimental facility as well as data collected from Wolsong-3 where the IX column remained in service well past the recommended time. In both cases, the breakthrough curves were similar to the collected data.

1. Introduction

Carbon-14 is produced in a CANDU reactor mainly by the (n,α) reaction with oxygen-17. Because of high neutron fluxes combined with the large volume of heavy water in the core, the majority of the carbon-14 (94.5%) is produced in the moderator. In the moderator system, carbon-14 is present mainly as a mixture of CO_2 in the cover gas in equilibrium with dissolved carbonates, bicarbonates and CO_2 in the water. The dissolved $^{14}CO_2$ will exist as a combination of $D_2{}^{14}CO_3$/ $D^{14}CO_3{}^{-}$/$^{14}CO_3{}^{-2}$ though predominantly in bicarbonate form under normal operating conditions and a pH of ~6 [1]. Emissions of carbon-14 from reactors occur through venting or leakage of the cover gas and can be minimized by removing the dissolved carbonates in the moderator water with an ion exchange (IX) purification system. Effective control of carbon-14 emissions therefore requires good performance of the moderator IX columns.

The moderator purification system in CANDU 6 stations consists of five IX columns, each containing a mixed bed of strong-acid cation and strong-base anion exchange resins. The function of this system is to minimize the concentration of ionic impurities that will cause a build-up of D_2 in the system, minimize the corrosion of components, and control various liquid poisons in the moderator system. Carbon-14 emissions have been reduced significantly over the last number of years due to initiatives such as changing resins more frequently and not using resins for general purification that had been previously used for gadolinium removal. The impact of these initiatives is that stations generate more solid waste.

AECL has developed a model to simulate the absorption of multiple anions commonly found in Moderator water. This model could become a useful tool to optimise resin bed usage and minimize the quantity of solid wastes that require disposal.

This paper describes the structure of the ion exchange column model and compares results from the simulation with experimental and station data.

2. IX Column Model

2.1 Basis for Model Equations

The model is based on a structure developed by Barber [2] to predict gadolinium precipitation in cases where gadolinium nitrate solutions have been exposed to strong-base anion resins. A short increment of an IX column was modelled that contains a mixed bed of strong-acid cation and strong-base anion resin. The model calculates the concentration of each species at several locations within a horizontal increment of the bed: the bulk fluid, the inner surface of the thin liquid film around the cation resin bead, the inner surface of the thin liquid film around the anion resin bead, and within the resin beads themselves. Unlike earlier models, cations were permitted to diffuse into the anion film, and anions were permitted to diffuse into the cation film.

A schematic of the short increment of column is shown in Figure 1. A complete IX column was modelled by linking a number of these increments together.

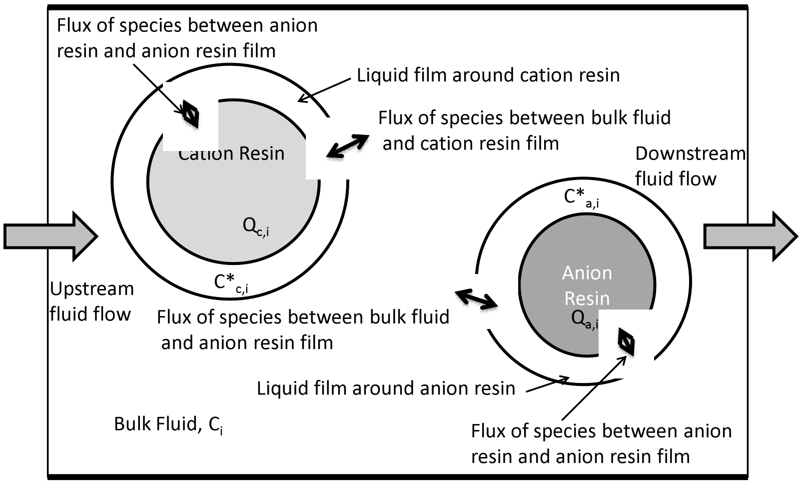

Figure 1 Schematic of IX column increment

A set of equations was derived to determine values for the unknown concentrations. These equations include diffusion flux equations, equilibrium relations between the concentrations in resin beads and the liquid films at the resin bead surfaces, equilibrium relations between chemical species, mass balance equations and electroneutrality equations. In all cases, film diffusion was assumed to be the rate-controlling step.

The model accounts for ionic species that are typically found in the moderator of CANDU nuclear reactors, such as nitrates, borates and carbonates/bicarbonates. The majority of the nitrates are introduced as $Gd(NO_3)_3$ through the liquid injection shutdown system (LISS) and the moderator liquid poison system (MLPS) for reactor shutdown and also for shim control in some CANDU stations.

