OVERVIEW OF SEPARATION METHODS APPLICABLE FOR THE MOLTEN SALT REACTOR FUEL CYCLE

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Abstract

1. INTRODUCTION

The processing of Molten Salt Reactor (MSR) fuel during and after the reactor operation requires evaluation and adjustment of various pyrochemical and/or possibly hydrometallurgical techniques to address the unique challenges posed by irradiated molten salts. The separation methods must address several key objectives in MSR fuel treatment, including:

- Removal of noble gas fission products (e.g., Xe, Kr) from the fuel salt
- Separation of insoluble fission products, such as noble metal particles
- Partitioning of fuel constituents and minor actinides both mutually and from lanthanides
- Extraction of soluble fission products, primarily lanthanides, from the carrier salt
- Purification of the carrier salt by removing cesium, strontium, alkali metals, and alkaline earth metals after lanthanide removal
- Elimination of atmospheric and corrosion contaminants, including O_2 and H_2O, from the carrier salt

A range of separation techniques developed globally are applicable to these goals, including molten salt–liquid metal reductive extraction, electrochemical techniques using molten salt media, fluoride and chloride volatility processes, oxide precipitation, zone melting, and aqueous extraction [1]. Additionally, polishing of MSR fuel during operation can be achieved through inert gas sparging, e.g., helium bubbling, to remove volatile noble gas fission products and noble metal particles [2] .

The presentation will provide an overview of the principles behind the most commonly applicable methods, aiming to support the evaluation of their suitability within the MSR fuel cycle back end. This abstract is limited to a brief description of selected examples, including electrochemical techniques, reductive extraction, and fluoride volatility methods.

Electrochemical separation methods

Electrorefining is one of the most advanced pyrochemical separation techniques [3] but is primarily applicable to reprocessing metallic alloy fuels in molten salt media and not to liquid MSR fuels. However, electrochemical methods remain promising for MSR fuel processing due to their precise control of separation performance and the fact that they do not require external chemical additives.

The principle relies on the selective electrochemical reduction of individual fuel components dissolved in the carrier salt. Separation is governed by the differences in electrochemical stability of the dissolved species, which are determined by their redox potentials [4]. While standard electrode potentials, based on ideal thermodynamic conditions, are often used to predict the separability of elements, the actual redox behavior in molten salt systems is influenced by factors such as complexation, melt composition, temperature, electrode material, and species concentration. These factors affect the observed redox potentials, which are more accurately described by apparent standard potentials. Apparent standard potentials are experimentally determined values that reflect the redox behavior of species under specific, non-standard conditions. Therefore, experimental measurements are essential to validate and calibrate predictions based on standard potentials.

Published data on the electrochemical behavior of actinides and lanthanides in molten chloride and fluoride salts (e.g. [5-8] where data on several relevant elements are summarized with references to original works) indicate that electrochemical methods can effectively extract actinides from MSR fuel while retaining lanthanides, cesium, strontium, alkali metals, and alkaline earth metals in the fuel. If removal of fission products is required, as is typically the case for MSRs, these elements would be removed together with the actinides. An additional step would then be needed to recover the actinides and return them to the fuel cycle. This fact is illustrated in Figure 1, which compares the apparent standard potentials of selected actinides and lanthanides in LiCl-KCl eutectic melt at 450°C, using an Ag/AgCl (10 wt.% AgCl) reference electrode. These values were experimentally determined at JRC Karlsruhe [7].

