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ACTINIDE RECYCLE

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HISTORICAL PERSPECTIVE

A multitude of studies and assessments of actinide partitioning and transmutation were carried out in the late 1970s and early 1980s. Probably the most comprehensive of these was a study coordinated by Oak Ridge National Laboratory [1]. The conclusions of this study were that only rather weak economic and safety incentives existed for partitioning and transmuting the actinides for waste management purposes, due to the facts that (1) partitioning processes were complicated and expensive, and (2) the geologic repository was assumed to contain actinides for hundreds of thousands of years.

Much has changed in the few years since then. A variety of developments now combine to warrant a renewed assessment of the actinide recycle. First of all, it has become increasingly difficult to provide to all parties the necessary assurance that the repository will contain essentially all radioactive materials until they have decayed. Assurance can almost certainly be provided to regulatory agencies by sound technical arguments, but it is difficult to convince the general public that the behavior of wastes stored in the ground can be modeled and predicted for even a few thousand years. From this point of view alone there would seem to be a clear benefit in reducing the long-term toxicity of the high-level wastes placed in the repository.

Secondly, the Nuclear Waste Policy Act of 1982 mandated that (1) EPA promulgate standards for protection of the general environment from off-site releases from radioactive materials in repositories and (2) NRC promulgate technical requirements and criteria, consistent with EPA standards, that NRC will apply in licensing of repositories. As a result, the NRC regulations were developed in 10 CFR Part 60, "Disposal of High-Level Radioactive Wastes in Geologic Repositories" and the EPA standards in 40 CFR Part 191, "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes." The place of actinide recycle today, therefore, must be reevaluated in the light of the technical performance requirements placed on the repository by these newly established NRC regulations and EPA standards.

Finally, IFR pyroprocessing has been developed only in recent years and it appears to have potential as a relatively uncomplicated, effective actinide recovery process. In fact, actinide recycling occurs naturally in the IFR fuel cycle. Although still very much developmental, the entire IFR fuel cycle will be demonstrated on prototype-scale in conjunction with the EBR-II and its refurbished Fuel Cycle Facility starting in early 1991. A logical extension to this work, therefore, is to establish whether this IFR pyrochemical processing can be applied to extracting actinides from LWR spent fuel.

Some history of the process development leading up to the present state of affairs in pyroprocessing is useful at this point. In the 1960s, the EBR-II Fuel Cycle Facility operated for five years using a simple slagging process, known as melt refining, in which the fuel was melted in an oxide crucible. The electropositive fission products were separated from the fuel alloy by reaction with the oxide crucible to form a slag. This was the main process, simple though it was. But pyrochemical processes for recovering the actinides included with the slag were also explored. These "skull reclamation" processes involved reduction of the oxide slag into metallic solvents, such as Zn, Cd, and Mg, and separation of actinides from fission products by solubility differences and preferential extraction into molten chloride salts. A skull reclamation process of this kind was successfully demonstrated on an engineering scale at that time.

In light of that success, the logical extension of these techniques to direct processing of UO_2 and UO_2-PuO_2 fast reactor fuels began. Rapid, reliable methods of reducing these dense oxide fuel pellets into liquid metal solutions were developed, followed by processes employing extractions between metals and salts to separate fission products from actinides. And because of the large volume of fuel handled by these processes, an important requirement from the start was to minimize the volume of liquid metal and salt solutions. This was accomplished by having most of the uranium present as a precipitated metal phase.

The IFR process development in recent years combined with the technology experience described above has led to a preliminary assessment at ANL of the feasibility of using pyrochemical processes for directly extracting actinides from the LWR spent fuel. The results of this assessment indicate promising potential. Two of the most promising flowsheet options have been identified for in-depth R&D efforts.

On the basis of this work, the Department of Energy has initiated an assessment of the R&D activities needed to provide the technical facts necessary to assess the practicality of actinide recycling, timed to allow timely policy decisions on implementation, if favorable results are obtained.

This report summarizes current thinking on the rationale for actinide recycle, its ramifications on the geologic repository and the current high-level waste management plans, and the necessary development programs.