In this full column model, anion species were considered since the goal is to predict carbon-14 emissions. Barber's model [2] was focussed on the relevant species required to predict that gadolinium hydroxide precipitates in the liquid film surrounding the anion resin beads.

2.2 Model Parameters, Initial Conditions and Boundary Conditions

Parameters required to solve the model equations are the diffusivities of ions in water at infinite dilution, resin characteristics (e.g., capacity, resin volume, volume ratio of anion and cation resins, average bead diameter) and selectivity coefficients for each anions with hydroxide ions and each cation with hydrogen ions. Initial conditions required are the feed water flowrate and concentrations of ionic species in the feed water. The pH of the feed water and the concentrations of ions within the films surrounding the ion exchange resin beads need to be determined accurately. These values are calculated within the program by solving the charge balance equation within the fluid region of interest.

Initial values for all species concentrations and their derivatives are required to start the simulation. The IX column is assumed to contain fresh resin. The bulk fluid in the IX column initially contains only hydrogen and hydroxide ions in concentrations determined by the specified pH of the fluid. The fluid film around the cation resin contains only hydrogen and hydroxide ions that are at the same initial concentrations as the bulk fluid. In addition to hydrogen and hydroxide ions, the fluid film around the anion resin contains inorganic carbon and chloride that are in equilibrium with the concentrations of these species in the fresh resin. Resin manufacturers provided specifications for maximum concentrations of all species present in the fresh resin. The concentrations of the other inorganic carbon species in the anion film were derived from equilibrium equations for these species. These concentrations were very small, but had to be specified correctly or the simulation would fail.

Initial estimates of the derivatives were zero for all unknowns except the bulk fluid concentrations in the column and the anion resin concentrations. The initial guesses for non-zero derivatives were calculated from the bulk fluid mass balance equations or resin-film equilibrium relations.

There was one boundary condition in the simulation. The feed flow and concentrations at the inlet of the IX column was specified, and it was assumed that these values did not vary.

2.3 Numerical Solution of the Model

The IX column was divided into a user-specified number of increments, which were assumed to act like continuous stirred tanks. The concentrations in each column increment were calculated sequentially down the column.

For each time step, the set of equations for each increment were solved simultaneously using the differential-algebraic equation [3] solver DDASKR available from NETLIB [4]. This equation solver uses backward differentiation formulas to simultaneously solve a system that contains both ordinary differential equations and algebraic equations.

3. Experimental System

An experimental facility was constructed to measure the time to breakthrough under known, controlled conditions so that the predictions from the model could be assessed.

Figure 2 shows a schematic diagram of the experimental set-up. The set-up was designed so that two ion exchange columns could be tested at the same time. The size of the columns was selected so that the residence time and superficial velocity of the fluid in the experimental system was similar to the values in the ion exchange columns within CANDU stations.

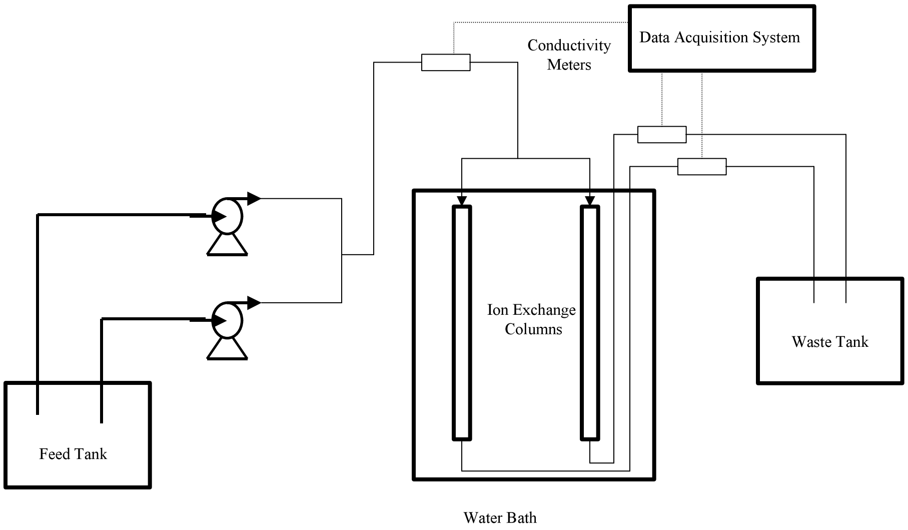

Figure 2 Schematic of Experimental Apparatus

The ion exchange columns were constructed of 12.7 mm diameter (1/2″) stainless steel tubing. The columns were 40 cm long. A small screen was spot welded to the bottom of the column to support the resin. Both IRN-150 and NRW-37 resins were used in the experiments. Once filled with resin, the columns were connected to the remaining tubing in the apparatus. The columns were then immersed in a temperature-controlled water bath to maintain the desired temperature throughout the experimental runs. The water bath controlled the temperature to ±0.1°C.

