Original Article

SEPARATION OF STRONTIUM AND CESIUM FROM TERNARY AND QUATERNARY LITHIUM CHLORIDE-POTASSIUM CHLORIDE SALTS VIA MELT CRYSTALLIZATION

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A B S T R A C T

Separation of cesium chloride (CsCl) and strontium chloride ($SrCl_2$) from the lithium chloride-potassium chloride (LiCl-KCl) salt was studied using a melt crystallization process similar to the reverse vertical Bridgeman growth technique. A ternary $SrCl_2$-LiCl-KCl salt was explored at similar growth rates (1.8—5 mm/h) and compared with CsCl ternary results to identify similarities. Quaternary experiments were also conducted and compared with the ternary cases to identify trends and possible limitations to the separations process. In the ternary case, as much as 68% of the total salt could be recycled per batch process. In the quaternary experiments, separation of Cs and Sr was nearly identical at the slower rates; however, as the growth rate increased, $SrCl_2$ separated more easily than CsCl. The quaternary results show less separation and rate dependence than in both ternary cases. As an estimated result, only 51% of the total salt could be recycled per batch. Furthermore, two models have been explored to further understand the growth process and separation. A comparison of the experimental and modeling results reveals that the nonmixed model fits reasonably well with the ternary and quaternary data sets. A dimensional analysis was performed and a correlation was identified to semipredict the segregation coefficient.

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1. Introduction

Pyroprocessing is a used nuclear fuel (UNF) reprocessing technology that has been proposed as an alternative to traditional aqueous methods. This technology is attractive because of its small footprint, resistance to proliferation, and relatively low waste generation [1—3]. At the heart of this design is an electrorefiner that electrochemically dissolves the uranium metal at an anode into a eutectic lithium chloride-potassium chloride (LiCl-KCl) salt electrolyte. The uranium is then transported

through the electrolyte and reduced onto a cathode for later reuse. Throughout this process, fission products, rare earth elements, and transuranic chlorides accumulate in the molten salt. Table 1 shows the electrorefiner salt composition after processing UNF from the experimental breeder reactor II (EBR-II). As concentrations of these contaminants accumulate over multiple batch processes, the efficiency of the electrorefiner diminishes. To keep the electrorefiner at its optimum operating condition, it is necessary to replace or recycle the molten salt over time. The used electrolyte salt constitutes a large portion of the waste generated during the pyroprocessing of UNF.

Several technologies such as oxygen sparging [5] and lithium drawdown [6] have been explored for rare earth element and transuranic element removal, respectively. These processes are effective; however, methods to remove the fission products are still needed. Ion-exchange technology has been explored as a means of removing fission product contaminants from the electrolyte salt [7]. However, this method only reduces the waste mass by an estimated 50% [8]. In several recent studies conducted by the Korean Atomic Energy Research Institute (KAERI, Daejeon, Korea) [9−11] and the University of Idaho (Idaho Falls, ID, USA) [12,13], a melt crystallization technique has been explored as a potential technique for salt purification. Results from these studies indicate that in some cases up to 90% of the used salt can be recycled *via* a melt crystallization process. The melt crystallization process used in several of these studies was a reverse vertical Bridgeman growth configuration, which is demonstrated schematically in Fig. 1. In this study, the material is advanced slowly upwards from a high temperature zone into a low-temperature zone. As a result, the melt is cooled from the top downwards at a controlled rate. As the melt solidifies, the contaminants tend to stay in the melt and yield higher contaminant concentrations at the bottom of the solidified salt ingot. The bottom portion, which contains the bulk of the impurities, can then be mechanically separated, mixed with zeolite, and formed into a stable ceramic waste form. The upper portion of the purified LiCl-KCl salt can be returned to the electrorefiner.

The focus of the melt crystallization works conducted to date has been on separating Cs and Sr from the waste salt.