RATIONALE FOR ACTINIDE RECYCLE

The LWR spent fuel waste consists of both fission product and actinide elements. Fission products comprise hundreds of various isotopes, which, along with energy, are the products of fissioning. Actinides (or more precisely transuranic elements) are produced from neutron capture, as opposed to neutron fission, reactions in the fuel.

The relative radiological toxicities of actinides and fission products contained in once-through LWR spent fuel are compared in Fig. 8-1, normalized to the toxicity of the natural uranium ore. Fig. 8-1 was derived in the following manner:

The International Commission on Radiological Protection (ICRP) Publication 30 gives estimates of the cancer risk to various body organs resulting from ingestion of a radionuclide. When this is multiplied by the number of curies of each isotope in the LWR spent fuel, the result is an estimate of the number of cancer doses from each radionuclide in the spent fuel. These cancer doses are then summed over radionuclides in two categories, fission products and actinides, for 1 metric ton of the spent fuel. This gives the total potential radiological hazard if all radionuclides in 1 metric ton of the spent fuel are ingested. This potential hazard is then normalized relative to the cancer hazard, calculated in the same manner, associated with natural uranium ore from which the spent fuel originated. Assuming 3.2% enrichment and tails assay of 0.2%, about 5.9 metric tons of natural uranium is needed to produce 1 metric ton of LWR fuel. In the natural uranium ore the uranium is assumed to be in equilibrium with its daughter products. The ingestion mode is assumed to be oral ingestion.

Instead of expressing the relative radiological hazard or toxicity based on cancer doses, one could measure the hazard relative to the "annual limits on intake" for each radionuclide. The "annual limits on intake" are also listed in ICRP Publication 30. Since these limits were established based on cancer risks, the final results when normalized to the natural uranium ore are very similar to those obtained based on the more detailed cancer dose methodology. The minor differences that do exist are due to the simpler metabolic model assumed in deriving the annual limits on intake.

Relative toxicity can be calculated based on other standards as well, such as the maximum permissible concentration in drinking water. However, all originate from ICRP data.

