ABSTRACT

ALLENSWORTH, JAMES ROBERT. Study of Highly Concentrated Fission Product Sorption into Zeolite-A. (Under the direction of Man-Sung Yim.)

An investigation into the ability of zeolite-A to absorb highly concentrated fission product salts lacking LiCl-KCl was conducted. Salt-zeolite powder blending experiments were performed to ascertain zeolite-A's salt absorption characteristics. Salts used were NaCl, RbCl, CsCl, SrCl₂, and BaCl₂. A time dependent reaction-diffusion mass transfer model was developed in order to better understand the dominant mass transfer mechanism of the sorption process and to calculate relevant physical parameters. Molten-state salt-zeolite contacts were performed to generate cesium and strontium loading data for the developed mass transfer model. Finally, both solid-state and molten-state experiments were performed to investigate whether the prior presence of chloride within the zeolite could enhance the rate of fission product cation uptake. In the powder contacts, zeolite-4A absorbed between 10-75% of each salt with the highest and lowest uptakes associated with NaCl and BaCl₂, respectively. Lithium substituted zeolite-A (Li-A) absorbed salts with nearly the same results as zeolite-4A. It is expected that greater salt uptake would be observed with longer heating durations and active mixing. Numerically determined effective diffusivities of cesium and strontium within the zeolite-4A material were 9.04E-6 cm² per second and 4.04E-7 cm² per second, respectively. Results of the study to determine the effect of prior chloride presence on fission product cation uptake were inconclusive. When exposed to powdered salt, cesium uptake in pelletized zeolite-4A was increased but strontium and barium uptake were not affected. When exposed to a molten salt, neither cesium or strontium uptake in pelletized zeolite-4A was affected by the prior presence of chloride within the zeolite. However, when Li-A loaded with lithium chloride was exposed to various salt powders at the same experimental conditions as the previous powder contacts, salt cation uptake was improved. Between 40-75% of each salt cation was absorbed with the highest and lowest uptakes associated with barium and strontium, respectively.

Study of Highly Concentrated Fission Product Sorption into Zeolite-A

by James Robert Allensworth

A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science

Nuclear Engineering

Raleigh, North Carolina

2011

APPROVED BY:

David McNelis

Wesley Henderson

Man-Sung Yim Chair of Advisory Committee

DEDICATION

To Jennifer. I would not be where I am without you.

BIOGRAPHY

The author attended the University of Texas at Austin and received a Bachelor of Science degree in chemical engineering. While at the University of Texas, he met the woman he would eventually marry. After graduation, they moved to North Carolina to obtain advanced degrees. She began pursuing a doctorate degree at Duke University while he started a master's program at North Carolina State University. After she graduates, they plan to return to Texas.

ACKNOWLEDGMENTS

I would like to thank Dr. Yim and Dr. Simpson for giving me this opportunity. Additionally, I want to thank Joanna Taylor and Will Smith for their help with sample analysis. Finally, thanks to Dr. Phongikaroon of the University of Idaho for the free room and board during my time in Idaho Falls.

TABLE OF CONTENTS

List of Tables	vi
List of Figures	vii
Chapter 1 Introduction	1
1.1 Goals	4
1.2 Scope	5
1.3 Background	5
Chapter 2 Materials and Methods	14
2.1 Solid-State Salt-Zeolite Contacts	15
2.2 Molten-State Salt-Zeolite Contacts	20
2.3 Development of Sorption Model	26
Chapter 3 Results and Discussion	31
3.1 Powdered Static Contacts	
3.2 Pelletized Static Contacts	34
3.3 Molten Contacts	
3.4 Molten Contact Model Fitting and Parameter Calculation	43
Chapter 4 Conclusion	52
References	

LIST OF TABLES

Table 1: Zeolite Pellet Classifications	23
Table 2: ImageJ XRF Map Calculations	
Table 3: Molten Experiment Salt-Zeolite Compositions	
Table 4: Comparison of Loading Results with Equilibrium Model	42
Table 5: Cesing Loading in Binder Volume	43
Table 6: Cesium Model Parameter Calculations	46
Table 7: Strontium Pure Diffusion Model Parameter Calculations	
Table 8: Strontium Reaction-Diffusion Model Parameter Calculations	
Table 9: Comparison of Calculated Diffusion Coefficients	

LIST OF FIGURES

Figure 1: Electrorefiner Separation Diagram	2
Figure 2: Zeolite-4A Crystal Structure	3
Figure 3: High Purity Argon Atmosphere Glove Box	15
Figure 4: Loaded Muffle Furnace	17
Figure 5: Li-A Synthesis Flowsheet	19
Figure 6: Loaded Magnesia Crucible	21
Figure 7: Zeolite Milling Setup	22
Figure 8: Zeolite Milling Results	22
Figure 9: Steel Mesh Basket	24
Figure 10: Molten Contact Apparatus	25
Figure 11: Analytical vs. Numerical Model Comparison	30
Figure 12: Chloride Uptake in Zeolite-4A	31
Figure 13: Chloride Uptake in Li-A	32
Figure 14: Salt Cation Uptake in LiCl Loaded Li-A	33
Figure 15: Cs Map of Blank Pellet	34
Figure 16: Si Map of Blank Pellet	34
Figure 17: Cs Map of Preloaded Pellet	34
Figure 18: Si Map of Preloaded Pellet	34
Figure 19: Sr Map of Blank Pellet	35
Figure 20: Sr Map of Preloaded Pellet	35
Figure 21: Ba Map of Blank Pellet	35
Figure 22: Ba Map of Preloaded Pellet	35
Figure 23: Cesium Loading in Blank Zeolite-4A	38
Figure 24: Strontium Loading in Blank Zeolite-4A	38
Figure 25: Pellet Contacted for 60 Seconds	39
Figure 26: Pellet Contacted for 120 Seconds	39
Figure 27: Pellet Contacted for 300 Seconds	39
Figure 28: Pellet Contacted for 600 Seconds	39
Figure 29: Pellet Contacted for 900 Seconds	40
Figure 30: Cesium Loading Preloading Comparison	41
Figure 31: Strontium Loading Preloading Comparison	41
Figure 32: Cesium Model Fitting with 1.71mm Pellets	44
Figure 33: Cesium Model Fitting with 2.08mm Pellets	44
Figure 34: Cesium Model Fitting with 2.08mm LiCl-KCl Loaded Pellets	45
Figure 35: Cesium Model Fitting with 2.32mm Pellets	45
Figure 36: Strontium Model Fitting with 1.23mm Pellets	47
Figure 37: Strontium Model Fitting with 1.71mm Pellets	47
Figure 38: Strontium Model Fitting with 2.08mm Pellets	48
Figure 39: Strontium Model Fitting with 2.08mm LiCl-KCl Loaded Pellets	48
Figure 40: Strontium Model Fitting with 2.32mm Pellets	49

CHAPTER 1

Introduction

Idaho National Laboratory (INL) is currently developing an electrochemical process to treat spent nuclear fuel from the Enhanced Breeder Reactor 2 (EBR2) program ⁽¹⁾. Designed to demonstrate the viability of a fast breeder reactor with onsite fuel reprocessing, the EBR2 reactor operated from 1965 until 1995. At the end of its operation, INL initiated a program to treat the spent fuel in order to make it suitable for a geologic repository. Due to the presence of metallic sodium used as a bonding agent in the fuel, conventional aqueous separation techniques were inapplicable. Metallic sodium reacts violently when exposed to water, and is thus incompatible with aqueous reprocessing methods and geologic repositories. In the electrochemical process, spent nuclear fuel rods are chopped and immersed in a molten salt consisting primarily of eutectic LiCl-KCl⁽²⁾. A voltage applied across two electrodes causes certain elements in the chopped fuel to dissolve into the molten salt, while other elements either remain in the fuel matrix or plate out on the cathode for collection. The Gibbs' free energy of formation of the associated chloride molecules determines where each element ends up after the voltage is applied. Figure 1 shows where each class of element resides after a typical electrorefiner operation ⁽²⁾.



Figure 1: Electrorefiner Separation Diagram

Elements with low chloride free energies like zirconium remain in the chopped fuel pieces, while group 1 and 2 elements, whose chlorides have very high free energies of formation, will dissolve into the molten salt. The electrorefiner can be operated such that very high purity uranium metal deposits onto a cathode for recovery. Plutonium recovery is also possible in a similar operation, but the recovered product is an impure mixture of uranium and plutonium. Ultimately, uranium and plutonium are removed from the electrorefiner while undesirable fission products are concentrated in the molten salt.

As the number of processed fuel elements increases, so does the concentration of impurities in the molten salt. Contaminated salt must be disposed of and fresh eutectic LiCl-KCl added when any of three impurity limits are met ⁽³⁾. The first limit, the sodium limit, is caused by the increased melting point of the salt mixture as a result of sodium buildup. Salt must be replaced when the melting point of the mixture nears the operating temperature of the electrorefiner. Second, salt must be replaced when the

fission product concentration in the salt results in a heat generation rate nearing the cooling ability of the electrorefiner. Finally, criticality concerns as a result of plutonium buildup dictate replacement of the salt.

