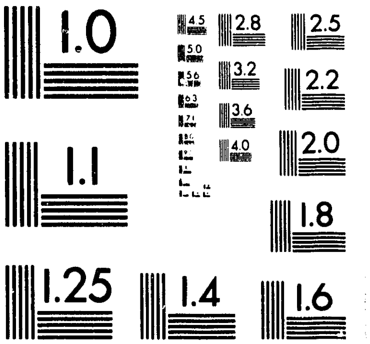
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NEW HIGH-LEVEL WASTE MANAGEMENT TECHNOLOGY FOR IFR PYROPROCESSING WASTES*

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To be presented at

GLOBAL '93

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ABSTRACT

The pyrochemical electrorefining process for recovery of actinides in spent fuel from the Integral Fast Reactor accumulates fission product wastes as chlorides dissolved in molten LiCl-KCl and as metals, some of which are in molten cadmium. Pyrochemical processes are being developed to recover uranium and transuranium elements for return to the reactor, and to separate and immobilize fission products in suitable waste forms. Solvent cadmium is recycled within the process. Electrolyte salt is treated in a series of salt/cadmium extraction steps; it is also returned to the process. Salt-borne fission products are concentrated on a zeolite bed that is converted to a stable, leach-resistant mineral. Rare earth fission products from the salt, noble metal fission products, and cladding hulls are dispersed in a metal matrix.

I. INTRODUCTION

Pyrochemical reprocessing of spent core and blanket fuels is an essential part of the advanced power reactor concept referred to as the Integral Fast Reactor (IFR).[1] More than 99.9% of the transuranium (TRU) elements – Pu, Np, Am, and Cm – in the spent core (U-Pu-10 wt% Zr) or blanket (U-10 wt% Zr) fuel alloys will be separated from fission products and recovered as metals by an electrorefining process. The reprocessed fuel will be returned to the reactor.

Minimization and ultimate disposal of radioactive and toxic wastes from the fuel cycle are important goals for the IFR Program. In the next few years, these waste treatment processes will be demonstrated on an engineering scale, and operations with irradiated fuel from the Experimental Breeder Reactor (EBR-II) will be conducted to establish a data base for the design and construction of a commercial IFR facility. Information will also be obtained to show that the salt and metal waste forms will be suitable for disposal in a geologic repository. Pyroprocessing of IFR fuel and all the essential associated waste treatment and fuel refabrication steps will be demonstrated starting in late 1993. This paper, however, describes an advanced IFR pyroprocess, including some refinements of IFR fuel reprocessing that are in an early development stage; these refinements are being pursued primarily to expedite removal and treatment of waste.

II. IFR FUEL PROCESSING

In the advanced IFR pyroprocess, spent core or blanket fuel rods are chopped into small segments, then thermal-bond sodium and alkali fission products are removed by distillation. The fuel segments are inserted in 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). Liquid LiCl-KCl electrolyte in the electrorefiner contains about 2 mol%, (total) uranium chloride and chlorides of the TRU elements. The basket containing the spent fuel is inserted into the electrolyte and connected to the positive pole of a dc power source (anode). The negative pole of the power source is connected to a cathode immersed in the same electrolyte.

For the spent U-Pu-Zr fuel from the core, the cathodes are simply steel rods. About two-thirds of the actinide metals is electrotransported from the anode baskets to the cathode rods, where it deposits as nearly pure uranium metal. The steel rod cathodes are replaced by cathodes consisting of liquid cadmium in ceramic crucibles, and the balance of the actinides in the spent fuel batch is deposited primarily as TRU elements, along with somewhat less uranium and relatively small amounts of rare earth fission products. In the case of the U-Zr fuel from the blanket, 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 is allowed to accumulate in the electrolyte until the next batch of U-Pu-Zr fuel is processed.

All products are 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 converted into fresh fuel assemblies. All steps -- from removal of spent fuel assemblies to re-insertion of processed fuel into the reactor -- are done remotely, under an inert atmosphere.

The fission products, with the exception of tritium, krypton, and xenon, accumulate in the electrorefiner during processing, although cladding hulls, zirconium, and some noble metal fission products are removed with the anode baskets after each batch of fuel has been processed. The three gases are released into the process cell, which has an argon atmosphere. They are recovered at high concentrations by the cell gas purification system.