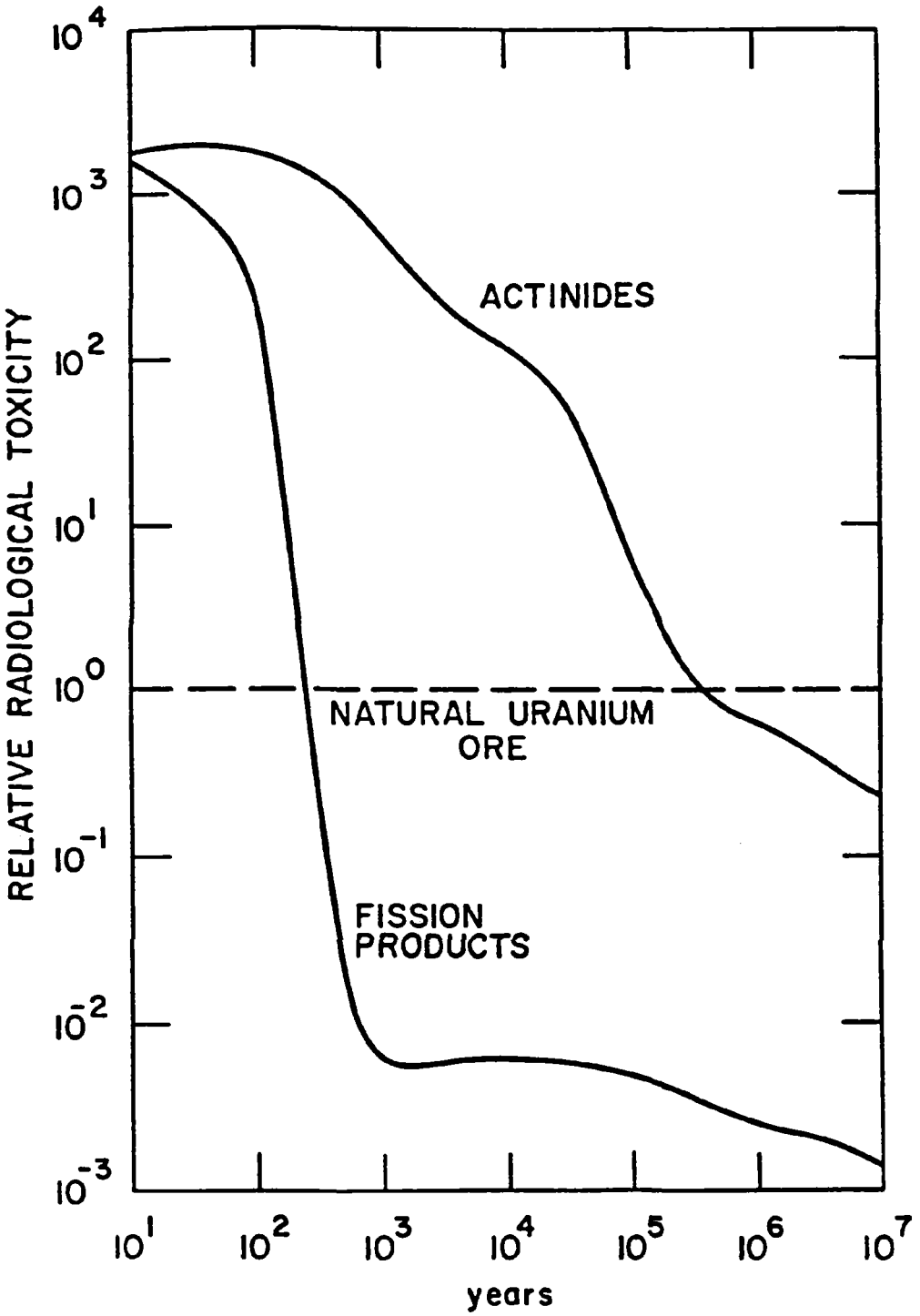

FIGURE 8-1: Relative Toxicity, Based upon a Single Ingestion, of High Level Radioactive Waste Constituents as a Function of Time following Reactor Shutdown.