To dispose of the contaminated salt, the salt is blended with powdered zeolite-4A at high temperatures. Zeolite-4A is a sodium aluminosilicate with a unit cell crystal structure given in Figure 2 ⁽⁴⁾. Upon blending, salt molecules are trapped inside the zeolite α and β cages. Additionally, the salt cations can react with sodium in the zeolite to become part of the zeolite framework.



Figure 2: Zeolite-4A Crystal Structure

Salt loaded zeolite mixed with glass frit is pressed at high temperature inside a metal canister to convert the mixture into a glass bonded sodalite form. The crystal structure transformation from zeolite-A to sodalite improves salt leaching characteristics of the final waste form ⁽⁵⁾. The pressed canisters are then ready for disposal at a geologic repository.

In the proposed INL salt treatment process, all salt removed from the electrorefiner is loaded into zeolite and disposed. A significant amount of usable LiCl-KCl is thus thrown away. Not only does this increase the amount of fresh salt required to continually operate the electrorefiner, it also decreases fission product loading in the final waste form. Currently, fission products make up only 1% of the final waste form mass ⁽⁵⁾. It is desirable to develop a process which selectively removes the fission product waste and produces a clean LiCl-KCl product. To accomplish this, INL is investigating the use of a zone melt crystallization process to concentrate the impurities in a very small salt mass ⁽⁶⁾. The waste product is a brick of highly concentrated fission product salt which would then be ground up and blended with zeolite-4A powder. However, it is currently unknown what effect the lack of LiCl-KCl in the waste salt would have in the salt loading process. Without LiCl-KCl, the salt mixture will remain solid at the 500°C operating temperature of the proposed blending process and the ability of zeolite-4A to absorb powdered salt is unknown.

1.1 Goals

The goal of this work is to assist in the development of a process to effectively absorb highly concentrated fission product salt into zeolite-A. Solid-state salt-zeolite contacting experiments will be performed to ascertain the ability of zeolite-A to absorb concentrated fission product salts lacking LiCl-KCl. In order to obtain a fundamental understanding of the salt-zeolite mass transfer mechanism, a model based on physical principles that captures the kinetics of the absorption process will be developed. Molten-state salt-zeolite contacting experiments will be performed to and data fit to the developed model in order to calculate relevant physical parameters useful to process optimization. Finally, both solid-state and molten-state salt-zeolite contacts will be conducted to study methods to enhance the rate of fission product uptake into the zeolite. Ultimately, the knowledge gained from this work will show whether INL's proposed salt treatment process can be used to treat highly concentrated fission product salts. In addition, the developed model and uptake enhancement work should be useful in improving the salt treatment process.

1.2 Scope

Only the absorption characteristics of group 1 and 2 chlorides are considered in this work. Sodium, cesium, strontium, and barium are major contributors to the purity limits of the electrorefiner salt, and thus a thorough investigation and optimization of their sorption into zeolite-A will have a major impact on the salt treatment process.

Diffusion mass transfer theory was used to model the transport of salt into the zeolite. Both pure diffusion and reaction-diffusion systems were considered. It was desired to have a model that was effective at modeling the sorption process but didn't require advanced computing methods. Thus, other mass transfer methods were not considered in developing the kinetic sorption model.

1.3Background

Johnson *et al.* ⁽⁷⁾ first investigated the treatment of electrorefiner salt with zeolite-A as part of a proposed integral fast reactor fuel cycle process. Experiments with molten electrorefiner salt and powdered zeolite-A were performed in order to investigate the process's effectiveness at concentrating alkali and alkaline earth fission products for waste form production. It was shown that the concentration of Rb⁺, Cs⁺, Sr²⁺, and Ba²⁺ in a molten LiCl-KCl solution decreased after contact with a zeolite bed. Analysis of the zeolite showed effective concentration of the surrogate fission products. Furthermore, it was determined that the LiCl-KCl solution was sufficiently decontaminated such that it could be returned to the electrorefiner.

Pereira *et al.* ⁽⁸⁾ showed that molten electrorefiner salt can be effectively occluded in zeolite-4A via a powder blending process. Powdered surrogate salt and

zeolite were blended at temperatures ranging from 450°C to 550°C for 20 hours. Samples were taken at the end of the blending process and analyzed for free chloride content. The initial salt to zeolite mass ratio largely affected the final free chloride content. It was found that for chloride to zeolite unit cell ratios less than 10, the final free chloride content was always less than 0.5 wt%. Such free chloride concentrations were deemed acceptable for final waste form production. Through X-ray diffraction, it was shown that the zeolite structure remained intact after the salt blending process.

Despite demonstrating the feasibility of using zeolite-A to treat contaminated electrorefiner salt, no attempt had been made to study the kinetics of the process. While pursuing a column-based contaminant removal system, Ahluwalia *et al.* ⁽⁹⁾ developed an analytical model combining exchange reaction equilibria with diffusion theory kinetics. They first performed batch experiments contacting powdered zeolite with an excess of surrogate electrorefiner salt in order to determine exchange factors (EF) relative to Li⁺ for each cation species in the salt. The EF is a useful quantity in predicting equilibrium concentrations of cation species inside the zeolite after the blending process. As shown in Equation 1, it relates the equilibrium coefficient of the exchange reaction to the mole fractions of species in the salt and zeolite

$$EF = \frac{\gamma_{Me}^{s} + \gamma_{Li^{+}}^{z}}{\gamma_{Me}^{z} + \gamma_{Li^{+}}^{s}} K_{Me^{+}} = \frac{x_{Me^{+}}^{s} + x_{Li^{+}}^{z}}{x_{Me^{+}}^{z} + x_{Li^{+}}^{s}}$$
(1)

where *EF* is the exchange factor, γ is an activity coefficient, superscripts *s* and *z* refer to salt and zeolite respectively, and *K* is the equilibrium coefficient. $x_{j^+}^i$ are the relevant mole fractions, and subscripts *Me*⁺ and *Li*⁺ refer to the cation of interest and lithium, respectively. Relative to Li⁺, exchange factors greater than one indicate higher affinity for the cation species to exchange into the zeolite.

To model the kinetics of the exchange process, the Nernst-Planck Equation was used to develop an equation for the diffusive flux of cation species *i*. The Nernst-Planck Equation combines concentration gradient driven diffusion with electric field driven diffusion. The developed equation for the total diffusive flux of cation species *i* is given by Equation 2

$$J_i = -D_i \nabla C_i^z - \frac{z_i F D_i C_i^z}{RT} \nabla \varphi$$
⁽²⁾

where D_i is the diffusion coefficient of cation species *i* inside the zeolite, C_i^z is the concentration of cation species *i* inside the zeolite, z_i is the charge of cation species *i*, *F* is the Faraday constant, *R* is the gas constant, *T* is the temperature, and φ is the electric potential. The differential equation governing the concentration of cation species *i* at time *t* and radius *r* within the zeolite is then given in Equation 3

$$\frac{\partial C_i^z}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_i \left(\frac{\partial C_i^z}{\partial r} - \alpha z_i C_i^z \right) \right]$$
(3)

where α is a simplification of the electric field term of Equation 1 subjected to the constraints of electroneutrality and zero net electric current. Ahluwalia *et al.* then implemented a similar equation lacking the electric field terms to account for the inorganic binder present in the zeolite pellets. The equations were then solved numerically using an implicit finite difference approach and concentration profiles for all relevant cations at various times were generated. The analysis showed dynamic behavior of the cations, with the concentration of monovalent and divalent species inside the zeolite often exceeding the local equilibrium values. After 72 hours of simulation, all cation concentrations in the zeolite were at equilibrium values. An important finding from this work is the concentration of certain cations in the zeolite can be maximized depending on the exposure time. For example, an integration of the Sr⁺ concentration profiles showed maximum loading in the zeolite occurred between one and five hours contact time.

Simpson and Battisti ⁽¹⁰⁾ then conducted mixing experiments using a mechanically fluidized vacuum (MFV) system with in-situ sampling ability. Eutectic LiCl-KCl was mixed with two separate forms of zeolite-4A powder and then blended in

the MFV at 500°C for up to 20 hours. The zeolite existed either as a very fine, pure zeolite-4A powder or as granules that include an inorganic binder. For both types of zeolite, Simpson and Battisti showed that steady state free chloride concentrations were attained after five hours at 500°C. The granulated zeolite performed better than the pure powder, attaining acceptable free chloride concentrations around 0.05 wt%. This was attributed to the granules' better mixing properties in the MFV. Finally, Simpson and Battisti found evidence that solid-state mass transfer was occurring by blending salt and zeolite slightly below the eutectic melting temperature. After four hours, the free chloride concentration had dropped to half the initial value.

