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WASTE REMOVAL IN PYROCHEMICAL FUEL PROCESSING FOR THE INTEGRAL FAST REACTOR*

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WASTE REMOVAL IN PYROCHEMICAL FUEL PROCESSING

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Abstract

Electrorefining in a molten salt electrolyte is used in the Integral Fast Reactor fuel cycle to recover actinides from spent fuel. Processes that are being developed for removing the waste constituents from the electrorefiner and incorporating them into the waste forms are described in this paper. During processing, halogen, chalcogen, alkali, alkaline earth, and rare earth fission products build up in the molten salt as metal halides and anions, and fuel cladding hulls and noble metal fission products remain as metals of various particle sizes. Essentially all transuranic actinides are collected as metals on cathodes, and are converted to new metal fuel. After processing, fission products and other waste are removed to a metal and a mineral waste form. The metal waste form contains the cladding hulls, noble metal fission products, and (optionally) most rare earths in a copper or stainless steel matrix. The mineral waste form contains fission products that have been removed from the salt into a zeolite or zeolite-derived matrix.

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INTRODUCTION

The Integral Fast Reactor (IFR) concept includes a passively safe, metal-fueled fast reactor and a pyrochemical fuel reprocessing scheme for recovering nearly all of the transuranic (TRU) elements – Pu, Np, Am, and Cm – in spent fuel and transferring fission products to acceptable waste forms. The TRU elements are incorporated in fresh fuel and returned to the reactor for consumption [1,2].

There are two kinds of IFR fuel – blanket and core. As inserted into the reactor, blanket fuel contains depleted uranium and 10 wt% zirconium; during irradiation, up to 4 wt% of TRU elements grow into the blanket fuel, along with up to 2 wt% of fission products. Fresh core fuel is similar, except that about one-fifth of its uranium is replaced by TRU. When removed from the reactor, core fuel typically contains about 18 wt% TRU, 63% uranium, 10% zirconium, and 9% fission products. In both kinds of fuel, plutonium makes up about 99% of TRU; neptunium and americium each constitute less than 1%, and curium amounts to less than 0.1%. There are no significant amounts of actinides lighter than uranium or heavier than curium.

The pyroprocess is required to return nearly pure uranium for fabrication of fresh blanket fuel and a TRU-U mixture containing 25% or more TRU for fabrication of fresh core fuel. It must also leave the fission products, the cladding metal, and any other high-level wastes in suitable waste forms for permanent disposal in a repository. A major objective of the IFR development program is to ensure that less than 0.1% of the TRU content of the spent fuel is lost with the wastes. Achieving this objective will result in a significantly decreased burden on the repository and a tolerable loss of valuable fuel. With the methods described below, it may be possible to keep TRU losses well below 0.1%.

After an overview of the pyrochemical process, we describe the processes that are being developed for removing the waste constituents from the electrorefiner and incorporating them into satisfactory waste forms.

FEED PREPARATION AND PRODUCT RECOVERY

The following describes the design for a commercial IFR pyroprocess as it is presently envisioned. It serves as the reference process for development of waste processing methods and waste forms. Process chemistry has been discussed previously [3].

Spent core or blanket fuel rods in their stainless-steel cladding are chopped into small segments, then thermal-bond sodium and alkali fission products are vacuum-retorted from the segments and collected. A 20-kg batch of the fuel segments is inserted into perforated steel baskets, which are taken to an electrorefiner for processing. The electrorefiner is a steel vessel that is maintained at 775 K (500°C). It contains 300 kg of liquid LiCl-KCl electrolyte in which about 2 mol%, total, of uranium chloride and chlorides of the TRU elements are dissolved. When the basket containing the spent fuel is inserted into the electrolyte, the active metals (alkaline and rare earth metals and any alkali metals that remain after retorting) react with some of the actinide chlorides. Oxidant, such as UCl_3, is added to maintain the concentration of actinide chlorides; oxidant addition is required after every few batches of fuel are processed.

The basket is connected to the positive pole of a dc power source (anode); the negative pole of the power source is connected to steel cathodes immersed in the same electrolyte. Sufficient current is passed to electrotransport about two-thirds of the actinide metals from the baskets to the cathodes; it deposits as quite pure uranium metal. Cathodes consisting of liquid cadmium in ceramic crucibles are used to harvest the balance of the actinides in the spent fuel batch. The cadmium cathode product comprises primarily TRU elements, along with somewhat less uranium and relatively small amounts of rare earth fission products. The liquid and solid cathodes may be operated simultaneously to increase throughput. In the case of U-Zr fuel, only the steel rod cathodes are used, and only uranium is recovered. The small amount of TRU in spent U-Zr fuel displaces uranium chloride and accumulates in the electrolyte until the next batch of U-TRU-Zr fuel is processed.

All cathode products are melted and retorted to remove salt (and cadmium from the cadmium electrode). Ingots from the retort are blended to appropriate composition, alloyed with make-up zirconium and uranium as required, and recast into fuel pins. The pins are inserted into cladding, welded, and reassembled into fresh fuel assemblies. Because of the radioactivity of the TRU and residual fission product elements, all steps, from removal of spent fuel assemblies to re-insertion of processed fuel into the reactor, are done remotely behind several feet of concrete shielding

At present, most critical processing steps, especially electrorefining, are in an advanced state of development and are about to be demonstrated on near-commercial scale [4].