Feed was prepared by dissolving measured amounts of the desired ions in deionized water. The typical batch of feed solution for an experimental run was 50-100 L. Since the feed contained carbonate species that could equilibrate with carbon dioxide in the air, a nitrogen cover gas was applied over the feed tank. Feed solution was pumped to the columns using one of two liquid pumps. Once the solution passed through the columns, it flowed to a waste tank.

Conductivity meters measured the ion conductivity of the solution at the entrance and exit of the ion exchange columns. The conductivity meters have a range of 0-2000 $\mu S \cdot cm^{-1}$ with an accuracy of ±1%. The conductivity meters were connected to a data acquisition system that recorded the conductivity as a function of time.

Liquid sample lines were installed at the inlet and outlet of each ion exchange column. Samples of the inlet liquid were taken at the start of each run. Samples of the outlet liquid were taken periodically when the conductivity of the liquid began to increase, indicating the beginning of breakthrough. The water samples were analysed for ion content using ion chromatography.

4. Simulation of Small Scale Experiments

Model output was first compared with results from the small-scale experimental system where the column was fed with a solution containing nitrates and inorganic carbon species (bicarbonate, carbonate and dissolved carbon dioxide).

4.1 Bicarbonate Feed

The first test conducted was where an IX column filled with fresh NRW-37 resin was fed a solution prepared by adding a known amount of sodium bicarbonate to water. Figure 3 shows the conductivity of the feed and effluent solutions over the entire experimental run as well as the simulated effluent conductivity. The simulated effluent curve matches the experimental curve very well both in shape and the predicted time to breakthrough. A similar test was conducted using IRN-150 resin, but the agreement between the experimental and simulated curves was not as good.

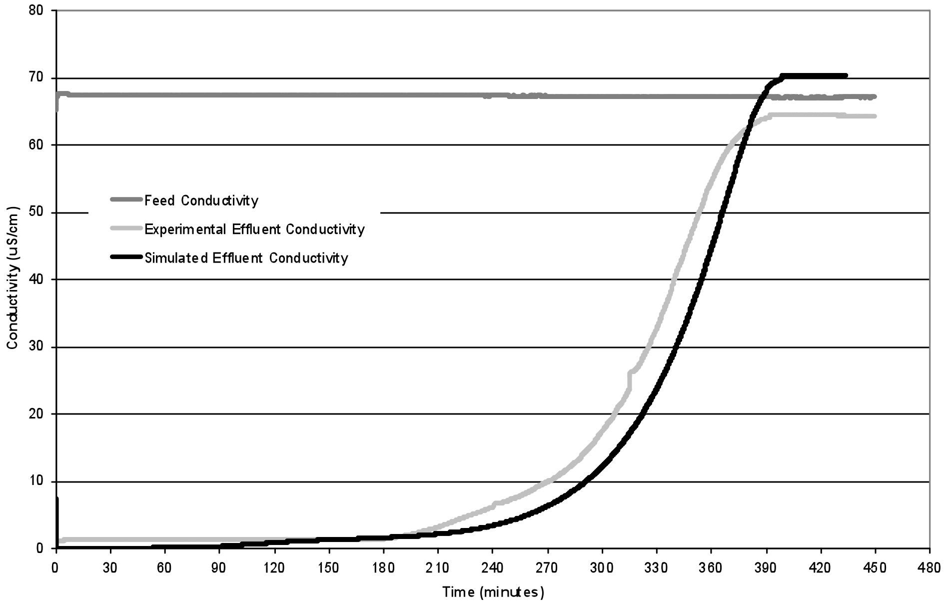

Figure 3 Effluent Conductivity: Inorganic Carbon Feed to IX Column with NRW-37 Resin

4.2 Nitrate Ion Feed

The next test was to feed an aqueous solution containing a known concentration of sodium nitrate to an IX column filled with fresh NRW-37 resin. Figure 4 compares the breakthrough curves, expressed in terms of the effluent conductivity, over the experimental run.