The blending process was then scaled up from the 24 L MFV system to a 220 L heated v-mixer by Simpson *et al.* ⁽⁵⁾. The purpose of this work was to demonstrate that the salt treatment process would perform on an engineering scale with radioactive salt. Radioactive salt and zeolite granules were blended at 500°C for 15 hours to ensure equilibrium. Free chloride concentrations of two separate experiments averaging 0.18 wt% showed the v-mixer to be in successful operation.

Simpson *et al.* ⁽⁴⁾ then attempted to formulate a mathematical model for the salt sorption process. A surrogate salt with composition similar to that of the radioactive electrorefiner salt was used in these experiments. Powdered salt and zeolite of various particles sizes were blended in a lab scale v-mixer at 500°C. Before inserting the experimental data to the model, several process variables were investigated to determine which were significant. It was found that variations in the batch size and initial moisture content did not affect the results, while zeolite particle size and time at 500°C were critical to the results. Free chloride concentration data were then fit to a first order kinetic model given by Equations 4 and 5.

$$\frac{\partial [salt]}{\partial t} = -k[salt] \tag{4}$$

$$k = k_o e^{-\frac{L}{RT}} \tag{5}$$

In the model, [*salt*] is the measured free chloride concentration, k_o is the first order reaction constant, *E* is the activation energy, *R* is the gas constant, and *T* is the operating temperature. It was found that the data fit the model reasonably well. Furthermore, Simpson *et al.* determined that available zeolite surface area explained the process dependence on zeolite particle size. Fine powdered zeolite will have a larger surface area than a similar mass of granular zeolite and thus have more available sorption sites.

Simpson's kinetic model successfully fits the results of salt/zeolite blending experiments, but does not explicitly describe the reactions occurring between the salt and zeolite. While useful in that it accurately accounts for the overall blending process, no attempt was made to understand principles behind the sorption mechanism. Lexa and Johnson ⁽¹¹⁾ described the sorption process as occlusion followed by ion exchange. Equilibrium constants for the exchange reactions referenced to Li⁺ were derived in the same manner as Ahluwalia *et al.* ⁽⁹⁾. Numerous experiments were performed where ternary LiCl-KCl-XCl salt mixtures were contacted with zeolite pellets at 550°C, with X representing Na⁺, Rb⁺, or Cs⁺. The calculated equilibrium constant for Cs⁺ was greater than one, indicating the possibility of selective removal of Cs⁺ from the molten salt. In their analysis, Lexa and Johnson assumed that ion exchange occurred rapidly compared to the diffusive mass transfer inside the zeolite. This led to the calculation of effective diffusion coefficients from experimental data using a method given by Breck ⁽¹²⁾. From this work, the effective diffusion coefficients for Li⁺, K⁺, Na⁺, and Cl⁻ were not appreciably different, and roughly twice the value of Cs⁺.

Simpson and Gougar ⁽¹³⁾ then developed a two-site equilibrium model that describes ion exchange and occlusion within the zeolite. Applicable to monovalent cations, the model is derived from equilibrium reactions between the salt and zeolite at the two reaction sites. The governing equation for the concentration of monovalent cation in the zeolite developed by Simpson and Gougar is given in Equation 6

$$C_{i,z} = \frac{k_{i,1}S_1C_{i,s}}{\sum_j k_{j,1}C_{j,s}} + \frac{k_{i,2}S_2C_{i,s}}{\sum_j k_{j,2}C_{j,s}}$$
(6)

where k_i is the equilibrium reaction coefficient for each cation *i*, *S* is the concentration of available sites, and $C_{i,s}$ is the concentration of cation *i* in the salt phase outside the zeolite. Subscript 1 refers to ion exchange with zeolite framework cations, while subscript 2 refers to occlusion within the zeolite cavities. Simpson and Gougar used a least squares method after fitting experimental ternary salt data to the model to solve for $k_{i,1}$ and $k_{i,2}$ for group 1 cations. Relative to Li, equilibrium coefficients were determined for K⁺, Na⁺, Cs⁺, and Rb⁺. With the calculated coefficients, the resulting model closely fit the experimental results from Lexa and Johnson ⁽¹¹⁾.

Gougar *et al.* ⁽¹⁴⁾ then extended the equilibrium model to include multivalent cations. Equation 7 gives their developed model equation

$$\theta_{i} = \frac{S_{1}K_{i}^{IX}C_{i,s}^{1/n_{i}}}{K_{i}^{IX}C_{i,s}^{1/n_{i}} + (1 - C_{i,s})^{1/n_{i}}} + \frac{S_{2}K_{i}^{Occ}C_{i,s}^{1/n_{i}}}{K_{i}^{Occ}C_{i,s}^{1/n_{i}} + (1 - C_{i,s})^{1/n_{i}}}$$
(7)

where θ_i is the total concentration of cation species *i* in the zeolite, n_i is the charge of the cation species *i*, and K_i^{IX} and K_i^{Occ} are the equilibrium coefficients for species *i* for ion exchange and occlusion, respectively. With data from ternary and quaternary salt mixtures, equilibrium coefficients were calculated for the following ions: Li⁺, K⁺, Na⁺, Cs⁺, Rb⁺, Ca²⁺, Sr²⁺, Nd³⁺, and U³⁺. In this model, the calculated equilibrium coefficients were not relative to Li⁺ as in the previous model, but absolute. While not fully based upon first principles, it was shown that the model fit the experimental data reasonably well.

Phongikaroon and Simpson ⁽¹⁵⁾ then set out to improve upon Gougar's multivalent model. The intent was to develop a model fully based on first principles that accounted for multivalent cations without requiring sophisticated numerical computations. Also, a limitation in Gougar's model was found involving cation species at very low concentrations in the salt mixture. In these instances, the calculated K_i^{IX} and K_i^{Occ} coefficients were inaccurate. To develop their model, Phongikaroon and Simpson used equilibrium exchange reactions with Li⁺ as a reference cation in order to simplify

the modeling process. The relevant equations for this model are given in Equations 8-10

$$y_{i}^{IX} = K_{i}^{IX} \left(\frac{x_{i}}{x_{Li}}\right)^{n_{i}} \left(y_{Li}^{IX}\right)^{n_{i}}$$
(8a)

$$y_i^{Occ} = K_i^{Occ} \left(\frac{x_i}{x_{Li}}\right)^{n_i} \left(y_{Li}^{Occ}\right)^{n_i}$$
(8b)

$$\theta_i = n_i (y_i^{IX} + y_i^{Occ}) \tag{9}$$

$$y_{Li}^{IX} + \sum_{i=1}^{IX} n_i y_i^{IX} = 12$$
 (10a)

$$y_{Li}^{Occ} + \sum_{i=1}^{M} n_i y_i^{Occ} = (\theta_T - 12)$$
(10b)

where y_i^{IX} and y_i^{Occ} are the mole fractions of cation species *i* located in framework and occlusion sites respectively, x_i is the mole fraction of species *i* in the salt phase, and θ_T is the total salt species equivalence in the zeolite. Equations 8a and 8b give the mole fraction of cation species *i* in the zeolite as a function of the equilibrium reaction coefficient, salt composition, and Li⁺ mole fraction in the zeolite. Equation 9 gives the total concentration of cation species *i* in the zeolite, while Equations 10a and 10b act as constraints to Equation 8. Effectively, Equation 10a limits the number of framework sites to 12, while Equation 10b relates the total amount of cation species in the zeolite function species in the zeolite to the total amount of occlusion sites. After fitting with the same experimental data that Gougar used as well as an additional data set, it was shown through the correlation coefficient R that this new model provided a better fit than Gougar's model.

Yoo *et al.* ⁽¹⁶⁾ then extended the previous model to include several rare earth elements in the group of elements considered. Experiments involving ternary salt mixtures of eutectic LiCl-KCl and either LaCl₃, PrCl₃, or YCl₃ were conducted to estimate the parameters for each new species. Experimental results suggest that La³⁺, Pr³⁺, and Y³⁺ have a strong affinity for sorption into the zeolite. A comparison of the model to a wide range of experimental results shows good agreement between the predicted and measured values. With the inclusion of La, Pr, and Y, model parameters have been

estimated for the major components of the contaminated electrorefiner salt, and the model can be used to predict the results of batch molten salt and zeolite blends.

Sachdev *et al.* ⁽¹⁷⁾ investigated the selective removal of Cs⁺ and Sr²⁺ from both molten and solid LiCl based salt mixtures using zeolite-4A. Analysis of zeolite pellets immersed in molten salt at 650°C for up to eight hours showed little to no loading of Cs⁺ or Sr²⁺. For Sr²⁺, a maximum of 0.06 molar equivalents per unit cell were measured. This is far less than the known maximum of roughly 24 equivalents per unit cell. Results were even poorer in the case of Cs⁺, whose peak loading reached less than 0.01 equivalents. XRD analysis showed an unknown lithium aluminosilicate present in all contacted zeolite pellets. It is thought that significant thermal degradation occurred in the zeolite as a result of prolonged heating at 650°C.