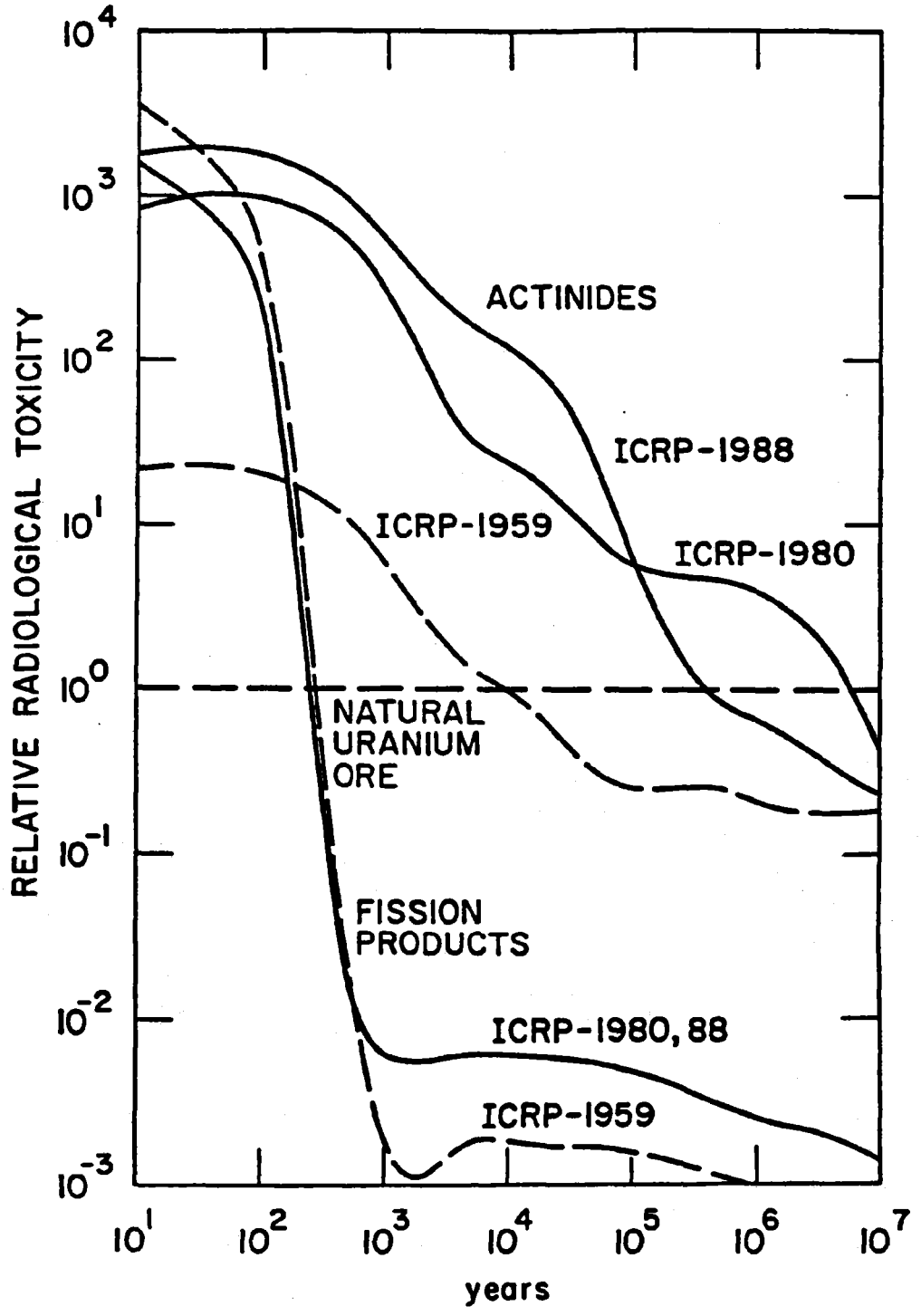

FIGURE 8-2: Relative Toxicity, Based upon Continuous Ingestion, of High Level Radioactive Waste Constituents as a Function of Time following Reactor Shutdown.

Discrepancies in relative toxicity comparison are generally due to differences in the particular ICRP source data used, rather than different methodologies. Metabolic data used in the ICRP publications on individual actinide nuclides key fission products were modified drastically in 1980 and 1988 from the original version of 1953. The sensitivities to different ICRP versions [2, 3, 4] are illustrated in Fig. 8-2. The important point to be noted is that the overall trend, relative toxicity as a function of time, is not affected to first order, from the 1980 to the 1988 versions. The 1959 ICRP data, however, substantially underestimates the toxicity of the actinides relative to both the later versions.

As shown in Fig. 8-1, most of fission products have relatively short half-lives, and their radiological toxicity drops below that of their original uranium ore in a timespan of the order of 200 years. Actinides, on the other hand, have long half-lives and their radiological toxicity remains orders of magnitude higher than that due to fission products for millions of years. In this lies the incentive to separate actinides from the waste stream and recycle them back into a reactor for *in-situ* burning, leaving a waste free of actinides.

It should be noted at this point, however, that Fig. 8-1 does not represent actual radiological risk from a repository, for example, because it does not take any account of pathways to the human body, and in effect assumes total release. The term "toxicity" is used in Fig. 8-1 instead of "risk" because the word "risk" has an implicit connotation that the radioactive nuclides in the repository are released to the environment causing ingestion by humans and hence involves cancer risks. The term "toxicity" is meant to indicate the potential hazard contained in the materials in the repository, without addressing the issue of actual pathways from repository to human body.

Another, more concrete, way of evaluating the benefits of actinide recycle is in terms of the ability to satisfy the technical performance requirements placed on the geologic repository. The EPA standards establish containment requirements that cumulative releases of radionuclides to the accessible environment for 10,000 years after disposal have a likelihood of less than one chance in 10 of exceeding the quantities specified as "cumulative release limits."

A proposed NRC rulemaking involves direct incorporation of the EPA cumulative release limits within 10 CFR Part 60. Even before this direct incorporation, 10 CFR Part 60 requires the repository to conform to such generally applicable environmental standards for radioactivity as may have been established by EPA. The EPA cumulative release limit is therefore a very important technical requirement placed on the geologic repository. The EPA cumulative release limits given in terms of curies per MTHM of spent fuel are listed in Table 8.1.