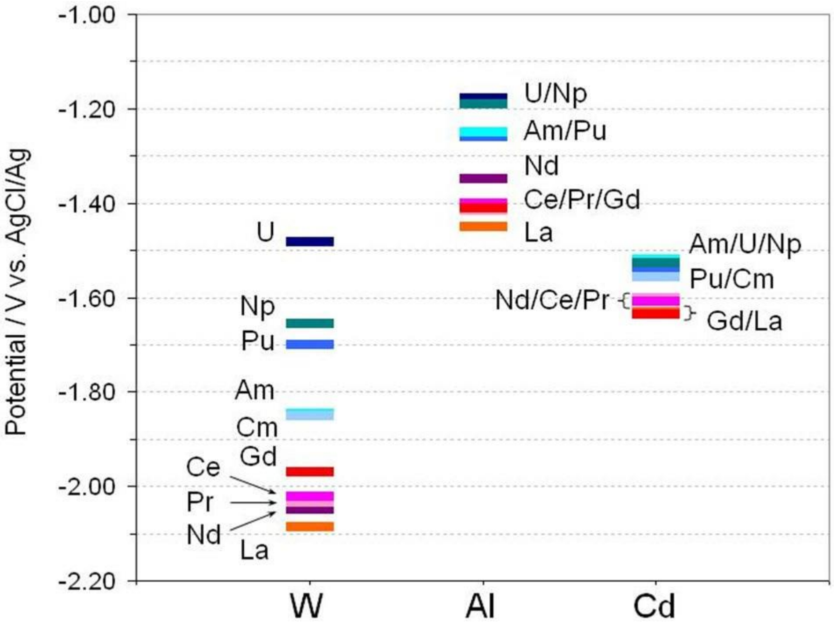

FIG. 1 *Apparent standard potentials of various Ln and An experimentally determined at JRC Karlsruhe on solid W, Al and liquid Cd working electrodes in a LiCl-KCl eutectic melt at 450°C, Ag/AgCl (10 wt.% AgCl) reference electrode*

Molten salt–liquid metal reductive extraction

Similar to electrochemical techniques, the selectivity of the reductive extraction is based on differences in chemical stability among the different MSR fuel components dissolved in the carrier salt. This process involves introducing a reducing agent and a liquid metal, commonly bismuth, cadmium, or aluminum, into contact with the salt phase. Metallic species with lower chemical stability are reduced and subsequently transferred into the liquid metal phase [9]. The extraction mechanism follows an equilibrium reaction (1):

$$M^{n+}\text{ (molten salt)} + n\text{Li (liquid metal)} \rightleftharpoons M^{0}\text{ (liquid metal)} + n\text{Li}^{+}\text{ (molten salt)} \quad (1)$$

Here, Li denotes the reducing agent, typically lithium metal, and M represents the metal species targeted for separation from the spent fuel.

The selectivity of the separation can be controlled by the choice and strength of the reducing agent, which can be fine-tuned by dilution or alloying. When a powerful reductant such as lithium is alloyed with a carrier metal like bismuth, the effective reducing effectiveness of the system diminishes in proportion to the lithium content. This approach was foundational in the conceptual design for Molten Salt Breeder Reactor (MSBR) fuel reprocessing at ORNL during the 1970s, which suggest possibility of selective extraction of protactinium, group separation of thorium from lanthanides, followed by selective extraction of divalent and trivalent lanthanides [10].

The method has therefore a great potential to be used for the separation of fuel constituents and minor actinides from lanthanides and for extraction of soluble fission products from the carrier salt and it is the basic process in many proposed flowsheets of the MSR fuel cycle back end [2, 11].

Fluoride volatility methods

Fluoride volatility is a separation method suited for MSR fuel, where actinides are dissolved in a high-temperature molten fluoride salt. The process involves fluorinating the salt with fluorine gas to convert specific species, typically uranium, neptunium, and plutonium, into volatile hexafluorides, which can be extracted from the system in the gas phase [12]. Lanthanides and minor actinides, forming non-volatile fluorides, remain in the salt.

This method was demonstrated at Oak Ridge National Laboratory (ORNL) during the MSRE program in the 1960s–70s, where uranium was effectively removed from carrier salts (e.g., LiF-BeF_2-ZrF_4) via continuous fluorination at 500–550 °C using nickel-based equipment [10] .

In MSR systems, particularly those operating on the ^{232}Th–^{233}U fuel cycle, this technique enables online or batch removal of uranium or other volatile actinides, improving breeding performance and reactivity control. Its compatibility with liquid fuel makes fluoride volatility a promising option for integrated fuel reprocessing in advanced MSRs.

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