In the solid-state experiments, powdered zeolite and salt mixtures were heated at either 500°C or 550°C and mixed inside a v-blender for up to 20 hours. For the 500°C tests, the measured uptake of Cs⁺, Sr²⁺, and Cl⁻ after five hours was 99.6%, 97.4%, and 56.0% respectively. This suggests that solid-state blending of electrorefiner salt and zeolite could be used to selectively remove Cs⁺ and Sr²⁺. Interestingly, experiments at 550°C showed smaller loading of all elements, and follow up XRD analysis indicated zeolite crystal degradation similar to the molten experiments. The solid-state experimental results showed promise with regards to the recycling of electrorefiner salt. A future goal of the authors was to determine what temperature maximized Cs⁺ and Sr²⁺ loading while minimizing total Cl⁻ loading in order to optimize the blending process.

Shaltry ⁽¹⁸⁾ performed experiments involving molten LiCl-KCl mixed with CsCl or SrCl₂ in an effort to compare various kinetic models of the sorption process. Pellet loading versus time data were generated in order to estimate parameters for the three models. Shaltry used an exchange reaction model which assumed rapid diffusion and chemical reaction limited kinetics, a first and second order sorption model developed by Lagergren ⁽¹⁹⁾ to model aqueous fission product ion exchange experiments, and a diffusion mass transfer limited model. Not surprisingly, the exchange reaction model

failed to produce reliable results. The model was derived similarly to previous equilibrium models, and thus should not give accurate results on kinetics. Also, the general assumption that mass transfer is the limiting step in ion exchange reactions contradicts the exchange reaction model's reaction limited basis. The Lagergren and diffusion models both fit the experimental results well with each model having total root mean square deviations around 10%. The calculated diffusion coefficients for Cs⁺ and Sr²⁺ in the molten salt unexpectedly varied as a function of concentration. This was likely a result of an oversimplification of the mass transfer mechanism in the diffusion model.

Much work has been done in the effort to characterize and model the loading of fission product salts into zeolite-4A. Kinetic models have been developed that describe the time dependence of the sorption process, while equilibrium models effectively predict the compositions of the salt and zeolite at equilibrium conditions. Zeolite-4A has been shown to selectively remove certain fission products, hinting at the potential to recycle salt back into the electrorefiner.

CHAPTER 2

Materials and Methods

Both solid-state and molten-state salt-zeolite contacts were performed in this work. In INL's current salt loading process, kilogram quantities of powdered salt and zeolite are actively blended in a V-mixer ⁽⁵⁾. As the V-mixer is heated, the powdered salt melts and the bulk of the loading occurs in the molten-state. However, with the highly concentrated fission product salts lacking LiCl-KCl, it is expected that the melting point of the salt mixtures will not be reached at the operating temperatures of the V-mixer. Solid-state powder blending experiments were performed to ascertain the viability of a powder blending process to absorb fission product salts into zeolite-A.

However, the creation of a mass transfer model which takes into account the large particle collisions that occur in the solid-state involved complicated mathematics beyond the scope of this work. Thus, in order to develop the mass transfer model, molten-state experiments were performed in a controlled setting with specific process conditions. When applied to the developed mass transfer model, the results of the molten contacting experiments ultimately allowed for the determination of relevant physical parameters such as diffusivity within the zeolite material.

Experimental work was performed at the Center for Advanced Energy Studies (CAES), a partnership between INL and the major Idaho state universities. All saltzeolite contacts were performed within high purity argon atmosphere glove boxes. The glove box used to perform solid-state contacts is shown in Figure 3.



Figure 3: High Purity Argon Atmosphere Glove Box

A similar but separate glove box was used to perform the molten-state contacts. The oxygen and water concentrations in each glove box were consistently below 1.0 ppm. A portion of the analysis work was performed at North Carolina State University. Surrogate salts were used in lieu of radioactive salts in order to eliminate the need for radiological controls.

2.1 Solid-State Salt-Zeolite Contacts

The solid-state powdered salt-zeolite contacting experiments were designed to represent as closely as possible INL's powder blending process. The key difference between the two processes is the lack of active mixing capability. In this work, all powder mixtures were hand mixed before static heating in a furnace. Ultra dry salts obtained from Acros Organics, Alfa Aesar, or Fisher were ground and sieved into a 45-250 μ m classification. This classification provided adequate contact area without sacrificing material handling characteristics. Salt particles smaller than 45 μ m stuck to surfaces and proved difficult to handle without significant waste. Zeolite-4A material in the form of roughly 2mm diameter pellets were acquired from Universal Oil Products (UOP) and classified into the same 45-250 μ m range. UOP's industrial zeolite-4A material is composed of 1 μ m zeolite-4A crystallites surrounded by a proprietary inorganic clay binder ⁽⁴⁾. Pure zeolite-A is brittle, and the added inorganic binder provides crush strength to the pellet.

Once classified into the appropriate particle size, the salt and zeolite powders were mixed together in a 12 chloride per zeolite unit cell ratio in order to allow for comparison between salt mixtures. Hand mixing was performed for several minutes in order to ensure adequate blending of the salt and zeolite into a semi-homogenous mixture. Blended salt-zeolite mixtures were placed in CoorsTek crucibles and inserted into the muffle furnace as shown in Figure 4.



Figure 4: Loaded Muffle Furnace

The ample space inside the muffle furnace allowed for multiple solid-state contacts to be heated simultaneously. Generally, five separate salt-zeolite mixtures would be heated together. For this work, most solid-state contacts were heated to 600°C for five hours. Previous work showed that salt uptake into the zeolite was enhanced when the mixtures were heated at 600°C compared to at 500°C. However, the zeolite-4A material degrades at temperatures exceeding 600°C ⁽¹⁷⁾. Thus, 600°C was selected as the optimum temperature for this work.

After the heating cycle, the salt-zeolite mixtures were rinsed with 50 mL of nanopure H_2O and shaken for roughly one minute. A Thermo Scientific chloride probe was used to measure the dissolved chloride concentration of filtered samples of the

rinse solution. In order to ensure the sample solutions fell within the calibration range of the chloride probe, the probe was calibrated to measure between 10 and 1000 ppm. Salt uptake into the zeolite was then inferred by assuming that any chloride not present in solution must have been absorbed by the zeolite.

While initially designed to investigate zeolite-4A's ability to absorb highly concentrated fission product chlorides lacking LiCl-KCl, the powder contacting experimental setup evolved to study a separate portion of INL's salt treatment program. In an oxide reduction step, pure LiCl becomes contaminated with fission product chlorides ⁽¹⁷⁾. While treatment with zeolite-4A has been shown to effectively remove the fission product salts, ion exchange reactions with the sodium in the zeolite framework can result in sodium being transferred into the LiCl salt. In order to recycle the cleaned LiCl salt back into the oxide reduction process, the sodium transfer must be minimized or eliminated. The use of lithium substituted zeolite-A (Li-A) would remove sodium from the process and potentially produce a high purity LiCl product. The absorption characteristics of Li-A were thus studied and compared to those of zeolite-4A.

Li-A was synthesized via an adaptation of a method developed by Breck ⁽¹²⁾. Powdered zeolite-4A material was added to 200 mL of 3.17M LiCl solution and mixed for several hours. The concentration of the LiCl solution was chosen such that the number of lithium ions in solution would double the number of sodium ions in the original zeolite mass. After mixing, the powder was filtered and added to a fresh batch of LiCl solution. This process was repeated again for a total of three mixing runs. A flow diagram of the Li-A synthesis process is shown in Figure 5.



Figure 5: Li-A Synthesis Flow Sheet

To produce Li-A ready for salt-zeolite contact experiments, a drying step was performed to remove any water the zeolite absorbed during the synthesis process. Samples of the Li-A powder were taken for analysis to determine the extent of lithium substitution. One sample of Li-A powder was dissolved and analyzed via inductively coupled plasma mass spectrometry (ICP-MS) to give quantitative elemental composition data. The amount of lithium in the sample was compared to the amount of sodium in the sample to give the extent of substitution.

