Development of a Reactive Transport Model for the Optimization of Ion Specific Media Used at the Fukushima Dai-ichi Nuclear Power Plant – 14579

Joshua Mertz *, Mark Denton *, Brian Powell **, Lawrence Murdoch **
* Kurion, Inc.
** Clemson University

ABSTRACT

On March 11, 2011, the magnitude 9.0 Great East Japan earthquake, Tohoku, hit off the Fukushima coast of Japan. This was one of the most powerful earthquakes in recorded history and the most powerful one known to have hit Japan. The ensuing tsunami devastated a huge area resulting in some 25,000 persons confirmed dead or missing. The perfect storm was complete when the tsunami then found the four-reactor, Fukushima-Daiichi Nuclear Station directly in its destructive path.

In June of 2011, Kurion, Inc. contracted with the Tokyo Electric Power Company (TEPCO) to begin immediate remediation of the cooling water using Ion Specific Media. As a result of the initial work, Kurion was able to develop new ISM (EH, KH and TS-G) for the constantly changing conditions of the cooling water.

The Fukushima Dai-ichi cooling water is in a constant flux of conditions; groundwater in-leakage, addition of chemicals to control building degradation and ongoing remediation of the water present ever changing chemistry that is not simple to predict. While equilibrium batch reactions are often used to predict distribution coefficients, such experiments rarely take chemical kinetics into effect. The fluctuating conditions and life-cycle estimates are beyond the scope of empirical research. Therefore, in order to predict the vessel lifetime, rotation of the vessels and the overall optimization of Kurion's EH, KH and TS-G media, a calibrated numerical model was developed. A series of batch reactions were used at different contact times (5 minutes to 48 hours) and different concentrations of seawater, Cs^{+}, Sr^{2+} and Ca^{2+} to characterize the sorption kinetics. The kinetic sorption model was then used as an input to an ion transport model that simulates Kurion's treatment train at Fukushima Dai-ichi. The models allow Kurion to predict the correct operating procedures in the ever changing influent.

INTRODUCTION

A little more than a month after the March 11, 2011 Great East Japanese Earthquake and Tsunami damaged the Fukushima Dai-ichi Nuclear Plant, TEPCO announced the selection of Toshiba (oil/grease separation), Kurion (cesium removal), AREVA (cesium downstream removal) and Hitachi (desalination) to provide an external reactor water cooling system rated at 1200 MT/day (317,000 gallons/day). The mission was to reduce the dose to workers, allow access to the turbine and reactor buildings and protect the environment by the removal of a very large volume of highly radioactive, oily and saline water.

After one year of actual operation (June 15, 2012), Kurion had achieved ~ 71% and SARRY 29%

activity removal (TEPCO press releases). Estimates from the latest public data available showed that the TEPCO full system had processed, by 2012 year end, a total of 540,000 MT (>140 million gallons). In doing so, the Kurion system had removed 17 x 10^{16} Bq (4.6 million curies) and the SARRY system 8 x 10^{16} Bq (2.16 million curies), an impressive total of 25 x 10^{16} Bq (6.75 million curies) to bring the total activity down to ~2% of the original value.

The Kurion Ion Specific Media (ISM) System at Fukushima Dai-ichi is comprised of a number of vessels containing Kurion ion-exchange media (Figure 1.). The system was designed to utilize several classes of Kurion ISM to remove cesium ($^{134/137}Cs^{+}$) and iodine (^{131}I) from the cooling water. At the time of system start-up, three media were used: Surfactant Modified Zeolite (SMZ) to pretreat the water and capture oils, Herschelite (H) to capture Cs^{+} and silver modified engineered herschelite (AGH) to capture ^{131}I. Dose loading on the vessels prevented TEPCO from using Kurion's other media: Engineered Herschelite (EH) and KCCF-Herschelite (KH).