The LWR spent fuel activities for various nuclides normalized to the EPA limits in Table 8.1 are summarized in Table 8.2. If this value is less than 1, it means that even if the entire inventory is released the EPA limit is not exceeded. If this value is 100, then only 1% of the inventory can be released before the limit is exceeded, and so on. Since the activity varies with time the last two columns in the table were based on average activity over the period of 10 to 1000 years and the period of 1000 to 10,000 years, respectively.

Following the 300-1000 years of containment period required by the NRC regulations, the long-lived fission products have decayed to the same magnitude as the cumulative release limit. However, the actinide (including plutonium) activity is about 1000 times the cumulative release limit. The allowable release is 0.001, or 0.1% over the 10,000-year period. Allowable annual release rates then would be 10^{-7} per year. This is a very stringent requirement to meet.

If actinides are removed from the waste stream, then the EPA standards on cumulative release limits can be met very easily. Table 8.2 also indicates the desirable level of actinide decontamination. If 99.9% of actinides are removed from the spent fuel, then their activity will be on the order of unity after 1000 years. This is also consistent with the toxicity level considerations. Referring back to Fig. 8-1, if the actinides in the waste stream are reduced to 10^{-3}, their toxicity is in the same range as that of fission products.

Table 8.1

RELEASE LIMITS FOR CONTAINMENT REQUIREMENTS

(Cumulative Releases to the Accessible Environment for 10,000 Years After Disposal)

Radionuclide	Release Limit per 1000 MTHM or Other Unit of Waste (Curies)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	1000
Technetium-99	10,000
Thorium-230 or -232	10
Tin-126	1000
Uranium-233, -234, -235, -236, or -238	100
Any other alpha-emitting radionuclide with a half-life greater than 20 years	100
Any other radionuclide with a half-life greater than 20 years that does not emit alpha particles	1000

Table 8.2

LWR SPENT FUEL ACTIVITY

(Normalized to the EPA "Cumulative Release Limit" Listed in Table 8.1)

	Activity at 10 yrs	Average Activity $10\text{-}10^3$ yrs	Average Activity $10^3\text{-}10^4$ yrs
Sr-90	60,000	2600	0.0
Cs-137	90,000	3800	0.0
I-129	0.3	0.3	0.3
Tc-99	1.4	1.4	1.4
Other Long-lived FP	5.0	5.0	5.0
Actinides	105,000	5000	800

IMPLICATIONS ON REPOSITORY

As discussed above, actinide recycle allows the technical performance requirements placed on the repository to be met more easily, and seems highly desirable from the point of view of public acceptance. Actinide recycle should make the entire geologic repository concept more viable. At the same time, however, actinide recycle is not a requirement for the high-level waste management, and actinide recycle does not replace the need for a geologic repository.

The geologic repository is needed, independent of actinide recycle, for the following reasons.

- The goal decontamination factor for the removal of actinides from the waste stream is 10^3, that is, 99.9% removal of actinides. The residual 0.1% of actinides means waste that is far from being qualified as a non-TRU waste. A decontamination factor of the order of 10^6 would be needed for non-TRU qualification. Therefore, a geologic repository is needed to store even the residual actinides.
- In addition to residual actinides, there are a number of long-lived fission products, such as Tc-99, I-129, Cs-135, etc., that will always need to be stored.
- There are solidified defense high-level wastes and other civilian high-level wastes right now that need to be disposed in a geologic repository.

Therefore, actinide recycle must not be allowed to interfere with the present high-level waste management plans leading to the first geologic repository. Actinide recycle is a long-term option. It requires much further R&D to establish the technical, economic, and institutional practicality.

Although actinide recycle does not replace the need for a geologic repository, if successful it should simplify the long-term waste management strategy dealing with the need and timing of the second repository.

The Nuclear Waste Policy Act (NWPA) of 1982 prohibits the emplacement of spent fuel in the first repository containing in excess of 70,000 metric tons of heavy metal until such time as a second repository is in operation. The intent was to prevent the first repository being the only one and hence expanding its capacity forever. However, if the radiological toxicity is reduced by orders of magnitude through actinide recycle, and the decay heat burden could be reduced through an interim storage of cesium and strontium, it is reasonable to suggest that the current NWPA be amended to allow more efficient use of the first repository capacity.