REMOVAL OF FISSION PRODUCTS AND WASTES

During chopping and electrorefining of spent fuel, tritium, krypton, and xenon are released into the process cell, which has an argon atmosphere. They are recovered at high concentrations by the cell atmosphere purification system and are stored as compressed gas and tritiated water.

All other fission products are incorporated into either a metal high-level waste form or a mineral high-level waste form. The fission products accumulate in the electrorefiner during processing, although cladding hulls, zirconium, and some noble metal fission products are removed from the anode baskets after each batch of fuel has been processed. The electrolyte is filtered to remove any zirconium or noble metal impurities that may be lost from the anode baskets and any oxides or carbide impurities. The basket contents, filters, and filter contents are incorporated in the metal waste form.

Several dozen batches of fuel are processed in a "campaign." The end of a campaign is reached when the fission product concentration in the electrolyte becomes sufficiently great that heating due to radioactive decay approaches design limits. At this point, the salt is treated by a series of steps in a continuous purification cycle to remove the fission products; these are subsequently incorporated in the mineral waste form. The steps in the purification cycle mostly involve reactions between salt and molten cadmium solutions. They are carried out in special high temperature centrifugal contactors, called “pyrocontactors,” which are being developed especially for purification of IFR pyroprocess salt [5]. Pyrocontactors can be used wherever molten salt and liquid metal can be contacted without formation of solid phases. They are small (typically 4 cm diameter) , but have large throughputs (on the order of 1 liter/minute), and are expected to give excellent phase separations.

Figure 1 shows the continuous flows in the salt purification cycle. In the first step of the purification cycle (reduction), nearly all the actinide elements are reduced from the salt into a cadmium stream containing a controlled amount of lithium. In the final step (oxidation), these actinides are re-oxidized into the salt so that it is ready for immediate use in the electrorefiner.

The second step (extraction) uses a multi-stage pyrocontactor bank for extraction of TRU from the salt with excess uranium in cadmium. Countercurrent flow of metal and salt greatly enhances the selectivity of the extraction process. All but a few ppm of the remaining TRU elements is extracted from the salt. Accordingly, very little TRU is lost to waste; the process losses are expected to be mainly tramp particles (perhaps of oxides or carbides) lost with cladding hulls or in salt filtration. It should be easily possible to achieve the goal of more than

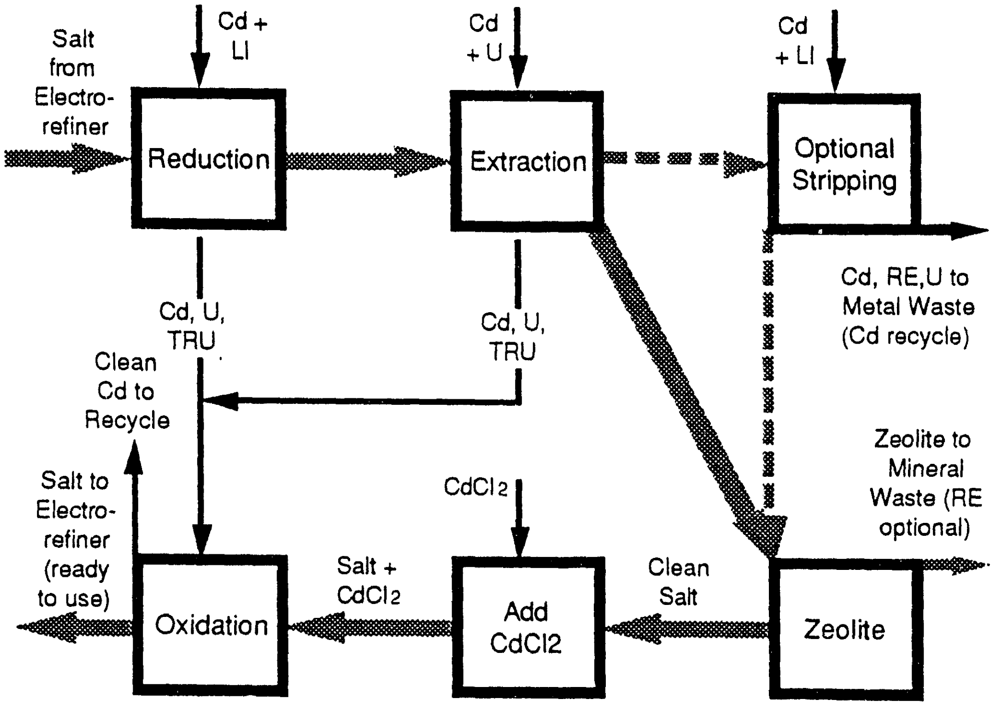

Fig. 1. Salt Purification Cycle
(RE= rare earths, TRU = transuranics)

99.9% overall TRU recovery for the IFR fuel cycle. At this point in the salt purification cycle, about 90% of the rare earths remains in the salt; the other 10% has been removed in the reduction or extraction steps.