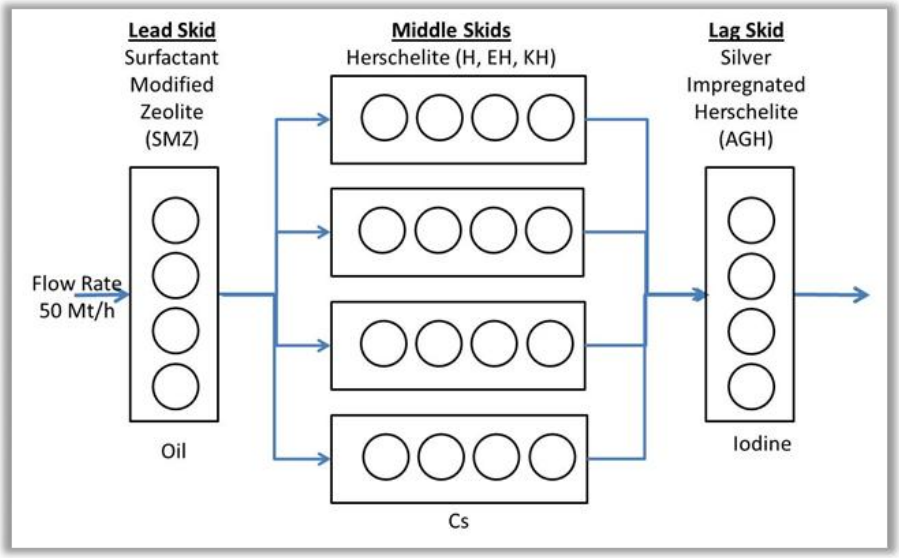

Figure 1. Kurion Process Flow Diagram describing initial conditions.

In any engineered ion exchange system, it is important to optimize the operation according to several factors: the dose of media on the vessel, the required effluent concentration or decontamination factor (DF) and the production of final waste volume. When the system started in June of 2011, operation was based on dose loading of the vessels. A few months after the start of operation, a preliminary model designed by a team at the Central Research Institute of Electric Power Industry (CRIEPI) was used to predict the rotation schedule of the vessels.[1-3]

The CRIEPI model was an adaptation based on the Versatile Reaction-Separation model for Liquid Chromatography (VERSE-LC) that describes a single column modeled with a one-dimensional grid equipped with particle models, corresponding to the adsorption of media solids. Batch tests were used to determine the Langmuir isotherm constants and column tests were used to help adjust and fit the model. The code was further adjusted to fit the effluent concentrations seen at the actual ISM system. The CRIEPI model has been the driving force for operation of the Kurion system since December of 2011. While the CRIEPI model was sufficient

during the emergency situation, it no longer can be used for predicting Kurion ISM optimization for several reasons. First the CRIEPI model restricts the media which can be used in the ISM system. Since the dose is now reduced considerably, a more effective media (EH or KH) can be used to remove Cs^+ and decrease waste production. Second, the CRIEPI model restricts the ions that compete with Cs as a function of percent seawater. However, the concentrations of individual ions such as Ca^{2+} are not a function of seawater concentration; Ca^{2+} is leached out of concrete in the basement where the cooling water is stored.[1-3]

The performance of Kurion's ISM system can be predicted using empirical data, however experiments to predict performance are costly and time consuming, making life-cycle estimates beyond the scope of empirical research. Therefore, in order to predict the vessel lifetime, rotation of the vessels and the overall optimization of Kurion's EH, KH and TS-G media, a calibrated numerical model was developed and combined with a transport model to predict the efficiency of the system with changes in solute concentrations.

MEDTHODS

Materials

Three Kurion ISM Media were used in these studies. EH and KH are engineered herschelite media that have been enhanced through Kurion's proprietary processes to remove Cs^+ more effectively than KUR-H media. For these tests, EH and KH were washed with 5M NaCl overnight to remove any impurities and simplify the model calculations by assuming only Na exists in the sorption sites.

To date Kurion's ISM system has focused primarily on Cs^+ removal. However, a large concentration of Sr^{2+} exists in the cooling water as fission products ($^{89,90}Sr^{2+}$) and as natural Sr^{2+} in seawater (^{88}Sr). To demonstrate the effectiveness of Kurion's new strontium specific media, TS-G, was also tested and modeled. Unlike the other media, TS-G did not have to be washed as all the sorption sites contained only Na^+.

Simulated seawater was prepared from commercial salts (NeoMarine®, InstantOcean®) by dissolving the salt into water and adjusting the salt added so that the density of solution was 1.023 g/mL. The salinity was measured and was found to be similar to the known values.[4] Seawater concentrations were varied from 2.5% to 50% by weight for the experiments. Concentrations of Cs^+, Sr^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ were varied according to Table 1.

Table 1. Compilation of the Concentration of Ions Tested.

