

PYROCHEMICAL PROCESSES FOR LWR SPENT FUEL

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ABSTRACT

Pyrochemical processes are under development at Argonne National Laboratory for recovery of transuranium (TRU) elements from light water reactor spent fuel. The recovered TRU elements will be used as fuel in the integral fast reactor (IFR). Burning these long-lived isotopes for electrical power generation has the additional benefit of reducing the burden on the geological repository for their long-term containment. The goals for the process include: greater than 99.9% recovery of TRU elements, a metal product that is compatible with the IFR fuel cycle, retention of some fission products in the TRU product to enhance proliferation resistance, and a simple process that is economically attractive. The TRU product will be inserted into the IFR fuel cycle for fission product decontamination and incorporation into the fuel.

Based on research and development at ANL in the 1960s and 1970s and a comparison of known processes for separation of TRU elements from uranium fuel, three conceptual processes were identified that seem to offer high potential for achieving the desired goals. All three conceptual processes include a reduction step to convert the oxide fuel to metal, an electrochemical step to recover the reductant (calcium) from its oxide, a TRU extraction step to separate TRU elements from the bulk uranium, and a retort step to recover the TRU product from a solvent metal. The candidate processes differ primarily in the methods used to separate the TRU elements from uranium. The salt transport process effects this separation by molten salt extraction; the magnesium extraction process uses the differential solubility of TRU elements in magnesium relative to that of uranium; and the zinc-magnesium process uses phase separation to recover TRU elements, which are soluble in a Zn-Mg alloy.

The chemical feasibility of each step of the three concepts has been demonstrated in small-scale experiments. Candidate containment materials have been selected and tested at the temperature and environmental conditions of the processes. The data from these small-scale experiments are summarized in this paper. The emphasis of current work is on selection of a single process concept for further development and scale-up of the process to a size that will address many of the design issues of a large system. This engineering-scale process system is being designed for 20-kg batch size, and fabrication of the process equipment and the containment glovebox are well underway.

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Introduction

Recovery of transuranium (TRU) elements from light water reactor (LWR) spent fuel for burnup, with net energy production, has been suggested as an attractive alternative to the current once-through LWR fuel cycle. The metal-fueled integral fast reactor (IFR)¹ is an effective burner for these TRU elements because of its high-energy neutron flux, and it offers the advantages of passive safety features and an integral fuel cycle that is resistant to diversion of TRU elements to weapons applications. The TRU elements in LWR spent fuel can be recovered in a metallic form suitable as feed material for the IFR fuel cycle, using pyrochemical processes that were developed at Argonne National Laboratory over the past three decades. Although these pyrochemical processes were developed for the early Experimental Breeder Reactor-n fuel cycle², they are being revised to recover TRU elements from LWR spent fuel.

· · Process Flowsheet Concepts

The goals for the pyrochemical processes include: greater than 99.9% recovery of TRU elements, a metal product that is compatible with the IFR fuel cycle, retention of some fission products in the TRU product to enhance proliferation resistance, and a simple process that is economically attractive. Three conceptual processes were identified that seem to offer high potential for achieving these goals. All three conceptual processes include a reduction step to convert the oxide fuel to metal using calcium reductant, an electrochemical step to recover the calcium from its oxide, a TRU extraction step to separate TRU elements from the bulk uranium, and a retool step to recover the TRU product from a solvent metal. The candidate processes differ primarily in the methods used to separate the TRU elements from uranium. The salt transport process effects this separation by molten salt extraction; the magnesium extraction process uses the differential volatility of TRU elements in magnesium relative to that of uranium; and the zinc-magnesium process uses phase separation to recover TRU elements, which are soluble in a Zn-Mg alloy. In all three flowsheet concepts, the reductions are done in a liquid-metal/molten-salt two phase system. The uranium and TRU elements are accumulated in the liquid metal phase, along with the more noble fission products and the rare earth elements. The alkali and alkaline earth fission products are accumulated in the salt

phase along with iodine, europium, and some of the samarium. In the salt transport process, the reduction metal phase is a Cu-Mg alloy, and the metal that accepts the TRU elements in the salt extraction step is a Zn-Mg alloy. In the magnesium extraction process, the reduction metal phase is a U-Fe eutectic alloy, and the extraction metal is magnesium. A Zn-Mg alloy is used as both the reduction alloy and the TRU accumulation alloy in the zinc-magnesium process. The TRU elements are separated from the bulk uranium by liquid/solid phase separation, in this latter case.

Experimental Studies

The chemical feasibility of each step of the three concepts has been demonstrated in small-scale experiments. The reductions have been shown to proceed to 97 to 100 % of completion for the actinide oxides of interest (UO_2 , PuO_2 , NpO_2 , and AmO_2). The degree of completion was determined by analyzing for actinide residues remaining in the salt phase at the end of the experiments. The assumption was that the residue would be in the form of oxides; however, when the salt phase was scrubbed with clean liquid zinc, all of the actinide residues were found in the zinc phase, indicating that the residues were present as entrained metals. Since the reduction salt is recycled in the processes, no loss of actinide elements would be expected in the reduction step.