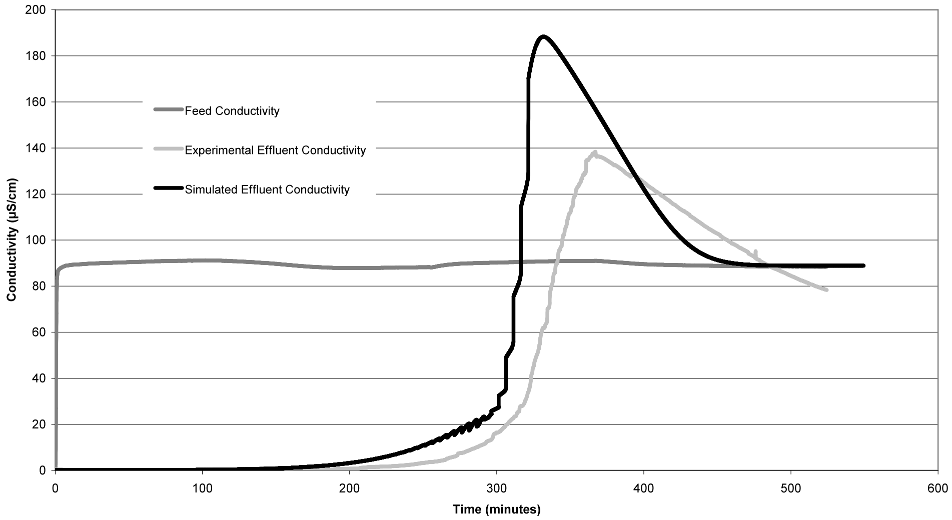

Figure 4 Effluent Conductivity: Nitrate Feed to IX Column with NRW-37 Resin

There are several similarities between the experimental and simulated breakthrough curves. Breakthrough begins at about the same time, and the simulation was able to predict the observed behaviour where the effluent conductivity was higher than the feed conductivity for a period of time.

However, the observed and simulated breakthrough curves also have differences. The peak in the simulated breakthrough curve occurs about 40 minutes earlier than in the experimental system and the peak conductivity is about 50 $\mu S \cdot cm^{-1}$ higher.

Figure 5 compares the observed and simulated effluent nitrate concentrations. While the effluent curves are similar in shape, the simulated curve is slightly sharper and predicts that the nitrate ion breaks through about 30 minutes earlier than was observed in the experiments.

The observed and simulated pH of the effluent solution is shown in Figure 6. The simulation correctly predicted that there would be a large decrease in pH when breakthrough began. The simulated drop in pH takes place at about the same time as was observed in the experiments. At this time, the anion resin was exhausted of hydroxide ions while hydrogen ions continue to be displaced from the cation resin. There is only a small change in hydrogen ion concentration, but the loss of balance between hydrogen and hydroxide ions in the bulk solution caused a large change in solution pH. Since hydrogen and hydroxide ions have large conductivities compared to the other species in the solution, the sharp change in the concentration of hydrogen ions caused the conductivity of the effluent solution to rise above the conductivity of the feed solution for a period of time.

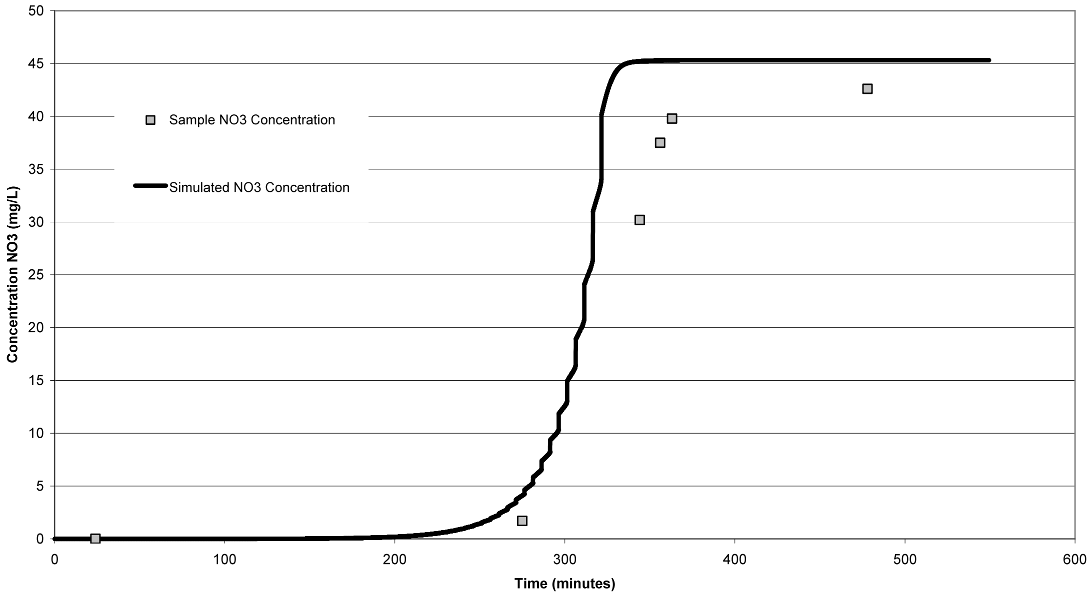

Figure 5 Effluent nitrate Ion Concentrations: Nitrate feed to IX column with NRW-37 Resin

The instabilities seen in the simulated curves are due to the near-zero concentrations of some of the carbon species. In these experiments, the only sources of carbon species are the residual amounts contained in the fresh resin. Thus, the concentrations of these species are extremely small in the bulk fluid and liquid films throughout the entire simulation. Instabilities in the simulated curves are caused by the presence of these near-zero values in the simulation and the strong linkage between the concentrations due to charge balances. The case shown used an IX column divided into 50 increments. Simulations with fewer column increments had large instabilities, but dividing the column into smaller increments did not reduce the instabilities in the effluent curves.