Several dozen batches of fuel are processed in a "campaign." At the end of a campaign, the salt in the electrorefiner is treated by a series of steps to remove active metal fission products, particulate noble metals, and any oxide or carbide impurities for incorporation in high-level waste forms. The salt and its associated TRU chlorides are returned to the electrorefiner. The TRU inventory in the electrorefiner amounts to about 20% of the TRU elements fed with the spent fuel; this must be recovered to achieve the goal of more than 99.9% overall TRU recovery for the IFR fuel cycle.

III. PROCESS CHEMISTRY

Separations in the electrorefiner are based on the partition of elements between metal and salt phases.[2] The alkali metals, alkaline earths, and rare earths collect in the salt as chlorides, along with halide and chalcogenide fission product anions. The noble metal fission products and zirconium alloy remain as metals throughout the process; they are largely removed with the cladding hulls in the anode dissolver baskets, but some are released into the electrolyte as fine particles. The actinides and rare earths exist in both the salt and metal phases; the rare earths favor the salt phase more than the actinides do.

At the 775 K operating temperature of the IFR electrorefiner, redox exchange reactions like

$$\frac{3}{y} M'Cl_y + \frac{3}{x} M \leftrightarrow \frac{3}{x} MCl_x + \frac{3}{y} M' \qquad (1)$$

are rapid, and a thermodynamic approach provides a good understanding of process chemistry. The elements in the spent fuel and its cladding may be ordered using the free energy of formation of their chlorides. Active metals, i.e., those elements having the most stable chlorides, will react with the chlorides of more noble metals (less stable chlorides). Under electrorefiner operating conditions, the highly active alkali and alkaline earth metals are immediately oxidized into the electrolyte salt; they remain in the salt until they are removed by an ion-exchange process in the salt purification step. Rare earth metals are significantly less active than the active metals, especially when formation of intermetallic compounds with cadmium reduces their activities considerably. They are removed from the salt by a reduction process, and they are a minor constituent in the TRU product. Transuranic metals are very much alike, and are slightly more active than uranium; they remain together throughout both fuel processing and salt purification. Metals more noble than uranium remain as metals through the process; they are separated by physical means, such as filtration and centrifugation. Zirconium, the most active of the noble metals, is a special case; under certain conditions, some electrotransport of zirconium is possible.

Transuranic metals also form intermetallic compounds with cadmium. Absent cadmium, they are considerably more active than uranium; in the presence of cadmium, they are only slightly more active. This difference in behavior is exploited in product recovery. Electrotransport to a steel cathode through an electrolyte containing even fairly small amounts of UCl_3 results in a pure uranium product, but electrotransport to a liquid cadmium cathode yields a mixture of U and TRU metals,[3] the composition of which depends on the TRU/U ratio in the salt. The differences in activity are also exploited in cadmium-salt extraction processes for purification of the electrorefiner salt. Because predicting the compositions of the salt and the cadmium phases is critical to process development, we have measured the distributions of actinide elements[4] and the most significant rare earth, alkali, and alkaline earth elements.[5,6]

The distributions of elements between molten cadmium and molten salt are described by pairwise "separation factors." These separation factors correspond to equilibrium constants for reaction (1), but they use concentrations rather than activities. At equilibrium, the distribution of elements is such that all pairwise separation factors are satisfied. By convention we write reaction (1) with the more active metal, M, on the left and speak of the M-M' separation factor. The separation factor, SF, corresponding to reaction (1)
is:

$$SF = \frac{[MCl_x]^{3/x}\,[M']^{3/y}}{[M'Cl_y]^{3/y}\,[M]^{3/x}} \qquad (2)$$

The concentrations can be measured in any units, as long as the separation factor remains dimensionless. With this choice of equation and definition, the separation factor remains constant with concentration as long as the ratios of the activity coefficients remain constant. Most actinides and rare earths form trichlorides, the separation factors defined as above usually reduce to simple ratios of concentrations in this case.

In the numerous measurements made to date, separation factors have been constant with concentration to within the available precision of the chemical analyses; they can, therefore, be multiplied and divided in the same way that equilibrium constants are combined when the corresponding chemical equations are added or subtracted. It is thus possible to calculate the separation factor for any element pair if the separation factors of both elements relative to a third element are known. This approach is used to derive a single set of separation factors for all the elements studied. That set of separation factors is given in Table 1, where the separation factors are all expressed relative to uranium.