Ions Tested	Range of Concentrations (ppm)
Cs^+	0.015-5000
Sr^{2+}	0.200-2500
Ca^{2+}	10-206
Mg^{2+}	30-650
K^+	9-200
Na^+	270-6000

Kinetic Tests

The sorption behavior of the three ISM were characterized by conducting batch test experiments where solutions with various concentrations of solutes were placed in contact with sorbing compounds and analyzed as a function of different times. 10 mL of a sample solution was combined with 0.1 g of media (V/m ratio of 100 mL/g) and contacted in a sample rotator at 30 RPM for 5, 10, 15, 20, 30, 60, 1440, and 2880 minutes (end over end rotation). The samples were then filtered through a 0.2 µm (nominal) syringe filter and the aqueous phase was analyzed by inductively coupled plasma, mass spectroscopy (ICP-MS).

RESULTS AND DISCUSSION

The ions of utmost concern at the Fukushima Daiichi nuclear power plant are Cs^+ and Sr^{2+} because of their long half-lives and high activity concentrations. However, unlike typically ultrapure fuel pool water, the cooling water in Fukushima contains large contaminants of other salts, mainly from the addition of seawater for emergency cooling. The major competitive ions found in seawater are Ca^{2+}, Mg^{2+}, K^+ and Na^+; the concentration of these competitive ions can directly affect the sorption of the target ions Cs^+ and Sr^{2+}. In designing a model it is necessary to include the sorption of these counter ions.

Modeling

The numerical transport model considers that a column can be symbolized as a function of batch test reactions, each with different influent and effluents. Each small batch test experiment can be considered a theoretical plate. The first plate sees the influent concentration into the column as a function of seawater concentration. However, after the ions exchange in the first plate, the influent to the second plate is no longer seeing Ca^{2+}, Mg^{2+}, K^+ and Na^+ concentration as a function of percentage of seawater. For this reason, it was necessary to test the individual exchange of the counter ions, while holding all other ions constant, instead of using the percent seawater as an individual variable.

Kinetic Model

In considering the kinetic model, there are two phase of each ion: an aqueous phase (*aq*), where the ion exists in the water, and a sorbed or solid phase (*s*). The concentration of the ions in solution are related to the concentration of ions sorbed according to:

$$\frac{dC_{Css}}{dt} = -\frac{n}{\rho_b}\frac{dC_{Csa}}{dt} \tag{1}$$

where C_{ab}, where *a* is the ion (e.g. Cs) and *b* is the phase.

When all of the phases and ions are considered, there are a total of 36 species of interest. An example is shown in Table 2.

Table 2. An example of the 36 species of interest. Not included are the phases of Mg^{2+}, K^{+} and Na^{+};

Aqueous Strontium	C_{Sra}
Sorbed Strontium	C_{Srs}
Aqueous Cesium	C_{Csa}
Sorbed Cesium	C_{Css}
Aqueous Calcium	C_{Caa}
Sorbed Calcium	C_{Cas}
Seawater	C_{Swa}
Sorbed seawater	C_{Sws}

It is assumed that a finite number of sorption sites are available to sorb Cs^{+} and/or Sr^{2+}, and the sorption rates will depend on the concentration of compounds filling those sites.

In the model the sites will initially be filled with Na, and this serves as a reference for the purposes of evaluating the effects of other ions on the sorption rate.

The sorption rate is be described by considering a Langmuir-type process with competition for sorption sites among *m* species. The ability of the competing species to exclude the sorbent of interest will depend on how similar the competing species are to the sorbent. This effect is considered by using a weighting function, w_i, between 0 and 1, which was determined from the empirical data. The *w* term for Na^{+} is w_{Na}=0, since Na^{+} is assumed to exist in all of the pores.

The sorption reaction is assumed to be characterized by a Langmuir-type process, so for example, the kinetics for the concentration of sorbed cesium can be described by

$$\frac{dC_{Css}}{dt} = \frac{n}{\rho_b} k_{1Cs} \left[C_{s,\max Cs} - \sum_{j=1}^{m} w_j C_{s,j} \right] C_{Csa} - k_{1des,Cs} C_{Css} \tag{2}$$

where $C_{s,maxCs}$ is the maximum total sorbed concentration of all species when considering Cs, $C_{s,j}$ is the concentration of the j^{th} sorbed species, w_j is the competition weighting function, k_{1des} is the desorption rate constant for Cs^{+}. The porosity of the sorbent is *n*, and the bulk density is ρ_b.[5]

A similar expression is used for strontium and other ions.

$$\frac{dC_{Srs}}{dt} = \frac{n}{\rho_b} k_{1Sr} \left[C_{s,\max Sr} - \sum_{j=1}^{m} w_j C_{s,j} \right] C_{Sra} - k_{1des,Sr} C_{Srs} \tag{3}$$

There are 3+*m* parameters to be determined for Cs^{+} and Sr^{2+} for each type of sorbent media. They are k_{1a}, $k_{1des,a}$, $C_{s,max,a}$, and the *w*'s.