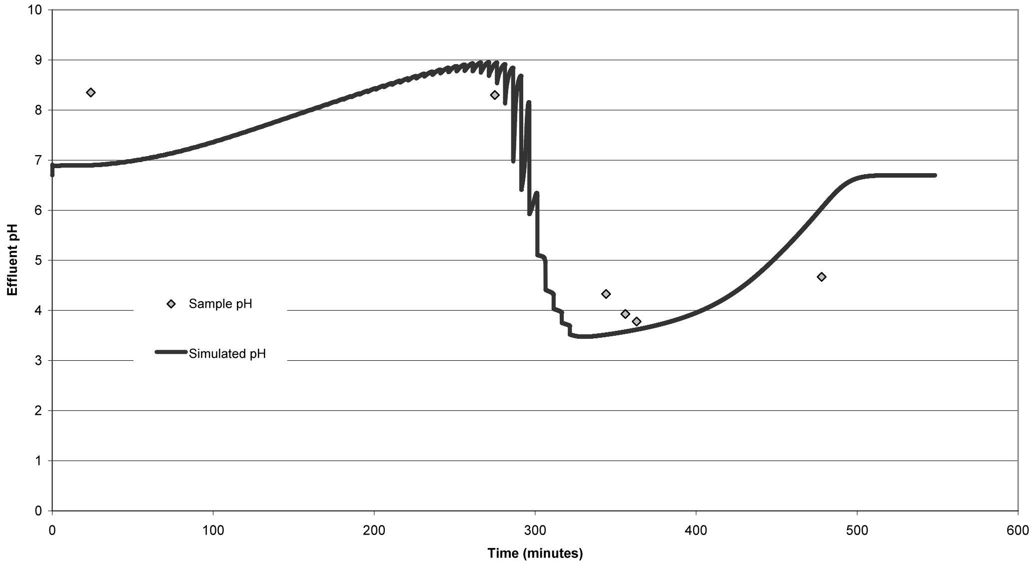

Figure 6 Effluent pH: Nitrate Feed to IX Column with NRW-37 Resin

4.3 Nitrate and Inorganic Carbon (Mixed) Feed

Another set of experiments considered cases where a column filled with fresh IX resin was fed a solution containing known concentrations of sodium nitrate and sodium hydroxide. The expectation was that there will be competitive absorption of ionic species in the anion resin. The nitrate ions, which have a stronger affinity for the resin, would ultimately displace the carbon species.

Figure 7 shows the experimental and simulated curves of the effluent conductivity. Unlike the cases where there is nitrate feed alone to the column, there was no time where the effluent conductivity was greater than the feed conductivity. The simulated time to the start of breakthrough was slightly less than seen in the experiments. The simulated curve predicted that the conductivity would eventually level off at a value just below the feed stream conductivity and then slowly rise to the value of the feed stream conductivity. The experimental effluent conductivity also levelled off at a value below the feed conductivity, but did not rise to the feed conductivity before the experiment was stopped.

Figure 8 shows the breakthrough curves for nitrate ions, inorganic carbon species and sodium ions. Both the experimental and simulated curves show similar behaviour. As expected, the nitrate and sodium curves are the expected S-shape. Fresh cation resin does not contain appreciable quantities of impurities and the only exchange is the displacement of hydrogen ions by sodium ions, so a standard breakthrough curve was expected. In the anion resin, nitrate ions have the strongest affinity and will displace all other anion species in the system, so an S-shaped breakthrough curve was also expected.

