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RECYCLE OF LWR ACTINIDES TO AN IFR

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INTRODUCTION

A large quantity of actinide elements is present in irradiated Light Water Reactor (LWR) fuel that is stored throughout the world. Because of the high fission-to-capture ratio for the transuranium (TRU) elements with the high-energy neutrons in the metal-fueled Integral Fast Reactor (IFR), that reactor can consume these elements effectively. The stored fuel represents a valuable resource for an expanding application of fast power reactors. In addition, removal of the TRU elements from the spent LWR fuel has the potential for increasing the capacity of a high-level waste facility by reducing the heat loads and increasing the margin of safety in meeting licensing requirements.

Argonne National laboratory (ANL) is developing a pyrochemical process, which is compatible with the IFR fuel cycle (ref. 1), for the recovery of TRU elements from LWR fuel. The proposed product is a metallic actinide ingot, which can be introduced into the electrorefining step of the IFR process. The major objective of the LWR fuel recovery process is high TRU element recovery, with decontamination a secondary issue, because fission product removal is accomplished in the IFR process. The initial goal is recovery of at least 99.9% of the TRU elements and production of the uranium in a form that can be stored safely until it is needed for future reactor blanket material Reagents are to be recycled to minimize wastes, and waste streams are to be suitab for storage in a high-level-waste reposito

The extensive pyrochemical processin studies of the 1960s and 1970s (ref. 2-3) provide a basis for the design of possible processes. Two processes were selected fo laboratory-scale investigation. One is ba on the Salt Transport Process studied at A for mixed-oxide fast reactor fuel (ref. 2) and the other is based on the blanket processing studies done for ANL's second Experimental Breeder Reactor (EBR-2) (ref. 3). This paper discusses the two processes and is a status report on the experimental studies.

SALT TRANSPORT PROCESS

A schematic flowsheet for the propos Salt Transport Process is presented as Fig. 1. It is assumed that the oxide fuel has been mechanically separated from the cladding. This step is not presently unde study at ANL, but its uncertainty is recognized. An alternative decladding procedure is melting the cladding from the fuel. This was explored at ANL briefly fo oxide fast reactor fuel and is currently u at Dimitrovgrad (ref. 4).

Following decladding the fuel is reduced with calcium in a reaction containing $CaCl_2$-20 mol% CaF_2 and an alloy of Mg-42 at.% Cu to which excess calcium has been added. The fuel need only be crushed into particles of a convenient size for charging to the reaction vessel. The reduction proceeds rapidly at 800°C, and the TRU elements go into solution in the liquid alloy, but the bulk of the uranium precipitates as metal. All the fission product metals except the alkalis and alkaline earths are reduced and go into the metal phase. The solubility limits and coprecipitation characteristics must be determined. The alkali and alkaline earth elements along with the halides and the CaO reaction product remain in the salt phase.

The reduction mechanism involves the solubility of calcium in the salt, but this solubility vanishes as the solution becomes saturated with CaO. Therefore, the quantity of salt is selected to dissolve all the CaO produced and have a final concentration that permits complete reductions. Following the reduction, the CaO is decomposed electrochemically. The oxygen is liberated at a carbon anode as CO and CO_2, and the calcium is collected in a liquid Mg-Cu alloy cathode to produce new reduction alloy. The salt and reduction alloy are recycled to the next reduction run. However, some salt must be processed as waste to limit heat generation from strontium and cesium fission products. Processing of salt wastes is under development as part of the IFR fuel process (1).

After removal of the reduction salt, the liquid metal is treated in a salt transport step to extract the TRU elements from the uranium and less-reactive fission products. In this step the TRU elements and rare earths are extracted from the Mg-Cu "donor" alloy into a $MgCl_2$ salt, and then they are extracted from that salt into a Zn-Mg "acceptor" alloy. This step is driven by the low activity of the actinides in zinc relative to their activities in the Mg-Cu. The salt transport of these elements to the acceptor is accompanied by an equivalent transport of magnesium from the acceptor to the donor alloy. The extractions obey chemical equilibrium reactions, and the extraction efficiency depends on the relative amounts of salt and metal equilibrated. High recoveries are achieved by cycling the sal between the donor and acceptor alloys. Although virtually all of the nobler fissi products and 99 % of the uranium remain wi the Mg-Cu, an amount of uranium about equa to that of plutonium transports with the T elements.