Separation of the TRU elements from the bulk uranium is a key step in these processes, and this separation has been demonstrated for all three processes. In the salt transport process, the reduction alloy (Cu-Mg) contains the TRU elements in solution while the uranium is present as a solid precipitate. The Cu-Mg is equilibrated with a molten MgCl_2 phase, then the salt is transferred to a separate vessel where it is equilibrated with a Zn-Mg alloy. The activity coefficients of the TRU elements are several orders of magnitude smaller in the Zn-Mg alloy than in the Cu-Mg alloy; therefore, the TRU elements are transferred to the Zn-Mg alloy while they are replaced in the Cu-Mg alloy with an equivalent quantity of magnesium, which moves in the opposite direction. Since all of the reagents (Cu-Mg, MgCl_2 , and Zn-Mg) are completely recycled in this process, no losses of TRU elements are expected to occur. This process has been successfully demonstrated in small-scale laboratory experiments.

In the magnesium extraction process, the TRU elements dissolve in the U-Fe reduction alloy during the reduction step. This alloy is then contacted with molten magnesium to extract the TRU elements. Experimental tests have shown that, while plutonium and americium are

extracted fairly well by the magnesium (distribution coefficients of about 1 and 5, respectively), the neptunium extraction is very poor (distribution coefficient of about 0.05). This poor distribution of neptunium between the magnesium phase and the U-Fe phase makes this process less attractive than the other two.

In the zinc-magnesium process, the TRU elements dissolve in the liquid metal phase while the uranium precipitates as a separate phase. Analysis of the Zn-Mg alloy from reduction experiments has shown that the TRU elements are quantitatively recovered in this alloy. While the uranium precipitates as a separate phase, it has been found that about 15 to 20% of the neptunium co-precipitates with the uranium. A final uranium treatment step was added to the flowsheet to recover this neptunium in which a chlorinating agent (such as UCl_3 in some experiments) is contacted with the uranium (as a liquid U-Fe alloy in these experiments). The neptunium tends to partition to the salt phase under these conditions, and the salt can be returned to the reduction step for recovery. This uranium scrubbing step is called halide slagging. This halide slagging step was explored during earlier pyrochemical research at ANL³.

Materials Development

Candidate containment materials for these high-temperature processes have been selected and tested at the appropriate temperatures and environmental conditions. The data from these experiments indicate that oxide ceramics, in general, are not stable in the presence of molten salts saturated with calcium metal. Consequently, most of the experimental work has focussed on development of other containment materials, including TiN, TiC, Ti(C,N), TaC, and refractory metals such as tungsten and Mo-30 % W. All of these materials have been found to be stable in these environments. The final process step, retorting and consolidation of the TRU product, will require a material that is capable of containing molten U-TRU-Rare Earth alloys. This is a corrosive combination of metals that is expected to be contained in a refractory-oxide-coated nitride or carbide compound.

Engineering-Scale Process Development

The emphasis of current work is on selection of a single process concept for further development and on scale-up of the process to a size that will address many of the design issues of a large prototype system. This engineering-scale system is being designed to be capable of processing 20-kg batch size of simulated LWR spent fuel. Fabrication of the

process equipment and the containment glovebox for the system are well underway. The process will be operated in a high-purity argon atmosphere glovebox to prevent contamination of the reagents and products. The equipment components include a reduction vessel for converting the oxides to metals, an acceptor vessel for accumulation of the TRU product in the Zn-Mg alloy, a retort for evaporating the solvent metal, consolidating the product, and conducting the halide slagging step, and an electrolytic anode assembly for converting the CaO to calcium for recycle. Construction of the glovebox is well underway, and design of the equipment components is in progress. The engineering-scale system is expected to begin operations in late 1993.

Future Plans

The long-term goal of the Actinide Recycle Program at Argonne National Laboratory is to demonstrate chemical, engineering, and economic feasibility of these pyrochemical processes. The chemical feasibility of most of the process steps has been adequately demonstrated in small-scale laboratory experiments. This work is continuing with emphasis on determining the behavior of the noble metal fission products, studying the halide slagging step, and conducting retorting, and product consolidation experiments. The engineering feasibility will be demonstrated during operation of the engineering-scale process and during future processing of actual LWR spent fuel in a shielded facility. The economic feasibility will be determined by preliminary design and cost estimate for a full-scale prototype plant. This design effort will commence after completion of the engineering-scale process demonstration.

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Acknowledgement

Work supported by the U. S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31 -109-Eng-38.