In addition to the powdered salt and zeolite contacts, a set of contacts were performed using pelletized zeolite-4A to study what effect the presence of chloride within the zeolite prior to exposure to fission product salts has on fission product uptake. It is theorized that the presence of chloride within the zeolite could enhance the rate of fission product uptake. It is thought that due to electroneutrality, fission product cations cannot diffuse through the zeolite particle without bringing along an associated chloride ion. The large, slow moving chloride ion decreases the rate of transport of the smaller, fast diffusing fission product cation. If chloride were already present in the zeolite, the fission product cation would merely have to exchange places with another small, fast moving cation. Cussler ⁽²⁰⁾ discusses this combined electrolyte diffusion argument and gives the effective diffusion coefficient of two associated salt ions as shown in Equation 11

$$D_{eff} = \frac{2}{\frac{1}{D_X} + \frac{1}{D_{Cl}}}$$
(11)

where D_x and D_{Cl} are the diffusion coefficients of cations x^+ and Cl^- respectively. Pelletized zeolite-4A was initially loaded with LiCl-KCl by mixing eutectic LiCl-KCl with pelletized zeolite-4A and baking in a furnace at 500°C for several hours. After removing exterior LiCl-KCl from the loaded pellets, loaded pellets were immersed in single component powdered fission product salts. The mixtures were heated in the furnace at 300°C for five hours. 300°C was selected as the operating temperature in order to prevent any LiCl-KCl that leaves the zeolite from melting. After the contact, pellets were cross sectioned and an X-ray fluorescence spectrometer (XRF) was used to generate qualitative spatial elemental composition maps. Comparisons between the empty and LiCl-KCl loaded cases were made using ImageJ software. By studying the uptake of each element within the pellet for both the blank and LiCl-KCl loaded cases, conclusions regarding the helpfulness of chloride presence prior to exposure were made.

2.2 Molten-State Salt-Zeolite Contacts

While not representative of INL's salt-zeolite blending process, the molten-state contacts were designed to provide salt loading vs. time data that could be used in the development of a kinetic model for salt sorption into zeolite-4A. The molten-state experimental process provided a method to closely control various system parameters. The parameters were chosen to fit the geometries and boundary conditions of the developed sorption model. All molten contacting experiments were performed in a glove box similar to that described in Figure 3.

CsCl or SrCl₂ was added to eutectic LiCl-KCl in order to generate a 2.5 wt% fission product chloride mixture. The salt mixtures were placed in magnesia crucibles obtained from Ozark Technical Ceramics as shown in Figure 6. Once heated above 350°C, the salt mixture will melt and fill the bottom centimeter of the crucible.



Figure 6: Loaded Magnesia Crucible

The zeolite-4A particle size was varied across the molten contacts. The roughly spherical material from UOP ranged from 1.8-2.4 mm in diameter. A portion of the zeolite-4A material was rolled between parallel plates of sandpaper in order to reduce

the zeolite particle size. Figure 7 shows the zeolite milling setup, while Figure 8 shows zeolite pellets before and after the sanding process.



Figure 7: Zeolite Milling Setup



Figure 8: Zeolite Milling Results

After milling, the particles were observed to maintain their roughly spherical shape. The four particle classifications used in this work are given in Table 1.

Table 1: Zeolite Pellet Classifications

Zeolite Pellet Diameter Classifications
1.23mm ± 0.07mm
1.71mm ± 0.04mm
2.08mm ± 0.06mm
2.32mm ± 0.08mm

All zeolite pellets used in the molten contacts were first dried in a furnace at 300°C to remove any absorbed water. Roughly 80 zeolite-4A pellets were placed inside the steel mesh basket depicted in Figure 9. Enough pellets were added so that repeated samples at each time point could be taken but without adding excess zeolite mass to the system.



Figure 9: Steel Mesh Basket

The salt loaded crucible was placed into a Kerr Auto Electromelt Maxi vertical furnace while the steel mesh basket was attached to a rotational motor above the top of the furnace. The completed experimental apparatus is shown in Figure 10.



Figure 10: Molten Contact Apparatus

To begin the experiment, the steel mesh basket containing zeolite was lowered into the furnace slightly above the top of the magnesia crucible. The furnace was switched on and set to 500°C. Upon reaching 500°C, the system was allowed to equilibrate for an hour before the molten contact would proceed. The mesh basket was lowered into the crucible such that the zeolite pellets were completely immersed in molten salt. The contact timer was started upon initial immersion. At the desired times, the timer was stopped and the basket raised to the level of the furnace lid. Several salt loaded zeolite pellets were then extracted from the basket. Once four or five pellets were removed, the basket was lowered back into the molten salt and the contact timer restarted. Salt loaded zeolite samples were obtained for both short and very long contact times, corresponding to the kinetic and equilibrium regimes of the sorption process.

One extracted pellet from each sample time was rinsed to remove excess salt adhered to the zeolite pellet, dried on a hotplate, and then massed. 600 μ L of concentrated HCl, 600 μ L of concentrated HNO₃, and 400 μ L of concentrated HF were used to completely dissolve each salt loaded zeolite pellet. After complete dissolution of the pellets, 6 mL of a 2.2% H₃BO₃ and 0.2% EDTA solution were added to each mixture in order to prevent the formation of insoluble fluoride complexes. The prepared sample was then analyzed via ICP-MS to quantitatively determine the elemental composition of each sample. Since the zeolite particles were not identical in size, the measured fission product loadings were normalized to the amount of aluminum in each pellet. In addition to accounting for the variation within each particle classification, the normalization allows experimental results to be compared across the various particle classifications used. The loading of fission product species is then related to the number of zeolite unit cells present via Equation 11

$$M_{t} = \frac{12 * a_{i} * [i] * MW_{Al}}{[Al] * MW_{i}}$$
(11)

where M_t is the zeolite loading at time t, a_i is ionic charge of species i, [i] and [Al] are the concentrations of species i and aluminum in the analyzed solution, while MW_i and MW_{Al} are the molecular weights of species i and aluminum. The factor of 12 relates the number of aluminum atoms per zeolite unit cell. The experimental M_t values are then used in developing the absorption model.

2.3 Development of Sorption Model

Diffusion mass transfer theory was used to model the transport of fission product salts into zeolite-4A pellets. Shell balance methods were used to derive the governing equation for transient diffusive mass transport into a spherical medium. Given in Equation 12, the governing equation describes the concentration of a given solute within the medium as a function of both time and radius

$$\frac{\partial C(r,t)}{\partial t} = \frac{D}{r^2} \left(r^2 \frac{\partial^2 C(r,t)}{\partial r^2} \right)$$
(12)

where C(r,t) is the concentration of solute within the medium, D is the diffusion coefficient of solute within the medium, r is radius, and t is time. In order to solve the governing equation for C(r,t), two boundary conditions and an initial condition must be specified. Application of the experimental conditions of the molten salt-zeolite system yields Equations 13-15.

$$C(r,0) = 0 (13)$$

$$C(a,t) = C_o \tag{14}$$

$$\frac{\partial C(0,t)}{\partial r} = 0 \tag{15}$$

Equation 13 states that the zeolite crystallite is devoid of fission products prior to immersion in the salt. Equation 14 gives the fission product concentration in the binder, which was assumed to equal the concentration of bulk salt external to the zeolite. In this work, the external salt concentration was assumed constant. This was accomplished experimentally by contacting relatively large masses of salt with small masses of zeolite. It was expected that the total mass of zeolite would not remove enough fission product salt to significantly alter the bulk salt concentration. Equation 15 maintains finiteness within the zeolite crystallite as *r* approaches zero.

Shown in Equation 16, Crank ⁽²¹⁾ gives the solution for Equation 12 after application of Equations 13-15

$$\frac{C(r,t)}{C_0} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{a}\right) e^{-\frac{Dn^2 \pi^2 t}{a^2}}$$
(16)

where a is the outer radius of the crystallite. C(r,t) is then integrated over the crystallite radius in Equation 17 to give the total amount of solute within the crystallite at exposure time t

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{Dn^2 \pi^2 t}{a^2}}$$
(17)

where M_t is the total solute within the crystallite at time t, and M_{∞} is the total solute within the crystallite at equilibrium. While the developed model is mathematically desirable, it oversimplifies the processes occurring within the zeolite into a single mechanism. The model combines both diffusion of solute through the zeolite cages and ion exchange with the zeolite framework into a single transport mechanism.

To separate the two transport mechanisms, chemical reaction terms were added to the governing equation. Shown in Equations 18 and 19, the ion exchange reaction is modeled as a first order reversible reaction.

$$\frac{\partial C(r,t)}{\partial t} = \frac{D}{r^2} \left(r^2 \frac{\partial^2 C(r,t)}{\partial r^2} \right) - \frac{\partial S(t)}{\partial t}$$
(18)

$$\frac{\partial S(t)}{\partial t} = k_f C(r, t) - k_r S(t)$$
(19)

where k_f and k_r are the forward and reverse reaction coefficients, respectively. S(t) is a construct used to model the total amount of solute which has reacted with the zeolite framework at time t. It is assumed that the amount of fission product trapped within the zeolite framework is initially zero. Physically, this model states that solute diffuses through the zeolite material, where it can simultaneously undergo a chemical reaction

and become trapped as part of the zeolite framework. Simultaneously, solute which has been trapped can react to become freely moving again.

Experimental M_t data were used to calculate the model parameters via a nonlinear optimization process. Initial guesses of model parameters were used to numerically solve each model equation subject to Equations 13-15. Calculated M_t values were optimized against experimental M_t data in order to generate best fit values of the model parameters. MATLAB's *pdepe* function was used to numerically solve the model equations. *pdepe* uses second order accurate finite difference methods to solve the spatial domain, and variable order Gear's method to solve the time domain.

pdepe solves for the solute concentration profile within each crystallite. The numerically generated concentration profile was then integrated with respect to radius using a Reimann sum method to generate the calculated M_t values. Based on previous experimental data, it was assumed that equilibrium was reached within 16 hours of contact, so the solver uses the 16 hour M_t value as M_{∞} . The total amount of solute within the pellet was calculated by summing the amount of solute in each individual crystallite at time *t*. This total value was then used in the optimization of model parameters.