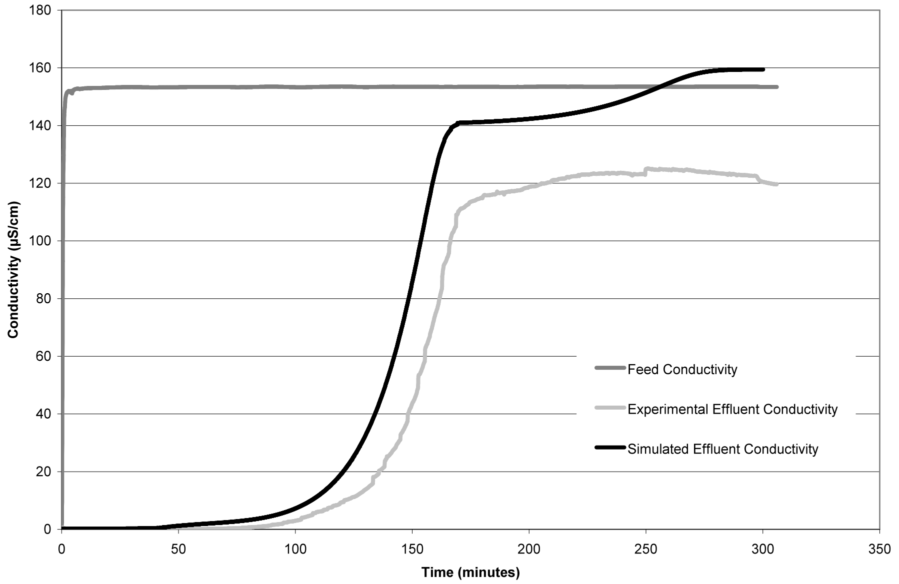

Figure 7 Effluent Conductivity: Mixed Feed to a Column Filled with IRN-150 Resin

The breakthrough curve for the inorganic carbon species showed the effect of competitive absorption. The Total Inorganic Carbon (TIC) concentration in the effluent rose well above the feed concentration and eventually returned to the feed concentration when nitrate ions broke through. At the start of the experimental run, both nitrate and TIC species displaced the hydroxide ions on the fresh resin. Once all the hydroxide was displaced from the resin at the entrance to the column, the nitrate ions entering the column began to displace the bicarbonate and carbonate ions in that section of the bed. The displaced TIC ions flowed down the column and displaced hydroxide ions located downstream. Eventually all the hydroxide ions were displaced from the column, but the nitrate ions continued to displace TIC ions in the column. This effect caused a build-up of TIC ions at the outlet of the column. Eventually the nitrate ions began to push the TIC ions out of the column. At this point, the concentration of TIC ions in the effluent was much higher than the feed concentration. When all TIC ions were displaced from the resin the TIC concentration in the effluent fell back to the feed concentration and the nitrate ion concentration in the effluent began to rise.

The simulated breakthrough curve for sodium matched the experimental curve very well. For nitrates the breakthrough curve was the expected shape but the simulated time to breakthrough was about 30 minutes later than seen in the experiments.

While the simulated TIC breakthrough curve showed the expected competitive absorption behaviour, the simulated time to breakthrough was earlier than seen in the experiments and the peak concentration predicted was much higher than that seen in the experiments. There was a large uncertainty in the measurement of total inorganic carbon concentration in aqueous samples, as these measurements are difficult to make accurately. Nonetheless, there was qualitative agreement between the experimental and simulated curves and a good prediction of the time to breakthrough.

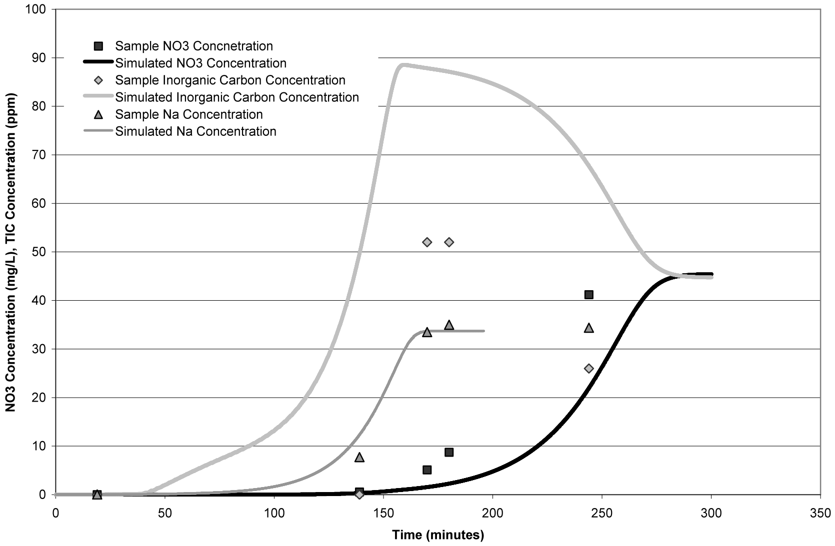

Figure 8 Ion Breakthrough Curves: Mixed Feed to a Column filled with NRW-37 Resin

Figure 9 shows the effluent pH changes in the column with time during column operation. Except for the first pH measurement, the simulated curve matched the experimental results very well. The pH of the column effluent was near 7.0 at the start of operation since the column is initially filled with water. There was a decrease in pH at the beginning of breakthrough as all the hydroxide ions were displaced from the anion resin before all hydrogen ions were displaced from the cation resin. Once TIC species started to be displaced from the resin, hydrogen ions were taken out of solution to maintain the bicarbonate/ carbonate equilibrium in the bulk fluid. When nitrate breakthrough was complete, the feed solution simply passed through the column and the effluent pH was the same as the feed pH.