After the salt transport step, the M Cu alloy is separated from the uranium precipitate and recycled until the fission product level reaches a limit, which has n yet been established. When the fission product limit has been reached, the magnes is distilled from the Mg-Cu alloy for recycle, and the copper-fission product mixture is fused and cast as a waste ingot

The acceptor alloy containing the TR product is charged to a retort where the z and magnesium are distilled off for recycl The actinide residue is cast into an ingot for charging to the IFR process. Because this alloy contains rare earths, it is charged to the electrorefiner where the ra earth-TRU element separation is made.

SALT TRANSPORT PROCESS EXPERIMENTS

Laboratory-scale experiments were performed to evaluate the chemical feasibility of the proposed Salt Transport Process. Three series of runs were made using simulated LWR fuel consisting of hig fired UO_2 pellets and powdered PuO_2, NpO_2, and representative fission product element (CeO_2, Nd_2O_3, ZrO_2, RuO_2, MoO_3, Pd, SrO, B and CsCl). The plutonium contained about americium. These runs consisted of a reduction step and three cycles of salt transport. The scale of the experiments i indicated in Table 1, which summarizes equipment dimensions and reagent charges.

Following the reductions, the melts were frozen in place. The reduction salt ingot were recovered by breaking the crucit and separating the solid phases. The phase separated cleanly into a bright silvery met ingot and a white salt ingot. The Mg-Cu alloy is very brittle and was easily crushe to locate the precipitated uranium, which generally was present as a single ball of near theoretical density. The entire ingot including the uranium, was retained for use as the salt-transport donor.

Based on the salt analyses, the reductions were greater than 99% for each of the actinides in all three runs. The salt from the reductions in the first two series were scrubbed with additional Mg-Cu-Ca with little additional actinide recovery. Based on the rapid formation of the uranium ball, as evidenced by interference with the agitator, the reductions were probably complete within 15 min. The extent of reaction may have been limited by the final oxide content of the salt. Reduction variables have not yet been studied. Although coprecipitation of plutonium and americium with the uranium was minimal, about 20% of the neptunium coprecipitated.

Three salt transport cycles resulted in recovery of 95% of the plutonium and neptunium and less than 1 % of the uranium in the acceptor alloy. Americium extracted more efficiently than plutonium and neptunium from the donor alloy, but about 15% of the americium remained in the transport salt. This is consistent with published distribution data for the Zn-Mg/$MgCl_2$ system (2). TRU elements in the transport salt represent an in-process inventory, which should reach a steady-state value for multiple runs. There have been major problems with the chemical analyses at the low concentrations involved, and material balances have been poor. These problems are being pursued actively. However, fission product behavior has been qualitatively as expected, and the actinides appear to extract as expected. It was recognized that higher plutonium recoveries will require more salt-transport cycles or a larger salt-to-metal ratio each cycle.

MAGNESIUM EXTRACTION PROCESS

A flowsheet for the proposed Magnesium Extraction Process is presented as Fig. 2. Again the fuel is assumed to have been separated from the cladding, and the first step is reduction of the fuel with calcium at 800°C. In this case, the reduced fuel is collected in a liquid U-Fe alloy. The $CaCl_2$-CaF_2 salt is again employed to promote the reduction by dissolving the calcium reductant and CaO reaction product. In this case the excess calcium over the solubility in the salt is present as a separate phase because of its low solubility in the liquid U-Fe. A in the Salt Transport Process, the reduction salt and calcium are recycled after the CaO is electrochemically decomposed. A small side stream from the salt recovery process provides for removal of alkali, alkaline earth, and halide fission products

The composition of the U-Fe alloy at the end of a reduction is about 80 at.% (94 wt%) uranium. The initial composition can be about 60 at.% (86 wt%) uranium, which requires adding iron and recycling about 40% of the uranium for each reduction. The composition range for the U-Fe alloy is selected to remain liquid during the step (ref. 5).