The batch tests experiments were able to determine the parameters and they were used to create the kinetic based model. The batch testing indicated that a first order model was insufficient for describing the kinetic rates. The batch tests for all media follow a Langmuir process and can be described by second order kinetics (Figure 2).

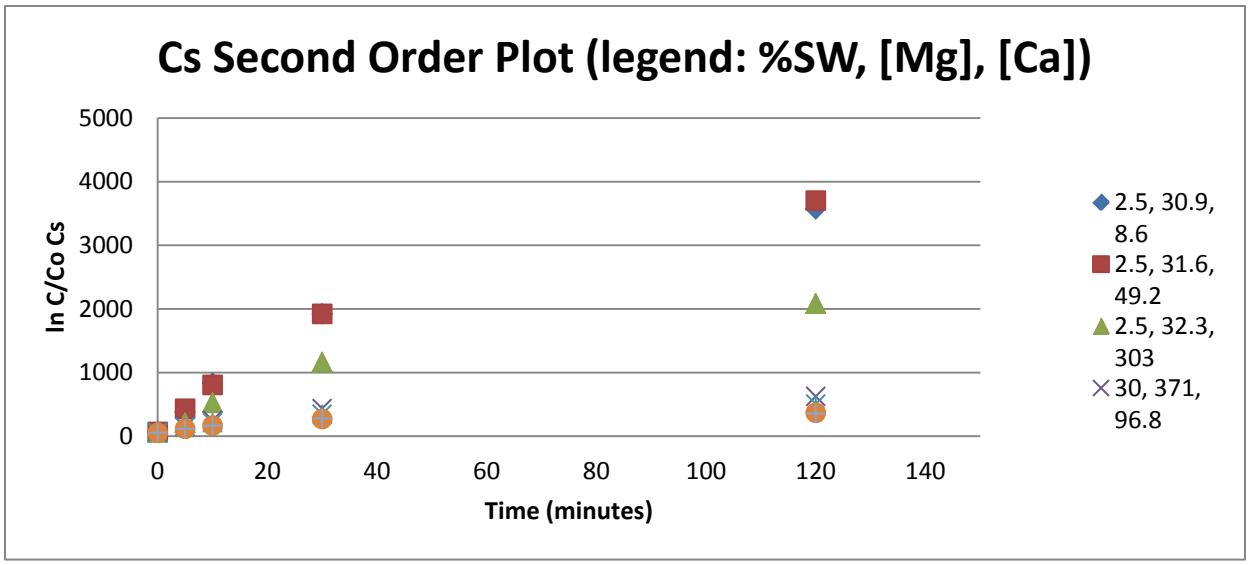

Figure 2. An example of how the media follows second order kinetics. Here the concentration of Cs is graphed against time and variable % seawater.

Transport Model

A numerical model was developed to simulate the fate and transport of radionuclides in the treatment columns. In order for the model to be finite, several assumptions had to be made:

- Concentrations in the input stream are known as a function of time.
- The flow through the columns is governed by continuity of momentum (Darcy's Law) and continuity of mass.
- Laminar conditions exist in the porous media.
- The flow is uniform, so there are no preferential pathways.
- The transport of radionuclides is governed by conservation of mass through the standard Advection-Dispersion-Reaction Equation.
- The columns will be treated as one dimensional as a consequence of this assumption.
- The parameters determined from the experiments are adequate for characterizing the sorption behavior in the field.
- Dispersion is relatively unimportant and average values of dispersivity were used

The Combined Model

The two models were combined by adding the kinetic parameters to the diffusion and transport parameters. The combined model is incredibly unique because it has the ability to be adjusted using over nine variables: system flow rate; the concentrations of Cs^{+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} or percent seawater; vessel duration. The model can also be reconfigured to have a variable amount of vessels, so that modifications to the Kurion ISM system can be theoretically justified. The model outputs the effluent of all of the input ions and through adjusting describes the longevity of the system.

