

# Pyrochemical process for electrochemically base metals in molten halides combined countercurrent electromigration and electrowinning methods

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Received 9 December 2004; received in revised form 3 March 2005; accepted 4 March 2005

Available online 7 April 2005

## Abstract

On reprocessing spent metallic fuels in molten salts it is indispensable to develop a pyrochemical process for the electrochemically base elements like alkali metal, alkaline-earth, rare-earth elements in order to use the melt baths repeatedly. For this purpose we have investigated the internal mobility of each cation from the electromigration methods and the electrochemical behavior of these base elements by electrochemical techniques. These experimental results allow us to conclude that the rare-earth, alkaline-earth, alkali metal halides were concentrated in the migration tubes and separated one another through electromigration process. In addition, in the following electrowinning process, each metal was selectively recovered in the liquid metallic cathodes. Furthermore, we suggested an originated pyrochemical process combined the countercurrent electromigration and the electrowinning methods in order to separate these elements effectively and recover them selectively each other. The characteristics of this process have the availability for the difference of the physicochemical properties such as the internal mobility and the decomposition potential for the electrochemically base metals in the molten halide baths.

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**Keywords:** Electromigration; Electrowinning; Molten halides; Pyrochemical process

## 1. Introduction

Pyrochemical treatment process has an advantage of its simplicity and less secondary wastes. Argonne National Laboratory has successfully accomplished the pyrochemical system using metallic fuels as the integrated fast reactor project [1]. States Scientific Center of Atomic Reactors in Russia has established another pyrochemical processes based on the oxide fuels. Central Research Institute of Electric Power Industry in Japan

has promoted the development of the pyrochemical practical plant using metallic fuels [2]. Japan Atomic Energy Research Institute has also extended the feasibility on the pyrochemical process concerned with the nitride fuels [3]. However, all these projects are mainly focused on achieving how to extract the fuel material including the transuranium elements from the ionic melts. From a standpoint of the harmonization of the nuclear systems with a global environment, we should make an effort to separate the fission products (FPs) each other for incineration or utilization of medical tracers, precious materials and at least decontaminating surrounding materials. After the electrorefining and the drawdown process, all alkali metal (AM), alkaline-earth (AE) and

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some amounts of rare earth (RE) halides from FPs still remain in the salt bath. Thus it is difficult to recover some FPs like AM and AE elements from the salt phase, because of their more negative reduction potentials [4] than those of the solvent components. For this purpose, we have applied a countercurrent electromigration method, which originated from the isotope separation [5]. For understanding the principle, a schematic diagram of the electromigration is shown in Fig. 1. When the electrical field is applied between the anode and the cathode, the cations migrate toward the cathode. The migration mobilities of each cation,  $b_1$  and  $b_2$  depend on the cationic radii, valences, polarizabilities, molar volumes, and so on. During electromigration, there occurs a back flow for cations, which is caused from the osmosis force keeping the liquid level constant. This flow is called a counter flow,  $b_c$  which is independent of a kind of species. Due to this counter flow, a cation with lower mobility is enriched toward the anode. We have already investigated the internal mobility of each cation using the countercurrent electromigration for RE, AE and AM [6–9] with theoretical estimations by MD simulations [9–11].

On the other hand, in order to recover each element as a metal, the alloy formation reactions between the FPs and the liquid metals were investigated by the electrochemical techniques [12–15]. As a result, we have successfully recovered RE and AE in the different liquid metal cathodes in the chloride bath. There were few references related with the possibility of recovery for the electrochemically base elements using the molten fluorides so far. We therefore executed the present experiment, which was investigation for the selective recovery of Cs, Sr and Ba in three kinds of liquid metal

cathodes in molten fluoride system from the technological aspects. Furthermore, we also have suggested an originated pyrochemical process combining electromigration and electrowinning methods in order to recover the base elements selectively each other in this paper.

## 2. Experimental

### 2.1. Electromigration method

The apparatus of the electromigration is illustrated in [6–9]. The anode was made of a super fine graphite rod with 5 mm  $\phi$ . The cathode compartment, which consists of the glassy carbon with 3.0 mm  $\phi$  was connected to the graphite rod with the ceramic binder for protection from corrosion because the glassy carbon was difficult to make the inter-metallic compounds with alkali metals. The migration tubes were made of the quartz glass. The upper part of the migration tube had an outlet of chlorine gas. The lower part of the migration tube was packed with alumina powder with 100  $\mu\text{m}$   $\phi$  in order to prevent convection of the melt in the migration tube. A constant direct current supplier fed electric currents less than 0.2 A. The transported charge was measured using a Cu or digital coulometer. After several thousand Coulombs of charge was transported, the migration tube was removed from the bath and the melt was quenched quickly. The migration tube was cleaned outside and cut into several pieces of about 10 mm length. The salt in each fraction was dissolved into the distilled water. The amount of Cs in each fraction was determined by absorption spectrometry. The other elements were analyzed by ICP emission spectrophotometry.

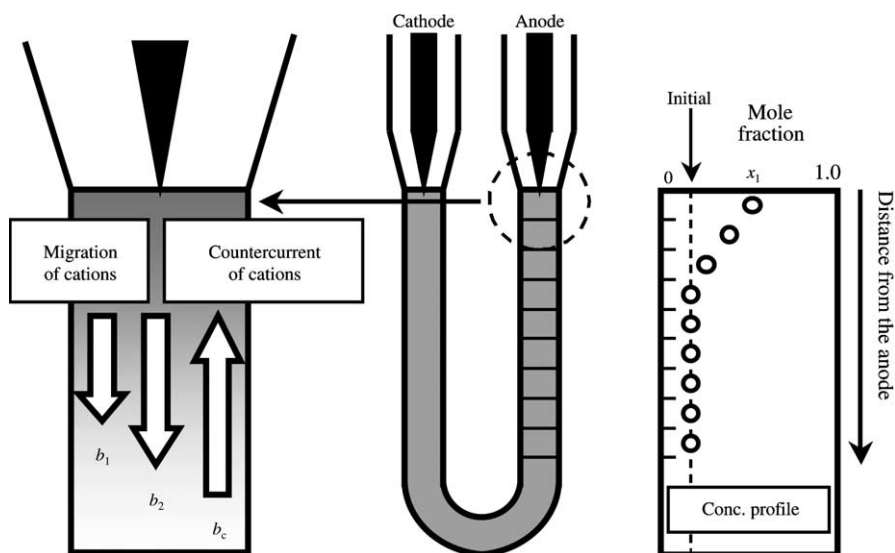


Fig. 1. The schematic diagram for countercurrent electromigration.

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