Following removal of the reduction sal for recovery, the TRU elements are removed from the U-Fe by magnesium extraction. Magnesium is immiscible with the uranium alloy, and the solutes in the uranium alloy distribute between the two liquid metal phases. The TRU elements distribute favorably into the magnesium. The magnesium solution is then removed to a retort where the magnesium is distilled off and recycled and metallic TRU elements are recovered for introduction into the IFR electrorefiner. Several magnesium extraction contacts are required to obtain the desired TRU recovery. Again, separation from the rare earths is minimal. The electrorefiner will provide an further isolation of fuel from fission products that may be required.

A portion of the depleted uranium allo is recycled along with fresh iron to the nex reduction step, and the balance is cast for storage for later use in a fast reactor blanket. An alternative to recycling uraniu following the magnesium extraction step is t feed fuel and iron proportionally to the reduction vessel while removing equivalent U Fe alloy for processing in the extraction step. This results in an essentially invariant liquid alloy composition in the reduction vessel, and the step can be operated with continuous feed and bleed streams.

MAGNESIUM EXTRACTION PROCESS EXPERIMENTS

Again, laboratory-scale experiments were performed to evaluate the chemical feasibility of the proposed process Three series of runs were made using the same type of simulated LWR fuel as used for the Salt Transport Process study. The Magnesium Extraction Process series consisted of a reduction run, several magnesium extraction steps, and a scrub step with the reduction salt. Table 2 summarizes the equipment dimensions and reagent charges for these experiments.

The reductions were at least 99.5% complete for plutonium and neptunium, but ranged from 93 to 98.7% for the americium. Because of analytical difficulties at the low concentrations, the results for the salt-scrub step are unclear.

The reduction salt was removed from the U-Fe ingot after the melts were frozen and broken out of the crucible. Some entrainment of heavy metal droplets in the salt phase was apparent after the runs. A dark region of salt near the metal-salt interface was analyzed separately from the bulk of the salt, which was white. The plutonium and neptunium concentration was significantly higher in the darker salt. There also were some light metal beads near the salt surface. These proved to be principally magnesium reduced from the crucible. The beads contained some calcium and about half of the americium, cerium, and neodymium.

The U-Fe ingots were next exposed to a series of magnesium extractions. Because liquid-phase separation was not practical in these small-scale experiments, $BaCl_2$-$CaCl_2$ eutectic was added to the melt, after equilibration, to separate the two metallic phases. The metal ingots were recovered after the melts were frozen. Analyses revealed no significant actinides in the separation salt.

Analysis of the U-Fe alloys has proven difficult and results are not consistent. Results to date indicate about 85% of the plutonium and 30% of the neptunium were extracted in each contact. Much of the americium was extracted by the magnesium beads in the reduction step, and little was found in the U-Fe ingot following the extraction; however, the total material balance was poor. Cerium and neodymium also were extracted into the magnesium, but no nobler metals were detected in that phase.

SALT RECOVERY EXPERIMENTS

Small-scale electrowinning experiments have been made to investigate the recovery o reduction salt for recycle of $CaCl_2$-CaF_2 and calcium to another reduction step. The experiments have been performed with 85-mm i MgO crucibles, carbon electrodes, and severa cathodes. The calculated reversible decomposition potential for CaO in these experiments ranged from about 1.0 V with a zinc cathode to 1.6 V with a solid cathode. For these electrolyses, the potentials generally were maintained at less than 2.7 V the reversible decomposition potential for $CaCl_2$ with a zinc cathode; however, in one run potentials as high as 3.4 V were used without chlorine formation.

The major problem encountered in these tests was carbon contamination of the salt. Carbon is sloughed of the anode during the electrochemical reaction and as a result of chemical reduction of carbonates formed between the CO_2 reaction product and CaO reactant. As carbon is unacceptable for sal recycle, these problems received major attention. The salt can be filtered to remove the carbon, but techniques to keep it from the product salt have been devised.

To date, the best results (75% current efficiency) have been obtained recovering th calcium in a zinc cathode, but this has the disadvantage that a distillation step would be required to recover the calcium from the zinc. Calcium has been recovered in a Mg-Cu cathode at 35% efficiency. This results in production of reduction alloy for the Salt Transport Process. Very low efficiencies (~10%) have been achieved with solid cathodes.

REFERENCES

1. Battles, J. E., W. E. Miller, and E. C. Gay, Pyrometallurgical Processing of Integral Fast Reactor Metal Fuels, Paper B-I 6, This Conference (Apr. 1991).