The model was verified and adjusted against the data from laboratory column experiments. However, the model cannot be currently verified against the Kurion ISM system at Fukushima,

because the media tested is currently not in use.

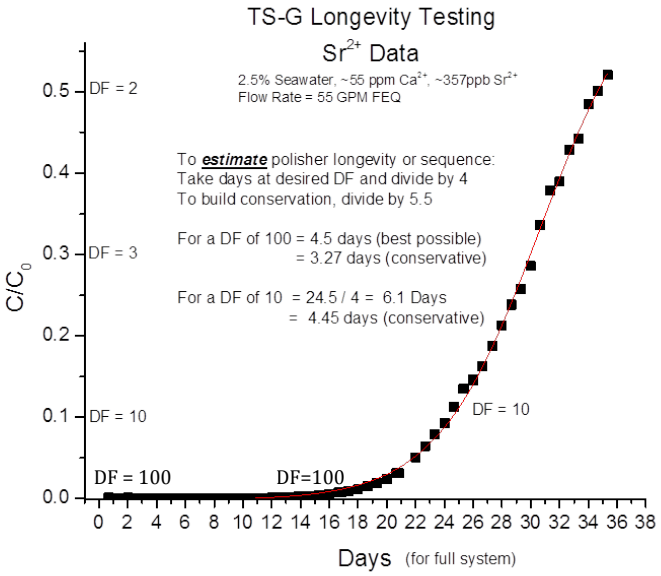

Figure 3. Experimental data in this figure was in agreement with the model.

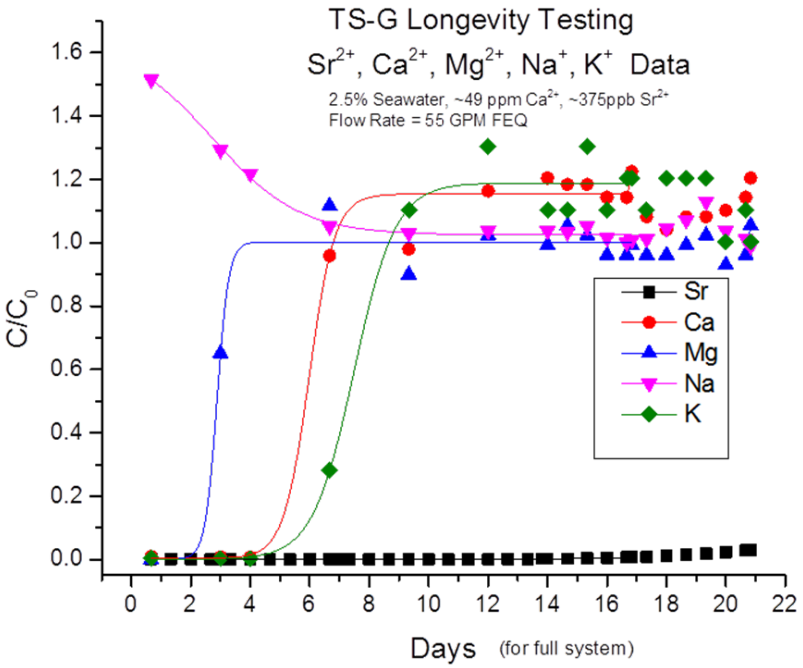

Figure 4. Results following multiple ions throughout the TS-G longevity experiment. This data was confirmed by the Kurion ISM Model.

ISM Optimization Based on the Model:
The combined model can be used to predict the longevity of Kurion ISM under certain conditions. The conditions of the inlet water as of April 2013 are listed in Table 3. In this run of the model, Kurion's system was set up as an extended train system to demonstrate the ability to remove both Cs^{+} and Sr^{2+}(Figure 5). While the experiment only tested a 10-10-10 rotation with KH and a 4-4-4 rotation with TS-G, the model was able to predict that the KH should actually last 25 days and the TS-G should last 6 days.

Table 3. Specifications as established in Kurion's Proposal to TEPCo in April 2013.

