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Ion exchange kinetics of fission products between molten salt and zeolite-A

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ABSTRACT

Experimentation, data analysis, and modeling of ion exchange kinetics between fission products (cesium and strontium) and zeolite-A beads in molten LiCl–KCl have been performed to support optimization of an electrochemical process to treat used nuclear fuel. Models based on pseudo-first- and pseudo-second-order sorption as well as diffusion have been adapted and compared to experimental data to assess their validity in describing the system. Individual experiments were performed with different concentrations of CsCl or $SrCl_2$ in the LiCl–KCl salt. Zeolite beads were removed from the molten salt at prescribed intervals of time and prepared for analysis by inductively coupled plasma-mass spectrometry. Results indicate maximum cesium (Cs) and strontium (Sr) loading occurred at approximately 31 min and 104 min of contact, respectively. The rate of loading and maximum loading were found to increase with increasing initial concentration of Cs or Sr. Data analysis included determination of rate constants and diffusion coefficients of the proposed models for each experimental condition. Results reveal that the diffusion model provides the best fit to the experimental data with average diffusion coefficients of 2.0×10^{-10} m^2 s^{-1} for Cs and 6.3×10^{-11} m^2 s^{-1} for Sr. This suggests that chemical diffusion is the dominant mechanism of mass transfer.

1. Introduction

Used nuclear fuel from the Experimental Breeder Reactor-II is currently being treated using an electrochemical process at the Materials and Fuels Complex located at Idaho National Laboratory. The electrorefiner is the most important component of the electrochemical treatment process and is used for the simultaneous dissolution of metal fuel at the anode and deposition of uranium metal at the cathode. This process takes place in molten lithium chloride–potassium chloride (LiCl–KCl) [1–4]. During this process, active metals (including fission products) accumulate in the molten salt. After several batches of fuel are treated, it becomes necessary to remove some of the molten salt from the electrorefiner to avoid the buildup of heat generating fission products, such as cesium (Cs) and strontium (Sr). Sodium accumulation, which increases the melting temperature of the molten salt, and criticality issues associated with increasing concentration of plutonium are also reasons for removing salt [4]. To address this issue, it is currently planned to remove salt from the electrorefiner, combine it with zeolite-A and glass frit, and consolidate the resulting powder into a ceramic waste form. This method leads to the disposal of relatively large volumes of high-level waste. An ion exchange column loaded with zeolite has been proposed for implementation in the process to reduce the volume of waste generated by enabling the recycle of LiCl–KCl back to the electrorefiner. This could dramatically lower processing costs, especially the cost to dispose of the waste.

Numerous studies of fission product removal from molten salt by zeolite-A have focused on equilibrium exchange conditions [5–9]. However, an understanding of the kinetic behavior of this system is fundamental for equipment design and optimization of the process. To explore the kinetic behavior of fission product removal, experiments were tailored to produce zeolite samples at times prior to and at equilibrium conditions. Several batches of salt were prepared with varying concentrations of active metal chlorides to span a wide range of conditions. The zeolite samples were analyzed to determine the change in their elemental composition as a function of time. Data analysis was carried out to assess how well each model fit the data. Ultimately, the objective of this research is to develop a simple model that is capable of predicting the kinetic and equilibrium ion exchange behavior.

2. Experiment

2.1. Materials and equipment

All chloride salts used in the experiments were procured from Alfa Aesar (99.9% LiCl, 99.95% KCl, and 99.995% $SrCl_2$) with the

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exception of 99.99% CsCl, which was an Acros Organics product. Zeolite-A beads (average diameter of 0.00213 m) were a commercial product obtained from UOP. The beads are composed of 2 μm–3 μm zeolite-4A (sodium-form) crystals held together by a proprietary clay binder. Dense magnesia (MgO) crucibles, with inside diameters of 0.0254 m and heights of 0.0508 m, were obtained from Ozark Technical Ceramics. The experiments were performed within an MBraun sealed-atmosphere glovebox using a KerrLab lab-scale furnace (see Fig. 1(a) and (b)).

2.2. Experimental procedure

Throughout the experimental duration, oxygen and moisture levels were maintained below 0.1 μL/L. Each salt mixture was prepared by adding 1.0 wt.%, 2.5 wt.%, or 5.0 wt.% of CsCl or $SrCl_2$ to approximately 0.0125 kg of LiCl–KCl salt (~72 mol% LiCl). The MgO crucible containing the salt mixture was placed into the furnace and heated to 773 K. The experiment was initiated by lowering a stainless steel mesh basket containing the zeolite-A beads, which was coupled to a rotating motor drive (shown in Fig. 1(b)). The mesh basket was rotated at a rate of 10.47 rad s^{-1} (100 rpm) while in contact with the molten salt. At the prescribed intervals, the mesh basket was raised to a height slightly above the furnace lid and a portion of the zeolite beads was retrieved and stored for analysis. Experiment durations were chosen to capture the kinetic and equilibrium regimes based on information from previous work [5,10]. Samples from the Cs experiments were taken at 5 min intervals during the first 30 min of contact and at 15 min intervals thereafter. Samples from Sr tests were taken at 20 min intervals during the first 120 min of contact and at 40 min intervals thereafter.