2. Steunenberg, R. K., R. D. Pierce, and L. Burris, "Pyrometallurgical and Pyrochemical Fuel Processing Methods," *Progress in Nuclear Energy Series III, Process Chemistry*, Vol. 4, 461-504, Pergamon Press, Oxford & New York (1969).

3. Pierce, R. D. and L. Burris, Jr., "Pyroprocessing of Reactor Fuels," *Selected Reviews in Reactor Technology 1964*, L. E. Link (Ed.), TID-8540, 411-476 (1964).

4. Bychkov, A. V., V. I. Lenin Research Institute of Atomic Reactors, Dimitrovgrad, USSR, Personal Communication (Dec. 1990).

5. Massalski, T. B. (Editor in Chief), *Binary Alloy Phase Diagrams*, Vol. 2, p. 1121, American Society for Metals, Metals Park, OH (1986).

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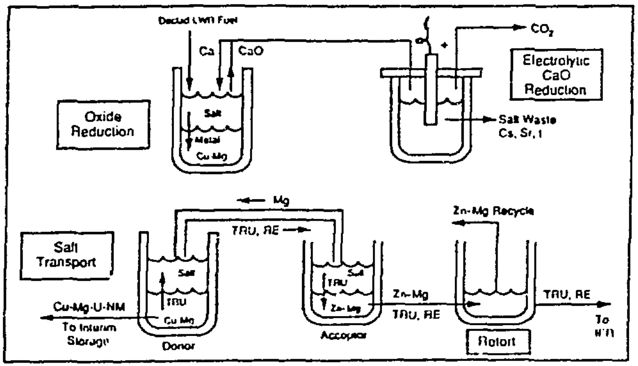

Fig. 1 Salt Transport Conceptual Process

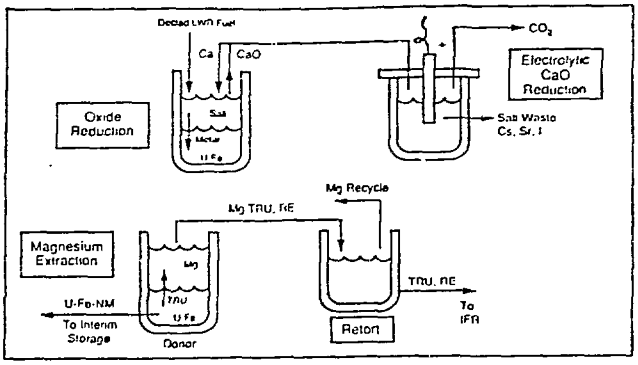

Fig. 2 Magnesium Extraction Conceptual Process

TABLE 1

Laboratory-Scale Salt Transport Experiments

MgO Crucibles with Integral Baffles		57-mm id
4-Blade Tantalum Turbine		28-mm di
Operating Temperature		795°C
Reduction Runs		
Reaction Time		4 h
Agitator Speed		900 rpm
Synthetic LWR Fuel		26 g
Metal Alloy:	Magnesium	48.5 g
	Copper	91.5 g
	Calcium	14.0 g
Salt:	$CaCl_2$	212 g
	CaF_2	38 g
Salt Transport Equilibrations		
Reaction Time		2 h
Agitator Speed		300 rpm
Donor Alloy (from Reduction Step)		160 g
Transport Salt:	$MgCl_2$	265 g
Acceptor Alloy:	Zinc	180 g
	Magnesium	20 g

TABLE 2

Magnesium Extraction Process Experiments

MgO Crucibles with Integral Baffles		57-mm id
4-Blade Tantalum Turbine		28-mm dia
Operating Temperature		795°C

Reduction Runs

Reaction Time		4 h
Agitator Speed		900 rpm
Synthetic LWR Fuel		26 g
Metal Alloy:	Uranium	43 g
	Iron	7 g
Reductant:	Calcium	14 g
Salt:	$CaCl_2$	212 g
	CaF_2	38 g

Magnesium Extraction Equilibrations

Reaction Time	2 h
Agitator Speed	300 rpm
U-Fe Alloy (from Reduction Step)	70 g
Magnesium Extractant (fresh magnesium for each extraction)	200 g