Table 1. Separation Factors (SF) Relative to Uranium in LiCl-KCl Salt at 775K

Element	SF	Element	SF
U	1.0	Ce	49
Pu	1.88	La	130
Am	2.85	Gd	150
Np	2.12	Dy	500
Cm	3.52	Y	6000
Pr	43.1	Sm, Eu, Li, Ba, Sr	$>10^{10}$
Nd	44.0		

IV. SALT PURIFICATION

After several dozen batches of fuel have been processed, heat release and radioactivity from the fission products in the electrorefiner will exceed operating limits for the electrorefiner. In that case, salt from the electrorefiner is pumped out through a filter to remove particulate. This will be the noble metal fission products and zirconium that are expected to escape from the anode baskets, as well as any oxides or carbides that may have formed. The salt is then treated as shown schematically in Fig. 1 to remove rare earth, alkali, and alkaline earth fission products. The discharged salt is sent through a series of centrifugal contactors and returned to the electrorefiner ready for continued use. Further details on these extraction steps and the high-temperature (775 K) extraction equipment being developed are given in a companion paper by Chow et al.[6]

The first step in the salt treatment sequence is to reduce about 98% of the actinide chlorides from the salt into a liquid cadmium stream. This (reduction) step is carried out in a two-stage bank of countercurrent extractors (centrifugal contactors), where the salt contacts a countercurrent stream of Cd-Li alloy. Only 10% of the rare earths is reduced in this step. The actinides are "stored" in the cadmium; re-oxidation in the final step of the sequence returns the actinides to the purified salt so that the salt is ready for further processing use.

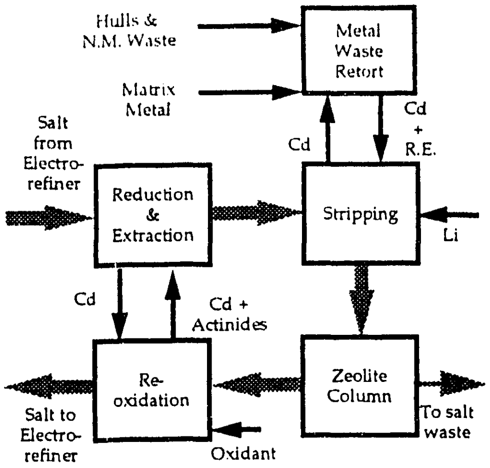

Figure 1. Schematic of Salt Purification Process

In the second (extraction) step, the TRU chlorides are removed from the salt by extraction with uranium in cadmium. With a 20-fold excess of uranium and four equilibrium countercurrent stages, the TRU content of the salt is estimated to decrease from 1400 ppm to 40 ppm. With additional stages, or more uranium, even greater removals are possible, but the amount of TRU remaining here is less than 1 part in 10^6 of the TRU in the fuel that is processed. In this step, 8% of the rare earths in the salt is removed, while about 83% of the rare earths in the unpurified salt remains. The cadmium stream from this step is combined with the cadmium from the first step.

Next, the salt is contacted with lithium in cadmium, again in two countercurrent stages. In this third (stripping) step, essentially all of the actinides and the bulk pf the rare earths are removed from the salt to the cadmium. The cadmium stream is processed to recycle the cadmium and to incorporate the rare earths and traces of TRU in the metal waste form. Samarium and europium are not as easily reduced as the other rare earths; most of these and small amounts of yttrium remain in the salt, along with alkali and alkaline earth fission products.

The salt is passed through zeolite beds to remove the remaining fission products. Multiply charged cations are strongly sorbed onto the zeolite, which is a dehydrated Li-K form of zeolite A.[8] It appears that Cs and I are also removed, although less strongly. The zeolite with its fission product loading is further processed to make a final waste form; the TRU content of that waste form will be exceptionally low. The only significant long-lived activity in this waste will be Se-79, I-129, and Cs-135; the total alpha activity should be less than 10 nCi/g. The loaded zeolite carries considerable amounts of electrolyte along with it as occluded and surface salt. This salt loss approximately balances the salt generated by each pair of oxidation (with

$CdCl_2$) and reduction (with Li) steps that are carried out. The Li/K ratio of the electrolyte is maintained by control of the lithium and potassium content of the zeolite used for fission product removal.

At this point, the radioactive species have been removed from the salt to the extent required for return to the electrorefiner. The salt is mixed with $CdCl_2$ and contacted with the cadmium streams from the reduction and extraction steps. The actinides are thus oxidized from the cadmium into the salt. This leaves the salt ready for use in electrorefining and the cadmium ready for re-use in the next salt purification cycle. The whole process can be made continuous, and thus can take place in a matter of only a few hours.

V. WASTE FORMS

A nonmetal and a metal waste form will accommodate all of the IFR high-level wastes. The nonmetal waste form will contain samarium, europium, and yttrium; the halogens and chalcogens; the alkali, and alkaline earth fission products; and a small amount of excess salt generated in the process. Zeolite A from the salt treatment process will contain all the fission product constituents of this waste form, as well as some "excess" process salt. It has been shown[8] that the zeolite has good radiation stability up to 10^9 rad.