To determine the size of the radial and time steps required for the solver to obtain sufficient accuracy, a comparison was made between the numerical and analytical solutions of the pure diffusion model given by Equation 12. For given *a* and *D*, analytical M_t values were plotted against numerical M_t values. Figure 11 shows the plot for a radial step (Δr) of 0.01µm and a time step (Δt) of 30 seconds.



Figure 11: Analytical vs. Numerical Model Comparison

As can be seen, the numerical solution matches quite well the analytical solution. As such, Δr and Δt were set at 0.01 µm and 30 s, respectively, for the remainder of this work. To perform the optimization, an error function given in Equation 20 was minimized by manipulating the model parameters to determine both best fit diffusion/reaction coefficients and loading vs. time curves.

$$Error = \sum \left(M_t^{numerical} - M_t^{experimental} \right)^2$$
(20)

MATLAB's *fminsearch* or *fmincon* were used to optimize the error function in Equation 19. *fminsearch* uses the Nelder-Mead simplex method to optimize, while *fmincon* uses an active-set method based on sequential programming methods.

CHAPTER 3

Results and Discussion

3.1 Powdered Static Contacts

Chloride uptake results for powdered salt and zeolite-4A mixtures are given in Figure 12. The mixtures were heated to 600°C for five hours. The salts were blended with zeolite at a 12:1 chloride to zeolite unit cell ratio.



Figure 12: Chloride Uptake in Zeolite-4A

Chloride uptake was surprisingly high given the lack of active mixing during the heating process. With just a few minutes of mixing followed by a static five hour heat cycle, greater than 30% of the chlorides were absorbed for all mixtures except BaCl₂. It

is expected that with longer heat cycles and active mixing, very high chloride uptake results would be observed. These results demonstrate that fission product salts lacking LiCl-KCl can be absorbed into zeolite-4A while in the solid phase.

ICP-MS analysis of the synthesized Li-A product revealed 73% exchange of sodium with lithium. While not complete, the extent of substitution was sufficient to effectively probe Li-A's sorption characteristics. Figure 13 shows the chloride uptake results for pure salts mixed with the synthesized Li-A.



Figure 13: Chloride Uptake in Li-A

With similar uptakes to zeolite-4A, the results suggest that Li-A does absorb some of the fission product salts at the experimental conditions. Slight improvements in cesium chloride and barium chloride absorption were seen. These results suggest that Li-A could be used instead of zeolite-4A to absorb fission product salts in the oxide reduction salt treatment process.

A portion of the synthesized Li-A was mixed with LiCl at a 12:1 molar ratio and heated several times in order to produce LiCl loaded Li-A. This was done to investigate whether the presence of LiCl within the zeolite enhanced the uptake of fission product ions. After each heat cycle, the salt/zeolite mixture was sampled to determine the free chloride level, and then stirred. Once sufficient free chloride results were obtained, the salt-zeolite mixture was rinsed with nanopure water to remove any unabsorbed salt. After drying, the LiCl loaded Li-A was mixed with pure salt and heated in the same manner as the previous powdered salt-zeolite contacts.

Due to the presence of LiCl within the zeolite, the chloride probe analysis method could not be used to determine the extent of salt uptake. Instead, filtered wash solutions were analyzed via ICP-MS to determine their salt cation content. Figure 14 gives the salt cation uptake results for each salt-zeolite mixture.



Figure 14: Salt Cation Uptake in LiCl Loaded Li-A

Nearly 40% of each cation was absorbed by the LiCl loaded Li-A. Most surprising were the divalent cation results, with both strontium and barium showing relatively high absorption into the zeolite. The presence of LiCl within the zeolite appeared to enhance the uptake of fission product ions. In addition, this result combined with miniscule additional chloride uptake in each case fit the combined diffusion argument.

The fission product ions merely exchanged places with occluded lithium ions without having to drag chloride ions along.

3.2 Pelletized Static Contacts

XRF maps of the blank and preloaded zeolite pellets exposed to powdered CsCl are presented in Figures 15-18. The silicon maps were used to define the boundaries of the zeolite pellet and generate a region of interest (ROI) for each sample.



Figure 15: Cs Map of Blank Pellet



Figure 17: Cs Map of Preloaded Pellet



Figure 16: Si Map of Blank Pellet



Figure 18: Si Map of Preloaded Pellet

Figure 17 shows a much higher density of cesium within the ROI of the preloaded pellet. In addition, the signal intensity corresponding to each color shade in Figure 17 is up to 4 times that of Figure 15. Thus, there is strong evidence that the presence of LiCl-KCl within the zeolite aids in the absorption of cesium. The corresponding maps of blank and preloaded zeolite contacted with SrCl₂ or BaCl₂ are given in Figures 19-22.



Figure 19: Sr Map of Blank Pellet



Figure 21: Ba Map of Blank Pellet



Figure 20: Sr Map of Preloaded Pellet



Figure 22: Ba Map of Preloaded Pellet

Shown in Figures 20 and 22, strontium and barium uptake in the LiCl-KCl loaded pellets did not appear appreciably different then the uptake in the blank pellets. In an

attempt to quantify the difference between the blank and preloaded measurements, ImageJ was used to calculate the total pixel value within each ROI. Darker shades of red correspond to smaller signals of the element of interest within the ROI, while brighter shades of red correspond to larger signals. The total pixel value was then divided by the ROI area to create a value comparable between the two pellet compositions. The results of the ImageJ calculations are given in Table 2.

Sample	Total Pixel Value	Pixel Area	Pixel Value Density	Maximum Relative Intensity
Blank CsCl	531,049	198,456	2.68	1
Preloaded CsCl	1,406,668	158,740	8.86	4
Blank SrCl ₂	3,074,622	694,890	4.42	2
Preloaded SrCl ₂	186,981	148,208	1.26	16
Blank BaCl2	258,992	148,208	1.75	2
Preloaded BaCl2	288,285	174,593	1.65	2

Table 2: ImageJ XRF Map Calculations

The results for cesium look promising, with both the pixel density and maximum intensity higher in the preloaded case. This result suggests that LiCl-KCl preloading aids in the absorption of cesium into the zeolite from a chloride salt. In the case of both strontium and barium, the pixel densities of the preloaded pellets were either equal to or less than that of the blank pellets, suggesting no helpful effect of LiCl-KCl preloading.

Results of the pelletized static contacts indicate that cesium absorption into the zeolite was aided by the presence of LiCl-KCl within the zeolite, while and strontium barium absorption were unaffected. The 300°C furnace temperature difference and lack of available contact area were likely responsible for the variation in results between the powdered/pelletized zeolite contacts.

3.3 Molten Contacts

Molten contacting experiments were performed to generate loading vs. time curves for salt and zeolite compositions given in Table 3. The use of multiple zeolite pellet sizes provided useful information of the limiting kinetics of the absorption process. An X signifies that the experiment was performed. The data from each experiment were used in the development of the diffusion based absorption model.

Table 3: Molten Experiment Salt-Zeolite Compositions

Zeolite Pellet Classification (mm)	2.5 wt% CsCl Mixture	2.5 wt% SrCl ₂ Mixture
1.23 ± 0.07		Х
1.71 ± 0.04	Х	Х
2.08 ± 0.06	Х	Х
LiCl-KCl Loaded 2.08 ± 0.06	Х	Х
2.32 ± 0.08	Х	Х

It was decided that four molten CsCl contacts were enough to provide sufficient modeling data to describe both the effects of particle size and LiCl-KCl preloading on Cs⁺ absorption into the zeolite. Figure 23 gives the loading vs. time curves for each 2.5 wt% CsCl mixture contacted with blank zeolite-4A pellets. The loading data were plotted against the square root of time in order to better visualize each curve.



Figure 23: Cesium Loading in Blank Zeolite-4A

In each case, cesium loading reached equilibrium in the pellet within roughly 900 seconds. Visual observation of the data indicated the smaller pellet sizes reached near-equilibrium loading only slightly faster than the larger pellets. Figure 24 presents the loading vs. time data for 2.5 wt% SrCl₂ contacted with blank zeolite pellets.



Figure 24: Strontium Loading in Blank Zeolite-4A

Time to equilibrium was much greater for each strontium contact. In addition to longer overall times to reach equilibrium, the difference between each particle size was also larger. For the smallest particle size, equilibrium was reached after roughly an hour, while the largest particle size took the entire eight hour duration to reach equilibrium.