Also note that the simulated effluent pH curve for the mixed feed case is much smoother than the corresponding curve for the case when there is nitrate feed alone. The presence of a significant amount of inorganic carbon species in the simulation greatly reduced the instability in the numerical solution.

In summary, the small-scale experimental cases demonstrate that the model predictions generally gave good predictions for the initial time to breakthrough. The simulations were able to reproduce the competitive absorption behaviour in the mixed feed case. In cases with nitrate feed alone, the model was able to predict the increase in effluent conductivity above the feed value at breakthrough. The predicted elution curves for nitrate and sodium were in fairly good agreement with experimental result in most cases. The prediction of pH values at various times was reasonably good.

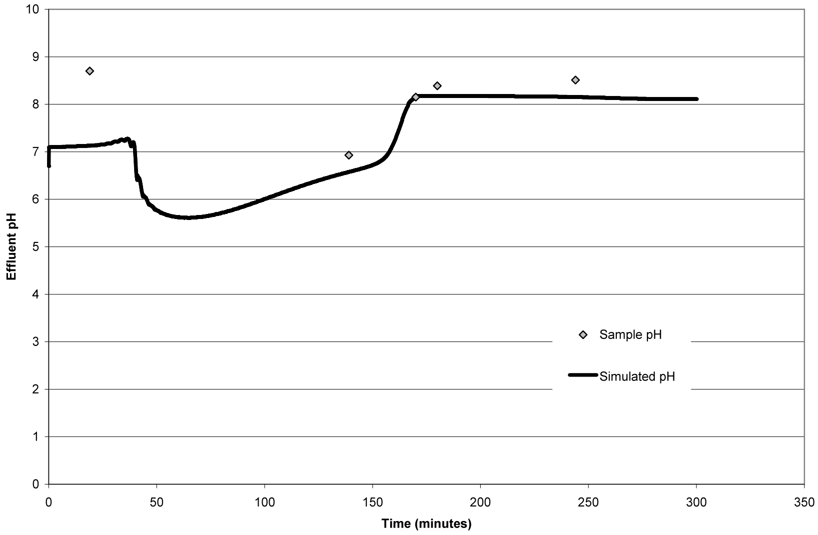

Figure 9 Effluent pH: Mixed feed to a column with NRW-37 resin

5. Simulation of Station Tests

Model output was also compared with data from an experiment where the moderator IX columns in Wolsong-3 were run to exhaustion [5]. During a 210-day period from July 2001 – January 2002, chemistry data on the moderator purification circuit was collected from Wolsong Unit 3 to characterize the water flowing through the moderator purification circuit. The service time of the ion exchange columns was extended beyond the accepted guideline and the emissions of C-14 from the stack were monitored. The stack emissions began to increase slowly after about 178 days in stream. After about 198 days, the stack emissions of C-14 increased significantly. The authors interpreted this increase in stack emissions as a sign of breakthrough in the moderator IX column. A reproduction of the breakthrough curve is given in Figure 10.

The authors of the paper also developed a computer model to simulate the observed behaviour. A graph in Reference [5] shows that the breakthrough curve generated by their model closely matches the time where the stack emissions from C-14 increase significantly. The authors state that the model simulates the removal performance of the IX resin column until exhaustion and suggest a new criterion for the time that a moderator IX column can remain in service.

Wolsong-3 uses IRN-150 resin in its IX columns. A mass balance, using the feed concentrations and the minimum anion resin capacity provided by the resin manufacturer (1.1 meq/mL), determined that the IX bed would be completely spent in about 44 days. A simulation of this case was consistent with this finding, as breakthrough began after about 20 days on stream and the column was completely spent after about 60 days.

However, the breakthrough data given in Reference [5] is consistent with an anion resin capacity of about 3.45 meq/mL. When a resin capacity consistent with the experimental data was input to the model, the model breakthrough curve showed good agreement with the station data. The simulated breakthrough curve is also shown in Figure 10. Consistent with the small-scale experiments, breakthrough started slightly earlier in the simulation than in the experimental data, and the simulated breakthrough curve was also not as sharp as the observed breakthrough curve.

The simulated breakthrough curve shown in Figure 10 is not smooth because the IX column was only divided into ten increments, which was consistent with a model outlined in Reference [5]. A smoother curve could be generated if the IX column were divided into more increments. However, the simulation with 10 increments took over 120 hours of real time to complete, so a case with a finer division of the IX column was not attempted.

