Ion Exchange in a Zeolite - Molten Chloride System

R. H. Woodman and C. Pereira
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

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ION EXCHANGE IN A ZEOLITE-MOLTEN CHLORIDE SYSTEM

R. H. Woodman and C. Pereira
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

ABSTRACT
Electrometallurgical treatment of spent nuclear fuel results in a secondary waste stream of radioactive fission products dissolved in chloride salt. Disposal plans include a waste form that can incorporate chloride forms featuring one or more zeolites consolidated with sintered glass. A candidate method for incorporating fission products in the zeolites is passing the contaminated salt over a zeolite column for ion exchange.

To date, the molten chloride ion-exchange properties of four zeolites have been investigated for this process: zeolite A, IE95$, clinoptilolite, and mordenite. Of these, zeolite A has been the most promising. Treating zeolite 4A, the sodium form of zeolite A, with the solvent salt for the waste stream—lithium-potassium chloride of eutectic melting composition, is expected to provide a material with favorable ion-exchange properties for the treatment of the waste salt. We constructed a pilot-plant system for the ion-exchange column. Initial results indicate that there is a direct relationship between the two operating variables of interest, temperature, and initial sodium concentration. Also, the mass ratio has been about 3-5 to bring the sodium concentration of the effluent below 1 mol%.

INTRODUCTION
Between 1963 and 1993, Argonne National Laboratory (ANL) operated a nuclear reactor facility known as the Experimental Breeder Reactor II (EBR-II).[1] Like most nuclear reactor facilities in the United States, EBR-II accumulated an inventory of spent fuel. However, unlike most spent fuel, the EBR-II inventory has properties that make it undesirable to dispose by repository burial. Consequently, research and development has been conducted
for treating fuel to produce more stable chemical and physical forms for disposal is underway.[2,3]

Electrometallurgical treatment involves dissolution of the spent fuel in an electrorefiner; a large electrochemical cell, with chopped fuel pins in an anode basket and a cathode selected to allow precipitation of desired materials. The electrolyte is a lithium-potassium chloride salt of eutectic melting composition (59.5 mol% LiCl, 40.5 mol% KCl), with a melting point of approximately 350°C.[4]

Certain fission products, notably the alkalis, the alkali earths, and the rare earths, remain dissolved in the electrorefiner salt. Eventually, either the heat load of the accumulated fission products or the accumulation of hypereuctectic sodium-lithium-potassium chloride will render this salt no longer serviceable.[5] Figure 1, the equilibrium phase diagram of the ternary system, reveals the sharp increase in liquidus temperature that occurs when sodium is present in amounts which exceed the ternary eutectic composition.[6]. Figure 1 also reveals the relatively low sodium content required to exceed the euctectic sodium content. Once the salt bath becomes unserviceable, the process flowsheet calls for one of two options: disposal of the salt or treating it to remove sodium and fission products.

Figure 1. Equilibrium Phase Diagram for the Ternary System Lithium-Potassium-Sodium Chloride, (Ref. 6).
Disposal plans include a waste form that can incorporate the fission products as chlorides. Certain mineral zeolites, such as sodalite, have chlorides in their structure, and may be able to accommodate some or all of the fission products.[7, p. 41] Certain synthetic zeolites, such as Linde Type A (often referred to as zeolite A), can, after dehydration, occlude salt within their structural cavities.[7, p. 585] Waste forms featuring one or more such zeolites, consolidated by sintering with a glass frit, are under development.[8]

Alternatively, it has been established since the late 1960s that zeolite A, when occluded with salts, exhibits cation exchange.[7, p. 587-8, and 9-13] Hence, the electrorefiner salt might be treated by exchange with zeolite A. Fission products and sodium would be incorporated with the exchange bed and, ideally, a eutectic lithium-potassium chloride salt would be returned to the electrorefiner.