Test Criteria	Value
Aspect Ratio	0.43
Configuration	1 Series of KH columns into 1 Series of TS-G columns and 1 TS-G polisher
Flow Rate	55 GPM / System
Cs^{+} Concentration	16.8 ppb
Sr^{2+} Concentration	~ 350 ppb +/- 15%
Na^{+} Concentration	270 ppm
Ca^{2+} Concentration	56 ppm
% Seawater	2.5%

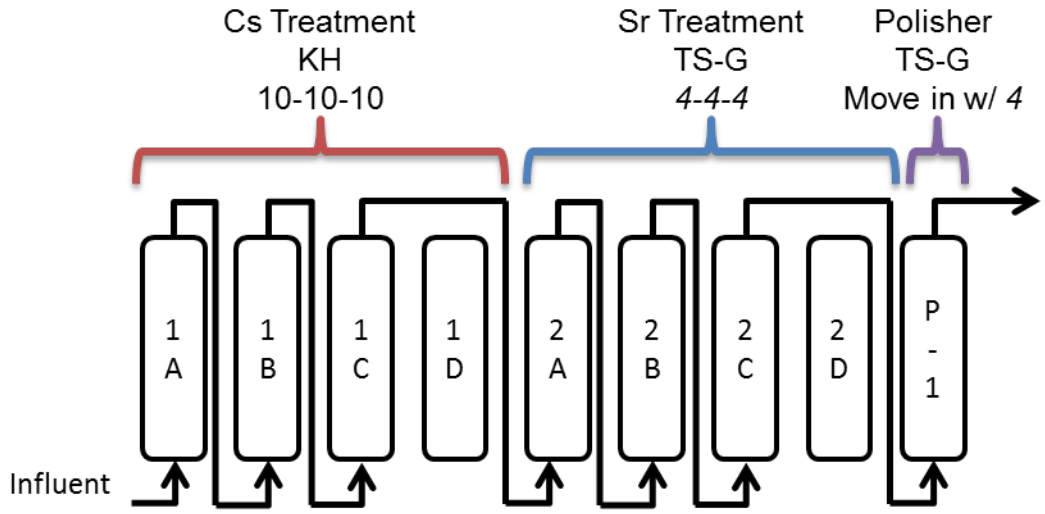

Figure 5. The experimental schematic for KH (10-10-10), TS-G (4-4-4) "Extended Train Configuration".

CONCLUSIONS

A calibrated numerical model was developed from an ion transport model and a kinetic model to predict and optimize the Kurion ISM system with new media. For EH, the determination was made that the vessel life times may be as long as 15 days in the lead position at a flow rate of 44 gallons per minute. Kurion's KH media may last as long as 20 days in the lead position. In the case that TEPCO wants to also treat Sr^{2+} in the upfront system, the system can be reconfigured to contain two trains in series, one for Cs^{+} and one for Sr^{2+}. In this case, TS-G will last 6 days in the lead position to have a Sr^{2+} DF of > 10 at a flow rate of 44 GPM. If the flow rate is reduced, the longevity is increased by a factor inverse to the decrease of the flow rate. This numerical model has proven to be very accurate when compared to the laboratory tests. Future work will adjust the model to testing proposed at Fukushima.

REFERENCES

1. Tsukada, T., et al., *Ion- Exchange Properties of Kurion Herschelite in the SImulated Solution of the Contaminated Water Accumulated at the Fukushima Daiichi Nuclear Power Station*, in *GLOBAL 2011*2011: Makuhari, Japan.
2. Ingaki, K., et al., *Development of a Simulation Code for the Zeolite Column System and its Application for the Cesium Adsorption Instrument Used in Fukushima Daiichi Nuclear Power Station*, in *GLOBAL*2011: Makuhari, Japan.
3. Hijikata, T., et al., *Small Zeolite Column Tests for Removal of Cesium from High Radioactive Contaminated Water in Fukushima Daiichi Nuclear Power Station*, in *GLOBAL*2011: Makuhari, Japan.

4. *CRC Handbook of Chemistry and Physics*, ed. D.R. Lide2008, Boca Raton, FL: CRC Press.
5. Berninger, J.A., et al., *A versatile model for simulation of reaction and nonequilibrium dynamics in multicomponent fixed-bed adsorption processes.* Computers Chem. Eng., 1991. **15**(11): p. 749-768.

ACKNOWLEDGEMENTS
The authors would like to acknowledge the analytical laboratories that helped with this data: Materials and Chemistry Laboratories, Inc, and Eberline Services, Inc., both of Oak Ridge, TN.