An optional third step (stripping) allows removal of rare earth and uranium chlorides from the salt, again by reduction with lithium in cadmium. If this step is omitted, the rare earths pass on to the zeolite beds and are incorporated into the mineral waste form. If stripping is used, the solutes in this cadmium stream are incorporated in the metal waste form by the methods discussed below. Europium, samarium, and yttrium are not easily reduced; therefore the bulk of these elements always passes on to the zeolite.

In the fourth step, alkali, alkaline earth, and (optionally) rare earth fission products are removed from the salt by means of a zeolite bed. Zeolite A has a strong affinity for the fission product cations relative to the sodium, lithium and potassium cations of the process salt. Anions such as iodide and telluride are also removed because the zeolite bed contains occluded salt within the molecular structure of the zeolite and salt on the zeolite surface. Even in the absence of specificity for anion exchange, this salt takes on the composition of the exiting salt flow, resulting in adequate removal of these minor anionic constituents. A string of beds in series is contemplated to achieve maximal fission product loadings. Periodically, perhaps after each purification operation, the first bed is taken away to the mineral waste form fabrication process. Succeeding beds are then "advanced," and a fresh bed is added to the salt outlet end of the string. The fresh beds are pre-loaded with clean electrolyte salt; fission products are removed by ion exchange.

After the zeolite step, cadmium chloride is added to the newly purified salt. Then, in the final step, the TRU elements are oxidized back into the salt by contacting it with the cadmium solutions from the reduction and extraction steps. After oxidation is complete, appropriate reagents are added to the cadmium, which is returned to the reduction and extraction steps for processing of the next salt batch. The salt is returned to the electrorefiner. About 90% of the fission products in the incoming salt are removed in the salt purification process. The quantity and composition (uranium and TRU content) of the purified salt are such that it is ready for immediate use in the electrorefiner.

Testing of the salt extraction process using pyrocontactors has recently begun [5]. Fuel retorting experiments have not yet begun because of the higher priorities assigned to the timely development of electrorefining and pyrocontacting.

PREPARATION OF MINERAL WASTE FORM

Salt-occluded zeolite and sodalite, which is formed by pyrolysis of zeolite, are both being evaluated for the mineral waste form. One form will be chosen for further development. They are both prepared from the zeolite removed from the salt purification process. A nominal unit cell of zeolite contains 12 AlO_2 and 12 SiO_2 units. The unit cell also contains exchangeable cations bearing 12 positive charges to balance the negative charges of the 12 AlO_2 moieties. In addition, neutral salt containing as many as 12 chloride ions can be occluded within the unit cell [6]. Particles of zeolite in a bed are also wetted by surface salt. The zeolite bed as brought to the waste-removal process contains both occluded and surface salt; the loaded bed exiting the process contains the same amount of salt, but the composition differs because of exchange with the electrolyte.

Dried zeolite that contains no occluded salt is blended with the fission product-loaded zeolite to make a waste form precursor. The blending is done near 725 K. Salt diffusion among zeolite particles appears to be rapid at this temperature, thus the blended zeolite is expected to be homogeneous. The blended zeolite contains a selected amount of occluded salt, but no surface salt. The amount of occluded salt in the blended zeolite must always be less than or equal to 12 equivalents of salt per nominal unit cell. If the zeolite is to be converted to sodalite (a naturally occurring mineral which is very similar to zeolite in composition and structure), the amount of occluded salt will be 4 equivalents per unit cell.

PREPARATION OF METAL WASTE FORM

Development of metal waste forms is discussed in a companion paper [7]. Methods for isolating the metal waste components are described here. Both a copper-based and a stainless steel waste form are undergoing initial investigation; one form will be chosen for further development.

The stainless steel waste form is made by melting the cladding hulls, filters, and noble metal fission products under a low-volatility flux containing an oxidant such as ferrous chloride. Any residual actinide or rare earth elements are oxidized into the flux. The flux is taken to the mineral waste preparation process, and the melt is withdrawn continuously and cooled to form ingots. The resulting metal waste form has very low TRU content [8]. If it should be necessary to incorporate the rare earth elements in the stainless steel waste form, the cadmium would be distilled away from them, and they would be alloyed with the balance of the waste in a second high-temperature melting.

The copper waste form is designed to incorporate the rare earth elements by extraction of the cadmium with a copper-aluminum alloy, which has a much higher affinity for the rare earths than does the cadmium. Most of the extracted cadmium is distilled and re-used; the still bottoms are returned to the extraction vessel. The copper-aluminum alloy is mixed with the hulls, noble metals, filters, and additional copper; the resulting high-copper alloy encapsulates and partially dissolves the noble metals and stainless steel components.

SUMMARY

The reference flowsheet for product recovery and waste isolation in commercial IFR pyroprocessing plants is designed and developed to support high product quality and throughput, and to facilitate fabrication of satisfactory waste forms having minimum volumes. With the exception of distillation of volatile metals from the feedstock, methods for carrying out the required steps are under development or about to be demonstrated at near-commercial scale.

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