Research and development at ANL has been directed towards establishing the feasibility of treating spent electrorefiner salt in this manner. Initial testing established that, of zeolite A, clinoptilolite, mordenite, and IE95®, zeolite A was by far the most effective ion-exchange medium.[8]

APPARATUS

A pilot-scale system for testing the ion-exchange column has been constructed. A schematic appears as Figure 2. The system is contained within a heated enclosure. The enclosure is maintained at temperatures ranging between 450 to 550°C. Because the chloride salt is hygroscopic, and the zeolites are dehydrated, the apparatus is housed in a glovebox with a helium atmosphere. The helium is circulated through absorbent beds to maintain the water vapor and oxygen gas levels below 1 ppm.

The primary feature of the system is the pair of stainless steel tanks, each capable of holding approximately 20 kg of salt. The tanks can be made gastight and pressurized to 2 to 3 psig. Each tank is also fitted with a cylindrical, annular cup that is filled with a braze. A cylindrical part that mates to the annular cup can be inserted. When the braze melts and freezes, a seal called freeze seal is formed.

Salt is transferred from one tank to the other by fitting a pipe to the freeze seal of the feeding tank and pressurizing the tank to force the salt through the pipe to the receiving tank. The lower end of the pipe is below the level of the molten salt. When the pipe is packed with beads of zeolite particles, it becomes an ion-exchange column. Because successful ion exchange requires a slow transfer rate, an electronic mass flow controller regulates the pressure.
The tanks themselves are mounted on piezoelectric load cells. The flow rate of the salt during the process can be measured by recording the weight change of the tanks over time.

The transfer pipe is fitted with a tube which permits sampling of the effluent stream from the column exit. The elemental composition of the effluent salt is determined by instrumental analysis techniques, typically inductively coupled plasma–atomic emission spectroscopy (for most species), inductively coupled plasma–mass spectroscopy (for ions, such as cesium, with emissions outside the detection window of the emission spectrometer), or ion chromatography (for chloride ion).

DISCUSSION AND RESULTS

Beaded particles of zeolite 4A are available in industrial quantities. While such beads exhibit ion-exchange behavior that is promising for treating fission product-laden molten chlorides, its physical and chemical form require modification to enhance the exchange. First, the beads must be dehydrated. Second, the channels need to be occluded with chloride salt. Third, sodium needs to be removed from the zeolite (for the same reasons that sodium should not accumulate in the electrorefiner).

The beads are dehydrated by implementing a controlled heating schedule under a flow of dry nitrogen.[14] At present, three methods for sodium removal and chloride occlusion are under investigation: (1) immersion of beads in
molten lithium-potassium chloride, (2) aqueous exchange of sodium with lithium or potassium chloride salts followed by salt occlusion, or (3) treatment of the dehydrated material in a column, using dehydrated beads as the column packing and lithium-potassium chloride eutectic as the feed salt. We explored the latter option.

Two control variables are of interest: temperature and residence time in the column. Two output variables are of interest: the concentration of sodium in the effluent salt over time and the mass of feed salt required to bring the sodium concentration of the effluent to a desirable level, such as 1 mol %, for a given mass of beads.

Figure 3 illustrates the change in composition of the effluent salt over the course of a representative column operation. As can be seen there, the initial effluent has the highest sodium concentration, and thus the greatest risk of the liquidus exceeding the operating temperature of the system. The concentration of sodium falls as more salt is transferred.

![Figure 3. Composition of the Effluent Salt versus Amount of Salt Transferred for a System of Dehydrated Zeolite 4A Beads and a Lithium-Potassium Chloride Eutectic Feed Salt. Test was conducted at 550°C (825 K) and a residence time of 25 minutes.](image)

At present, we do not have definitive data that describes the relationship between the operating variables. However, there does appear to be a direct proportion between residence time and the initial sodium concentration. Also, the
mass ratio to bring the sodium concentration of the effluent below 1 mol % is typically between 3 and 5.

SUMMARY
A pilot-scale system for investigating ion-exchange behavior between molten chloride and zeolite A has been developed. To date, most operations of the column system have been devoted to treatment of dehydrated zeolite 4A beads to a chloride-loaded form with minimal sodium. While the relationship between the operating variable is not definitive, initial sodium concentration and residence time appear to be directly linked. The mass ratio is about 3 to 5 for optimum sodium concentration in the effluent.

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