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PROPOSED METHODS FOR TREATING HIGH-LEVEL\*

PYROCHEMICAL PROCESS WASTES

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Introduction

Pyrochemical processes are being developed for recovering driver and blanket fuels from advanced LMFBRs. Several approaches are being investigated for converting high-level, TRU-contaminated wastes from these processes to metal alloys or glass. There are several potential methods for converting the pyrochemical wastes to glass, but other options to simplify waste processing and reduce costs are being explored.

From the pyrochemical process<sup>1</sup> chosen for the Integral Fast Reactor, the principal wastes are the chloride salt electrolyte and cadmium anode metal from electrorefining, fuel cladding, fission gases, and miscellaneous TRU-contaminated wastes from fuel melting operations. Except for tritium, krypton, and xenon, the fission products, including iodine, will be contained almost completely in the salt and cadmium. The salt, which is a mixture of lithium, sodium, calcium, and barium chlorides, will contain most of the alkali metal, alkaline earth, rare earth, and halogen fission products. In addition to the noble metals and zirconium, the cadmium waste will include the steel anode baskets and some of the cladding. The balance of the cladding, consisting of the plenum sections with some of the bond sodium, will not be fed to the pyroprocess, and is expected to be a TRU waste. The miscellaneous wastes are the damaged crucibles and fume traps

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(fibrous aluminum silicates) from fuel melting operations, as well as pin-casting molds. The fume traps will contain small amounts of volatilized materials, primarily halide salts. The fission gases will be released during fuel element chopping and electrorefining into argon, from which they can be easily separated by state-of-the-art cryogenic techniques. Proposed methods for treating only the solid wastes are discussed in this paper.

#### Proposed Waste Treatment Methods

Cadmium Containment. Based on calculations and laboratory scouting experiments,<sup>2</sup> it appears possible to lower the long-lived alpha activities in the waste electrolyte salt below 100 nCi/g by reducing the actinides with a strong reductant, such as lithium or calcium, and dissolving the actinides in liquid cadmium. The salt will then be a non-TRU waste. Most of the alkali metals and rare earths will also be transferred into the cadmium, but most of the strontium, barium, and iodine (as an iodide) will remain in the salt. The cadmium alloy would be combined with the other TRU process wastes, which are the cadmium metal from electrorefining, the plenum cladding, and the miscellaneous wastes, in a single, heavy-walled, steel container. After a 7- to 10-y interim storage period, the steel container would be placed in a secondary container of a corrosion resistant material, such as copper, and sent to a geological repository.

Steel Alloy Containment. After reducing the TRU elements into cadmium and separating the salt, this cadmium and the cadmium in the electrorefining metal wastes can be vaporized, leaving a metallic residue of steel, actinides, and fission products. We expect that only a very

small amount of fission products would be volatilized with the distilled cadmium, which could be recycled in any case. The residue would be melted to produce a solid steel ingot in which the actinides and fission products are dispersed. About 4 wt % carbon and boron would be added to the steel alloy to lower the melting point to about 1200°C. The ingot would be encased in secondary steel and copper containers for ultimate disposal. This technique adds two process steps, cadmium distillation and steel melting, that would add to costs and generate additional wastes. However, the total volume of TRU wastes would be decreased, and a dispersion of the alpha emitters and fission products in steel should be an acceptable waste form.

Oxidative Slagging. If glass is the required waste form for ultimate disposal, it appears to be possible to transfer the actinides from the cadmium or steel dispersions produced by the above methods into an oxide phase amenable to glass making. Where the TRU elements are dispersed in cadmium, they would be oxidized into a low-melting mixture of hydroxides, borates, and carbonates using oxidizing agents, such as sodium peroxide or air. From the steel dispersion, the actinides would be extracted into an oxide slag. To facilitate glass making, an acid slag and oxidants such as iron oxide or manganese oxide, or air would be used.

Based on the large differences in the free energies of formation of the oxides, either method will result in an almost quantitative transfer of actinides into the hydroxide or oxide phase along with a large fraction of the electropositive fission products. The hydroxide or oxide product would be made into glass by the addition of silicates and phosphates. The products would not contain any of the noble metals that tend to volatilize

during glass making and accelerate devitrification of the glass. In either method, the noble-metal fission products and cladding scrap would remain in the metal phase, which would be a non-TRU waste.

Direct Conversion of Chloride Salts. Rather than transfer the actinides in the salt and metal wastes from electrorefining into a metal phase, as described in the preceding techniques, the actinides in the metal wastes could be transferred into a chloride salt phase. In this general technique, the TRU elements remaining in the cadmium anode wastes and plenum cladding would be oxidized into the waste salt to produce a metal waste free of actinides. If cadmium chloride is used as the oxidant, the noble-metal fission products, with the possible exception of zirconium, will remain in the metal waste. To convert the resulting chloride salt to glass, the chlorine must be removed and the cations converted to oxides or other compounds amenable to glass making. Two methods for removing chlorine have been considered: pyrohydrolysis and electrolysis.

Pyrohydrolysis, the reaction of the chlorides with steam and air to produce oxides or hydroxides and HCl, is thermodynamically unfavorable for the components of the pyrochemical electrolyte. However, laboratory results have shown that the chlorine can be removed from the salt if a second reactant, such as pyrex glass, boron oxide, or phosphoric acid, is employed.

Chlorine can also be removed by electrolysis of the molten salt mixture in an apparatus similar to the Downs cell used commercially to produce metallic sodium. Chlorine gas would be produced at one electrode, and a metal alloy of the actinides, rare earths, sodium and other alkali

metals, and some of the alkaline earths at the other electrode. The product alloy would be reacted with air and steam to produce oxides and hydroxides that would then be fed to the glass-making furnace. The TRU-contaminated fume traps and damaged crucibles from fuel melting operations would also be fed to the glass furnace.

Electrolysis of an aqueous solution of the chlorides would accomplish much the same ends at lower temperatures. The products in this case are HCl and a water solution of the hydroxides. The solution would be dried and fed to a glass-making furnace.

Although this general approach would produce a glass product acceptable as a high-level waste form, it is less attractive for pyrochemical processes. Several process steps are added, which would add to the costs and would generate other radioactive wastes. The most significant additional waste stream is the off-gas from either pyrohydrolysis or electrolysis. Because these off-gases will contain fission-product iodine, they must be trapped, thereby producing a large volume of a low-level waste.

### Conclusions

This survey illustrates the large variety and number of possible techniques available for treating pyrochemical wastes; there are undoubtedly other process types and many variations. The choice of a suitable process is complicated by the uncertainty as to what will be an acceptable waste form in the future for both TRU and non-TRU wastes.

References

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