Stored samples were then removed from the glovebox and prepared for compositional analysis via an inductively coupled plasma-mass spectrometer (ICP-MS). Zeolite beads were prepared for analysis by combining 600 μL of hydrochloric acid, 600 μL of nitric acid, 400 μL of hydrofluoric acid, and 6 mL of a 2.2% boric acid + 0.2% ethylenediaminetetraacetic acid solution [11–13]. Dissolution took place under a fume hood at room temperature. The zeolite beads were not crushed or rinsed prior to analysis. Once dissolved, the zeolite/acid solutions were diluted to a total dissolved solid of less than 0.001 kg L^{-1}. Internal and external standards were prepared for calibration of the Agilent 7200c ICP-MS. The diluted sample solutions were placed on the ICP-MS autosampler in random order. Uncertainty associated with the ICP-MS measured value is in the range of 7–10%.

3. Results and discussion

3.1. General data interpretation

Measurement of the elemental composition of the samples yielded information about the loading of the cations in the zeolite as a function of time. The zeolite loading, y_i, was calculated using the equation:

$$y_i = \frac{12 u_i w_i M_{Al}}{w_{Al} M_i} \tag{1}$$

where 12 represents the moles of aluminum per unit cell, u_i is the molar equivalent of species i per mole of species i, w_i is the mass fraction of species i to the total dissolved solid of the sample, and M_i is the molar mass of species i.

Results of the Cs and Sr ion exchange tests are depicted in Fig. 2(a) and (b), respectively. Maximum loading in the zeolite increases with increasing initial concentration of CsCl and $SrCl_2$ in the salt. This observation is consistent with previously reported studies [5,7,8].

Further data analysis was facilitated by determining a critical time ($t_{critical}$) in the transition from the kinetic to equilibrium regions of the plots in Fig. 2. The critical time is the value of the time coordinate at the intersection of the average line of regression in the kinetic region and the equilibrium value of a particular data set. This method is illustrated in Fig. 3. In this case, the slope of the line in the kinetic region (m_{ave}) is formulated by averaging of the slopes of several lines (dashed lines) fitted to one or multiple data points in the apparent kinetic region of the plot. It was found that the average value for loading in the zeolite at the critical time for the Cs and Sr experiments is approximately 76% and 81% of equilibrium loading, respectively.

The critical time value is useful for plotting the data in a dimensionless format, as shown in Fig. 4. From this, it can be seen that the data sets from both the Cs and Sr experiments collapse upon each other indicating universal behavior. Moreover, the time at which equilibrium loading occurs in the zeolite, indicated by the dashed line ($t_{eq}/t_{critical}$), is easily obtained from Fig. 4.

In this particular case, the average values of $t_{eq}/t_{critical}$ for Cs and Sr are 2.38 ± 0.142 and 2.11 ± 0.122, respectively. This result can be extended to systems of any initial concentration of Cs or Sr. For the Cs experiments, equilibrium was achieved at an average of 31 min of contact. For Sr, the average was 104 min. Additionally, the average rate of loading (y_{eq}/t_{eq}) prior to equilibrium was calculated for each of the experiments. Table 1 lists the values associated with Figs. 3 and 4 for the Cs and Sr experiments.

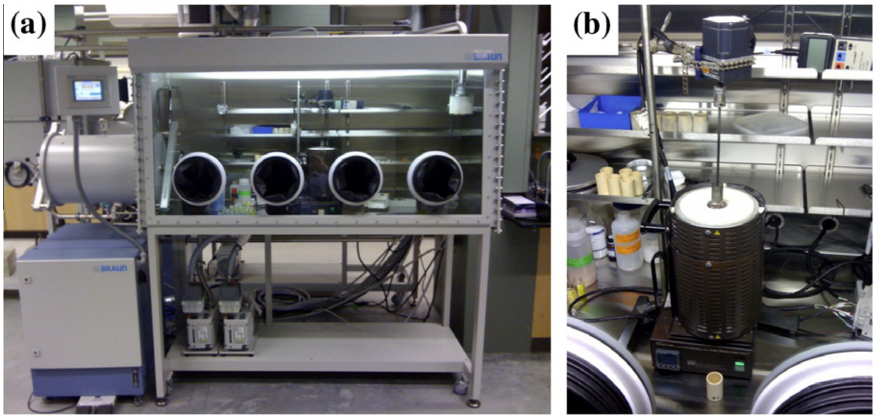

Fig. 1. (a) The MBraun glovebox and (b) the KerrLab melting furnace.