These fission products constitute the bulk of the fission products in the waste salt. In addition, Cs and Sr are major contributors in the heat generated because of radiation decay. In works by Cho et al [9], Cho et al [10], and Choi et al [11] at KAERI, the feasibility of this technology has been addressed. However, key operating parameters were not fully explored. In a work conducted by Williams and coworkers [12], various parameters were explored such as temperature, rate of advancement, initial composition, and a variation of the lid/no-lid configuration for separating CsCl from the electrolyte. Optimal parameters were determined in this study for the CsCl case. However, no experiments were conducted using $SrCl_2$, which provided a motivation for this study to explore melt crystallization using $SrCl_2$ alone and $SrCl_2$-CsCl in the LiCl-KCl salt. The effects of the advancement rates for the ternary $SrCl_2$-LiCl-KCl and quaternary $SrCl_2$-CsCl-LiCl-KCl salt systems will be explored to gain a fundamental understanding of Cs and Sr behaviors. In addition to these experiments, several models have been proposed and compared with experimental data sets to understand and describe this crystallization process further.

2. Methods

2.1. Materials, equipment, and variables

Four salts were used in the experiments: $SrCl_2$, CsCl, LiCl, and KCl. The LiCl (99.99%) and KCl (99.999%) salts were purchased from Rare Earth Products, Inc. (Beverly, MA, USA). Strontium chloride $SrCl_2$ (99.995%) and CsCl (99.99%) were purchased from Alfa Aesar (Ward Hill, MA) and Sigma Aldrich (St. Louis, MO), respectively. In this study, 50-g batches were mixed using a eutectic LiCl-KCl base salt (56 wt% KCl and 44 wt% LiCl). For the ternary experiments, 1 weight percent (wt%) of $SrCl_2$ was added to produce a $SrCl_2$-LiCl-KCl mixture. For the quaternary experiments, 1 wt% of $SrCl_2$ and 3 wt% of CsCl were added to make a $SrCl_2$-CsCl-LiCl-KCl salt mixture. Mixed salts were placed in magnesia [i.e., magnesium oxide (MgO), 99.4%] crucibles purchased from Ozark Technical Ceramics (Webb City, MO). The dimensions of the crucibles were 3.8 cm for the outer diameter with a 3.5-mm wall thickness and 7.6-cm height.

Experiments were conducted using a top loading retort furnace (TC100R furnace; OXY-GON Industries, Inc., Epsom, NH) that consisted of a high-temperature zone, a low-temperature zone, an adiabatic zone, and an inert retort tube. All experimental setup and routines in the current study were the same as those in the crystallization studies reported by Williams [12,14]. Further details regarding the system are explained by Williams [14]. The high- and low-temperature zones of the furnace were maintained at 450°C and 250°C, respectively. The adiabatic zone was set at 2.5 cm thick. The alumina [i.e., aluminum oxide (Al_2O_3)] retort tube was attached to a step motor system, which advances the retort tube up and down at various rates. The dimension of the retort tube is 90.0 cm in height with an inside diameter of 7.0 cm. The retort tube within the furnace could be sealed to draw a vacuum or to maintain an inert gas environment. Three retort advancement rates were used in this study: 1.8 mm/h,

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Table 1 — The composition of the used electrorefiner salt from processing used nuclear fuel from the experimental breeder reactor II [4].

Composition (mol%)

LiCl (36.12)	$SrCl_2$ (0.57)	$NdCl_3$ (1.48)	$PuCl_3$ (1.05)
KCl (26.13)	UCl_3 (0.59)	$PmCl_3$ (0.02)	$AmCl_3$ (0.003)
NaCl (29.35)	$BaCl_2$ (0.58)	$SmCl_3$ (0.28)	$PrCl_3$ (0.44)
RbCl (0.26)	$LaCl_3$ (0.47)	$EuCl_3$ (0.02)	YCl_3 (0.34)
CsCl (1.37)	$CeCl_3$ (0.89)	$GdCl_3$ (0.01)	$NpCl_3$ (0.03)

$AmCl_3$, americium (III) chloride; $BaCl_2$, barium chloride; $CeCl_2$, cerium chloride; CsCl, cesium chloride; $EuCl_3$, europium (III) chloride; $GdCl_3$, gadolinium chloride; KCl, potassium chloride; $LaCl_2$, lanthanum (III) chloride; LiCl, lithium chloride; mol%, mole percent; NaCl, sodium chloride; $NdCl_3$, neodymium (III) chloride; $NpCl_3$, neptunium (III) chloride; $PmCl_3$, promethium (III) chloride; $PuCl_3$, plutonium (III) chloride; RbCl, Rb chloride; $SmCl_3$, samarium(III) chloride; $SrCl_2$, strontium chloride; UCl, uranium (III) chloride; YCl_3, ytterbium chloride.