To investigate the vast difference in time to equilibrium between the cesium and strontium loadings, a set of zeolite samples exposed to the SrCl₂ mixture were cleaved along the cross section and imaged under a light microscope. The purpose of this work was to determine the amount of contact time required for the liquid salt to fully penetrate the intraparticle space within the pellet. Figures 25-29 show the depth of salt penetration of 2.32mm pellets contacted for up to 900 seconds.



Figure 25: Pellet Contacted for 60 Seconds



Figure 26: Pellet Contacted for 120 Seconds



Figure 27: Pellet Contacted for 300 Seconds



Figure 28: Pellet Contacted for 600 Seconds



Figure 29: Pellet Contacted for 900 Seconds

As shown in Figures 25-29, the salt saturation time for 2.32 mm pellets is between 600-900 seconds of contact. This saturation time matches up with cesium loading equilibrium times given in Figure 24. This is indicative of intraparticle limited transport where cesium diffusion into the zeolite crystallites is rapid compared to the bulk movement of salt through the pellet. However, the long equilibrium times in Figure 24 show intracrystalline limited transport of strontium. Diffusion of strontium into the zeolite crystallites is slow relative to the bulk transport of salt into the pellet.

Loading vs. time data for blank and LiCl-KCl loaded zeolite are presented in Figures 30 and 31. For the LiCl-KCl loaded pellets exposed to the CsCl mixture, sampling was stopped after two hours because it was believed equilibrium had been reached.



Figure 30: Cesium Loading Preloading Comparison



Figure 31: Strontium Loading Preloading Comparison

As can be seen in Figures 30 and 31, the presence of LiCl-KCl within the zeolite does not appreciably increase the rate of uptake of cesium or strontium from a molten salt into the zeolite pellet. While the uptake of strontium in the LiCl-KCl loaded dataset

show slightly higher loading at early times, long time loading approaches equilibrium at the same rate regardless of initial pellet composition.

In Table 4, the equilibrium loading results for each data set were compared to the results from Yoo's equilibrium model ⁽¹⁶⁾. Strangely, Yoo's cesium loading results were a factor of 5 times greater than the experimental value, but Yoo's strontium calculation closely matched the experimental results.

DatasetAverage Equilibrium Loading (Eq./unit cell)2.5 wt% CsCl0.49Yoo 2.5 wt% CsCl2.782.5 wt% SrCl24.57Yoo 2.5 wt% SrCl24.55

Table 4: Comparison of Loading Results with Equilibrium Model

To investigate the cesium loading difference, an attempt was made to quantify the mass of cesium within the inorganic binder of each pellet. Yoo's model uses pure zeolite-4A, while the zeolite used in this work is a composite material. The mass of cesium within the zeolite pellet binder volume was estimated by assuming a binder volume fraction ε and then filling the binder volume with bulk salt. Low, medium, and high values of binder volume fraction were used. The mass of cesium within the binder was then determined from known bulk salt cesium concentration.

Table 5 gives the average calculated masses of cesium within the binder at equilibrium compared to experimental equilibrium masses. The binder volume fraction largely determined the fraction of total cesium loading located within the binder. While the true binder volume fraction is unknown, it is expected to be low and much closer to the small values used in the calculation. Thus, while a portion of the total loading is present in the binder phase, the majority of the cesium within the pellet is located in the zeolite crystallites. While the calculation does not explain the difference between the predicted and observed loading results, it does show that the zeolite crystallites do in fact absorb cesium from the molten phase.

Cesium Particle	Cesium Mass	Cesium Mass	Cesium Mass	Experimental
Size (mm)	when $\varepsilon = 0.25$	when $\varepsilon = 0.50$	when $\varepsilon = 0.75$	Cesium Mass
	(mg)	(mg)	(mg)	(mg)
1.71	0.02	0.05	0.08	0.14
2.08	0.05	0.10	0.15	0.27
2.32	0.07	0.13	0.20	0.31

Table 5: Cesium Loading in Binder Volume

3.4 Molten Contact Model Fitting and Parameter Calculation

The cesium loading curve in Figure 23 and the light microscopy images in Figures 25-29 suggested that cesium transport into the zeolite pellet was intraparticle transport limited. That is, the transport through the binder in the space between zeolite crystallites was much slower than transport into the crystallites. The model was thus simplified to include only bulk diffusion into the pellet. The pellet was considered to be a large porous sphere of binder material, and no reaction terms were used to model mass transport.

For strontium transport, Figure 24 and the light microscopy images suggested that transport into the pellet was limited by transport into the zeolite crystallites. Thus, the binder was ignored and the pellet modeled as a single zeolite crystallite. Both diffusion and reaction terms were considered.

Figures 32-25 plot experimental data with the results of the model calculation for each cesium data set.



Figure 32: Cesium Model Fitting with 1.71 mm Pellets



Figure 33: Cesium Model Fitting with 2.08 mm Pellets



Figure 34: Cesium Model Fitting with 2.08 mm LiCl-KCl Loaded Pellets



Figure 35: Cesium Model Fitting with 2.32 mm Pellets

Table 6 shows the calculated effective diffusion coefficient and error function value from each cesium dataset. The three blank zeolite data sets each give fairly consistent results, with an average effective diffusion coefficient of 9.03E-06 cm² per

second. For the LiCl-KCl loaded dataset, the model calculates a D_{eff} roughly one third that of the blank zeolite average value. This result shows that the presence of LiCl-KCl within the zeolite did not enhance the rate of molten salt phase cesium uptake.

Cesium Dataset	D_{eff} (cm ² /s)	Optimized Error Function
		Value
1.71 mm	9.57E-06	0.057
2.08 mm	7.82E-06	0.12
2.08 mm LiCl-KCl Loaded	2.75E-06	0.064
2.32 mm	9.72E-06	0.12

Table 6: Cesium Model Parameter Calculations

Figures 36-40 give the experimental strontium loading data as well as the model fitting result for both the pure diffusion model and the reversible reaction-diffusion model. In all datasets except the LiCl-KCl loaded dataset, the reaction-diffusion model produced essentially the same curve as the pure diffusion model. As can be seen on Figure 39, the reaction-diffusion model had not reached equilibrium by the end of the 8 hour experiment. This result suggests that in the case of the molten salt contacting experiments, the presence of LiCl-KCl within the zeolite did not increase the rate of strontium uptake into the zeolite.



Figure 36: Strontium Model Fitting with 1.23 mm Pellets



Figure 37: Strontium Model Fitting with 1.71 mm Pellets



Figure 38: Strontium Model Fitting with 2.08 mm Pellets



Figure 39: Strontium Model Fitting with 2.08 mm LiCl-KCl Loaded Pellets



Figure 40: Strontium Model Fitting with 2.32 mm Pellets

A summary of the calculated model parameters is presented in Tables 7 and 8. The calculated diffusivities for each dataset were fairly consistent across models with the exception of the LiCl-KCl loaded dataset. The calculated reaction-diffusion D_{eff} was an order of magnitude larger than in pure diffusion model, while the calculated k_f and k_r for the LiCl-KCl loaded dataset were an order of magnitude smaller than any other dataset.

Table 7: Strontium Pure Diffusion Model Parameter Calculations

Strontium Dataset	D_{eff} (cm ² /s)	Optimized Error Function
		Value
1.23 mm	8.33E-07	0.099
1.71 mm	3.58E-07	0.110
2.08 mm	1.97E-07	0.009
2.08 mm LiCl-KCl Loaded	2.34E-07	0.159
2.32 mm	2.26E-07	0.013
2.32 mm	2.26E-07	0.013

Strontium Dataset	D_{eff} (cm ² /s)	k _f (s ⁻¹)	k _r (s ⁻¹)	Optimized Error
				Function Value
1.23 mm	9.85E-07	0.017	0.086	0.100
1.71 mm	4.43E-07	0.014	0.065	0.110
2.08 mm	2.27E-07	0.011	0.065	0.009
2.08 mm LiCl-KCl Loaded	3.13E-06	1.19E-04	1.02E-04	0.046
2.32 mm	5.08E-07	0.054	0.047	0.014

Table 8: Strontium Reaction-Diffusion Model Parameter Calculations

In the reaction-diffusion model, the calculated diffusion coefficients were always several orders of magnitude less than the reaction coefficients, thus suggesting diffusion limited transport within the zeolite crystal. The small difference in diffusion coefficients and fits between models suggests that the reaction terms are insignificant.

The results of the model optimization were then compared to several works studying liquid diffusion through porous media. Walker and Weatherly ⁽²²⁾ investigated the transport of aqueous dyes into granular activated carbon. El-Kamash ⁽¹⁹⁾ studied fission product transport from aqueous solutions into zeolite-A, while Lexa and Johnson ⁽¹¹⁾ examined molten salt transport into zeolite-A. Table 9 summarizes the results from each work. Most important is the agreement between the results of this work and that of Lexa and Johnson. Ultimately, the results of the developed model suggest that while the physics of the salt-zeolite system are not completely captured by the developed models in this work, the models still give an effective and reasonably accurate description of the mass transfer process.