The nominal formula for one unit cell of zeolite A is $M_{12}(AlO_2)_{12}(SiO_2)_{12}$, where M represents a singly charged cation. Up to twelve equivalents of chloride salt can be occluded in cages within one unit cell of the zeolite structure. In addition, the twelve equivalents of "M" ion can be exchanged with salt cations. Net removal of salt (meaning cation-anion pairs) from the process stream occurs by occlusion; fission product cations, especially multiply charged cations, are also removed from the salt stream by ion exchange. Finally, zeolite particles in the beds from the salt purification process are covered with "free" or "surface" salt that is essentially identical to the salt exiting the zeolite bed. This excess salt in the zeolite is sorbed into additional zeolite A in the course of preparing the final waste form; the composition of this additional zeolite is not critical, since it does not affect the composition of the electrolyte salt. Blending of the zeolite bed contents and the additional zeolite at elevated temperature (nominally 700-750 K) results in a homogeneous material with no excess salt and a controllable amount of occluded salt of up to 12 equivalents/unit cell.[9]

Two methods are being considered for consolidating blended zeolite into a monolithic waste form. In the first method, the blended zeolite is consolidated directly. Infusion of the blended zeolite powder with a relatively low melting glass binder appears to be one effective method of consolidation; initial leach tests show that a composite structure made in this way exhibits satisfactory leach rates and mechanical properties.[8] The second method is to convert the zeolite into sodalite. Sodalite is a feldspathoid mineral that is closely related to zeolite A and is one of the few naturally occurring minerals that retain chlorides in their structure. It has recently been shown[9] that the loaded zeolite A can be converted in high yield. If leach rates from the loaded sodalite are encouraging, we intend to consolidate the sodalite to form a monolithic waste form.

Metal wastes from the electrorefiner - noble metals, zirconium and cladding hulls from the anode baskets, and salt filter elements - will be combined with any process scrap such as broken crucibles and the rare earths from the salt purification process in the metal waste form. The metal waste form will have a very low TRU content, because of the effective TRU recovery in the IFR process, but its TRU level will not be quite as low as that of the nonmetal waste form.

Two candidate metal waste forms are under consideration. In the first, the constituents are melted together to form a stainless steel ingot having relatively high levels of homogeneously dispersed zirconium and (fission product) noble metals. Ceramic fragments might be dispersed in this ingot. The volume of the hulls vis-à-vis the fission products is large enough to form the stainless steel matrix for this waste form, but additional stainless steel is available from subassembly hardware which would otherwise be discarded as low-level waste. The rare earth fission products would be extracted from the cadmium process stream by either selective oxidation, relying on the immense difference in stability of the rare earth oxides and cadmium oxide, or by distillation of the cadmium. In either event, the cadmium is recycled to the process and does not appear in the waste. Work on this waste form has recently begun.

The second candidate metal waste form results from extracting rare earths from the cadmium using molten copper-aluminum eutectic, which is nearly insoluble in cadmium. Aluminum forms very stable intermetallic compounds with the rare earth metals, so that the extraction results in effective removal of rare earths from cadmium. Cladding hulls and other insolubles would be encapsulated with the extraction alloy. The eutectic composition would then be adjusted with additional copper or aluminum to yield an optimal trade-off among corrosion resistance, mechanical properties, cost, and processing ease; experiments in support of that trade-off decision are underway.

VI. SUMMARY

Advanced waste treatment concepts that maximize the electrorefiner throughput and thereby minimize the volume and cost of the fuel processing facility have been defined; the chemical basis for these process steps is firmly established. These concepts include methods for taking advantage of the inherently high capacity of centrifugal contactors. With modified versions of these contactors, it appears possible that the entire salt treatment process can be completed and the salt returned to the electrorefiner in a single work shift. Developing equipment and establishing experimental conditions to implement these steps are in progress. One metal and one nonmetal waste form will contain the IFR process wastes; the nonmetal waste form has received most attention heretofore; it appears that an economical and effective waste form will result. Because of recent progress with the nonmetal waste form, it has recently become possible to focus on development of the nonmetal waste form as well.

VII. ACKNOWLEDGMENTS

The work described herein would not have been possible without numerous conversations with many of our colleagues, most especially William Miller, or without the guidance and encouragement of Leslie Burris, James Battles, and James Laidler.

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