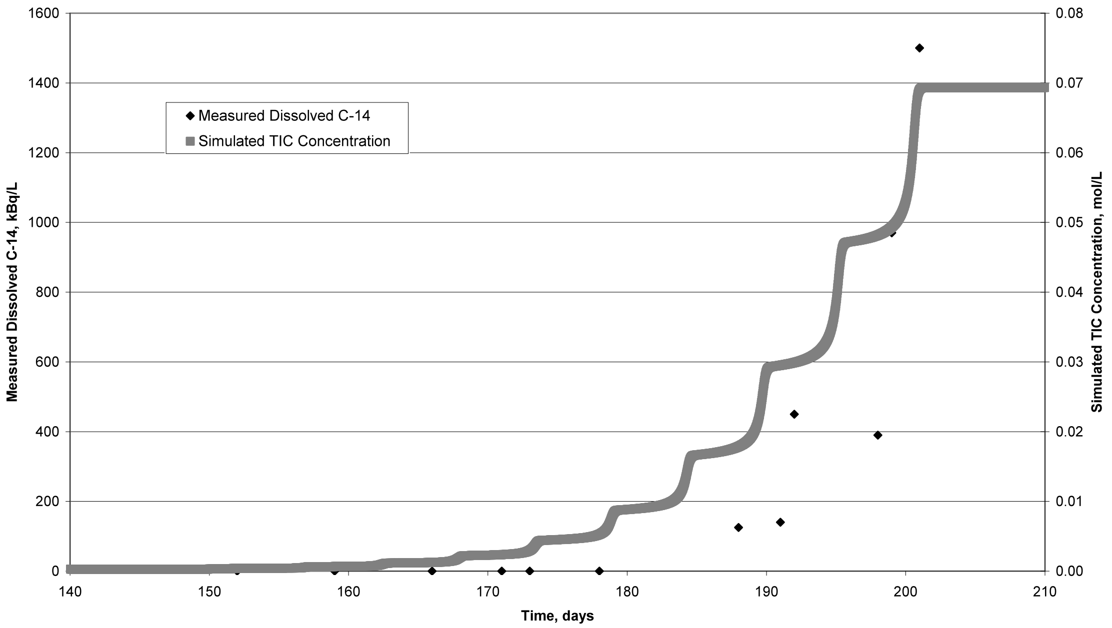

Figure 10 Breakthrough data for Wolsong-3 IX column

6. Conclusion

A mechanistic model has been developed to simulate the dynamic behavior of absorption in ion exchange columns with the goal of estimating the exchange behaviour of inorganic carbon species that contain carbon-14. The model consists of a set of equations that specifies relationships between the concentrations in the bulk fluid, the films around the resin beads, and inside the resin. This formulation assumes that absorption is controlled by diffusion through the thin film surrounding the resin beads.

Model output was compared to experimental data gathered under well-known, controlled conditions. Breakthrough curves for each case were recorded and compared with simulated breakthrough curves. The model is able to reproduce key features observed in small-scale experiments conducted, such as the time to breakthrough, elution curves for some ions and the trend in pH during operation. The model was able to demonstrate competitive absorption when both nitrate and inorganic carbon ions were fed to the column. In cases where nitrate ions alone were fed to the column, the model was able to correctly predict that the effluent conductivity would rise above the feed stream conductivity for a short time at breakthrough. The presence of species in very small quantities resulted in instabilities in the numerical solution.

The current version of the model does not match all the behaviours observed. The model was not successful in predicting the elution curves for the chloride ions that are an impurity in the fresh resin. Simulations with IRN-150 resin gave results that suggest that the assumed capacity of the resin is too low.

A preliminary model validation exercise, where model output was compared to emission data from Wolsong 3, was also successful. The model gave a reasonable prediction of the time to breakthrough when an appropriate value of resin capacity was input.

7. References

[1] Danckwerts, P.V. and M.M. Sharma. "The Absorption of Carbon Dioxide into Solutions of Alkalis and Amines (with some notes on hydrogen sulphide and carbonyl sulphide)", The Chemical Engineer, **202**, CE244-280, 1966.

[2] Barber, D.H., "The Kinetics of Strong-Acid Cation/Strong-Base Anion Mixed-Bed Ion Exchange of Gadolinium Nitrate from Dilute Solution", M.Sc. Thesis, University of Toronto, 1996.

[3] Brenan, K.E., S.L. Campbell, and L.R. Petzold. Numerical Solution of Initial-Value Problems in Differential-Algebraic Equations, 2nd Edition, SIAM Philadelphia, Pa., 1996.

[4] Netlib website www.netlib.org/ode/ddasrt.f

[5] Sohn, W., D.W. Kang, H.K. Ahn and I.H. Rhee, "Prediction Model for Exhausted Point of Ion exchange Resin Column of Moderator Purification Circuit at Korean CANDU Plant", Journal of Nuclear Science and Technology, 42, 833-838, 2005.