Dataset	Reported $D_{eff}(cm^2/s)$
Walker and Weatherly	10-5-10-13
Lexa and Johnson	10-6
El-Kamash	10-9
Allensworth	10-6-10-7

 Table 9: Comparison of Calculated Diffusion Coefficients

CHAPTER 4

Conclusion

An investigation into the fission product uptake characteristics of zeolite-A was conducted to ascertain zeolite-A's ability to absorb powdered fission product salts. Additionally, physical parameters relevant to fission product transport within the zeolite material were determined in an effort to understand the mass transfer kinetics of the absorption process. Both solid-state and molten-state experiments were conducted in this study.

Solid-state powder blending contacts demonstrated that zeolite-4A effectively absorbs pure fission product salts. The powder contacts were designed to resemble INL's proposed process as closely as possible. Thus, powdered salt and zeolite were hand mixed before undergoing a static heat cycle. Despite the lack of active mixing and relatively low contact times compared to the proposed blending process, between 10-75% of each salt was absorbed. Additionally, Li-A was synthesized using an aqueous method achieving nearly 75% substitution. Powdered salt uptake in Li-A was almost identical to zeolite-4A given the same experimental conditions. The results of the powder contacts were significant in that they demonstrated that waste salt lacking LiCl-KCl can still be effectively absorbed as a powder by zeolite-A material. Ultimately, the results showed that the proposed INL process needs no modification to treat the waste salt from a zone melt crystallization waste reduction step. Additionally, results of the Li-A contacts proved the usefulness of Li-A to an oxide reduction salt treatment step of INL's proposed process.

An investigation into the use of LiCl or LiCl-KCl loaded zeolite as a method to enhance the rate of solid phase fission product uptake yielded mixed results. Significant increases in fission product uptake were seen in the LiCl loaded Li-A mixtures compared to blank zeolite-4A/Li-A. An XRF study using blank and LiCl-KCl loaded pelletized zeolite contacted with powdered salt showed an increase in cesium uptake, while prior chloride presence had no effect on barium or strontium uptake.

A model has been developed to study the kinetics of molten fission product transport into zeolite-A. The salt absorption process was modeled as a basic reactiondiffusion system that effectively captures the time dependent nature of the process without requiring advanced mathematics. Experimental fission product loading vs. time data were generated and used to calculate best fit model parameters. Several zeolite pellet size ranges were used to investigate the significance of both intraparticle and intracrystalline transport through the zeolite pellet. Cesium transport into the zeolite pellet occurred much quicker than strontium transport, and the calculated model parameters reflected this result. It was found that cesium transport through the inorganic binder was limiting, and that a significant portion of the total cesium loading never entered the zeolite crystallites. Diffusion into the crystallites was determined to be limiting for strontium transport. The calculated effective diffusivities of both cesium and strontium fell within the range of other work studying liquid diffusion into porous media. Results of molten contacts using blank and LiCl-KCl loaded zeolite showed little to no uptake enhancements. With this work, the rates of uptake of cesium and strontium into zeolite-4A from a molten salt can be compared relative to one another. While not truly indicative of the proposed INL salt-zeolite blending process, the fundamental aspects of the salt mass transfer process captured by the model should be useful in future process design optimization.

To continue this work, the developed kinetic model should be adapted to include simultaneous transport of multiple species. This will allow more complete and realistic modeling of the salt-zeolite system that could be useful in studying fission product selectivity. Additionally, the salts investigated should be expanded to include multicomponent mixtures that are more indicative of the actual waste salt.

For the powdered salt-zeolite contacts, the most logical path forward is to conduct similar experiments using a lab scale V-mixer to exactly resemble the proposed

process setup. The salts used should move from pure single component salts to multicomponent mixtures which better resemble waste salt lacking LiCl-KCl. The gram scale actively mixed experiments should then evolve to kilogram scale experiments using a large V-mixer to demonstrate the effectiveness of the blending process on a greater scale. Finally, actively mixed powder blends using chloride loaded zeolite would continue the investigation on the use of chloride loaded zeolites to enhance fission product uptake.

References

1. Behavior of uranium and zirconium in direct transport tests with irradiated EBR-II fuel. Ahluwalia, R., Hua, T. Q., Geyer, H. K. 1999, Nuclear Technology, Vol. 126, pp. 289-301.

2. *Chemical basis for pyrochemical reprocessing of nuclear fuel.* Ackerman, J. P. 1991, Ind. Eng. Chem. Res., Vol. 30, pp. 141-145.

3. *Pyroprocessing progress at idaho national laboratory*. Benedict, R. W., Solbrig, C. Westphal, B., Johnson, A., Li, S. X., Marsden, K, Goff, K. M. Boise : s.n., 2007. GLOBAL.

4. *Kinetics of molten chloride salt sorption into zeolite-4A*. Simpson, M. F., Lance, S., Moore, G. Seattle : s.n., 2002. Light Metals: Proceedings of Sessions, TMS Annual Meeting. p. 51.

5. A description of the ceramic waste form production process from the demonstration phase of the electrometallurgical treatment of EBR-II spent fuel. Simpson, M. F., Goff, K. M., Johnson, S. G., Bateman, K. J., Battisti, T. J., Toews, K. L., O'Holleran, T. P. 2001, Nuclear Technology, Vol. 134, p. 263.

6. *Immobilization of Salt from Zone Freezing Process in Zeolite-A*. Simpson, M. F. Dmitrovgrad : s.n., 2010. International Pyroprocessing Research Conference.

7. *Treatment of high-level wastes from the ifr fuel-cycle*. Johnson, T. R., Lewis, M. A., Newman, A. E., Laidler, J. J. 1992, Abstracts of Papers of the American Chemical Society, Vol. 204, p. 111.

8. *Mixing of zeolite powders and molten salt.* Pereira, C., Zyryanov, M. A., Lewis, M. A., Ackerman, J. P. 1996, Ceramic Transactions, Vol. 72, p. 485.

9. *Modeling of a zeolite column for the removal of fission products*. Ahluwalia, R. K., Geyer, H. K., Pereira, C., Ackerman, J. P. 1998, Ind. Eng. Chem. Res., Vol. 37, p. 145.

10. Adsorption of eutectic LiCl-KCl into zeolite 4A using a mechanically fluidized vacuum system. Simpson, M. F., Battisti, T. J. 1999, Ind. Eng. Chem. Res., Vol. 38, p. 2469.

11. Occlusion and ion exchange in the molten (lithium chloride-potassium chloride-alkali metal chloride) salt + zeolite 4A system with alkali metal chlorides of sodium, rubidium, and cesium. Lexa, D., Johnson, I. 2001, Metallurgical and Materials Transactions B, Vol. 32B, p. 429.

12. Breck, D. W. Zeolite molecular sieves. Malabar : Kreiger Publishing Co., 1984.

13. *Two-site equilibrium model for ion exchange between monovalent cations and zeolite-A in a molten salt.* Simpson, M. F., Gougar, M. L. D. 2003, Ind. Eng. Chem. Res., Vol. 42, p. 4208.

14. Two-site equilibrium model for ion exchange between multi-valent cations and zeolite-A in a molten salt. Gougar, M. L. D., Simpson, M. F., Scheetz, B. E. 2005, Microporous and Mesoporous Materials, Vol. 84, p. 366.

15. Equilibrium model for ion exchange between multivalent cations and zeolite-A in a molten salt. Phongikaroon, S., Simpson, M. F. 2006, AIChE Journal, Vol. 52, p. 1736.

16. Salt-zeolite ion-exchange equilibrium studies for a complete set of fission products in molten LiCl-KCl. Yoo, T., Frank, S., Simpson, M. F., Hahn, P.A., Battisti, T. J., Phongikaroon, S. 2010, Nuclear Technology, Vol. 171, p. 306.

17. Selective separation of cs and sr from LiCl-based salt for electrochemical processing of oxide spent nuclear fuel. Sachdev, P., Simpson, M. F., Frank, S. M., Yano, K., Utgikar, V. 2008, Separation Science and Technology, Vol. 43, p. 2709.

18. Study of ion exchange kinetics between Cs+ or Sr2+ and zeolite-A in molten LiCl-KCl. Shaltry, M., Phongikaroon, S., Simpson, M. F. Salt Lake City : s.n., 2010. AIChE Annual Student Conference.

19. Evaluation of zeolite A for the sorptive removal of Cs+ and Sr2+ ions from aqueous solutions using batch and fixed bed column operations. El-Kamash, A. M. 2008, Journal of Hazardous Materials, Vols. 151(2-3), p. 432.

20. Cussler, E. L. Diffusion mass transfer in fluid systems. Cambridge, UK : Cambridge University Press, 1997.

21. Crank, J. The mathematics of diffusion. New York : Oxford University Press, 1975.

22. *Kinetics of acid dye adsorption on GAC*. Weatherly, L.R. and Walker, G.M. 8, Oxford : Water Research, 1999, Vol. 33.