The characteristics of the geological formation in which the repository is to be located limits the quantity and configuration of the spent fuel or process wastes that are to be replaced therein. Analysis of the Yucca Mountain Site, for example, indicates that the maximum heat burden that the site can handle without damage to the rock (chemistry, structure, and mechanical strength) is about 57 kW/acre. For ten-year cooled spent fuel, the heat load considerations limit the boreholes to only 16 per acre. If the heat load is not a constraint, then more boreholes can be drilled. The structural considerations during borehole drilling then determine the maximum number of boreholes, which is conservatively estimated to be 130 per acre. This is a factor of 8 increase in the effective capacity. Furthermore, if heat load considerations were no longer limiting, the waste form could be compacted for each borehole to fairly easily gain a further factor of about 2.5. So the overall potential for the first repository capacity increase is of the order of a factor of 20, if heat loads were eliminated.

As shown in Table 8.3, the heat load is dominated by Cs and Sr in the short term, and by actinides in the long term. Therefore, if actinides are recycled and Sr and Cs are stored in interim on the surface, the effective capacity of the first repository could be extended to the point where a second repository is not needed for a very long time.

Table 8.3

DECAY HEAT OF LWR SPENT FUEL
(Watts/MTHM)

Year	Actinides	Sr and Cs	Other F.P.	Total
1	610	8270	3430	12310
5	280	1550	430	2260
10	280	940	80	1300
20	270	650	30	950
50	250	320	2	572
100	215	97	0	312
200	174	9	0	183
500	110	0	0	110

Fig. 8-3 illustrates the capacity increase possible for a given heat load constraint as a function of the storage time of Cs and Sr. If Cs and Sr are separated and stored on surface for 85 years, in addition to the actinide recycling, the first repository capacity can be increased by a factor of 10. To fully realize the maximum of 20 improvement, a 125-year storage is required. After their interim storage, the waste containing Sr and Cs can be put into the repository for permanent disposal.

Even after most of the long-lived actinides are separated from the waste stream, other long-lived fission products remain. A logical question is whether incentive exists to partition and transmute these fission products as well. As summarized in Table 8.2, the concentrations of these long-lived fission products are low and the activities are in the same range as the EPA cumulative release limits. Furthermore, their combined toxicity level is at least two orders of magnitude less than that of the natural uranium ore as shown earlier in Fig. 8-1. Therefore, there seems to be no strong incentive to partition and transmute these long-lived fission products.

However, it should also be noted that previous repository risk assessment has shown that Tc-99 and I-129 dominated the long-term risk. This is because during an assumed leach incident at the repository the models used for risk analysis predict that technetium and iodine migrate through the geosphere rapidly enough to reach the biosphere within one million years, while actinides are sorbed in the geosphere and do not reach biosphere within one million years. That is why the risk is dominated by Tc-99 (92%) and I-129 (8%). In perspective, however, the health effects of Tc-99 and I-129 that arise from a repository leach incident are about a factor of 20 less than the expected health effects from natural background.

ACTINIDE RECYCLE IN THE IFR

A distinguishing element of the IFR concept is its unique fuel cycle based on metallic fuel and pyroprocessing. The key step in the IFR process is electro-refining. A cadmium pool in the bottom of the electrorefiner vessel serves as one electrode. The electrolyte is LiCl - KCl eutectic with about 2 mol % heavy metal chlorides, rare earth chlorides, and active metal (sodium, cesium, strontium) chlorides. Suitable electrodes for anodic dissolution of fuel and for product recovery are placed in the electrolyte.

Spent fuel pins are chopped and put in a basket for dissolution in the electrorefiner at 500°C. Cadmium chloride is then added to oxidize alkali, alkaline earth, and most rare earth metals to their chlorides, which become a part of the molten chloride electrolyte. Essentially pure uranium is electrotransported to a solid cathode and mixed U-Pu product is electro-transported to a liquid cadmium cathode. These cathodes are removed from the electrorefiner

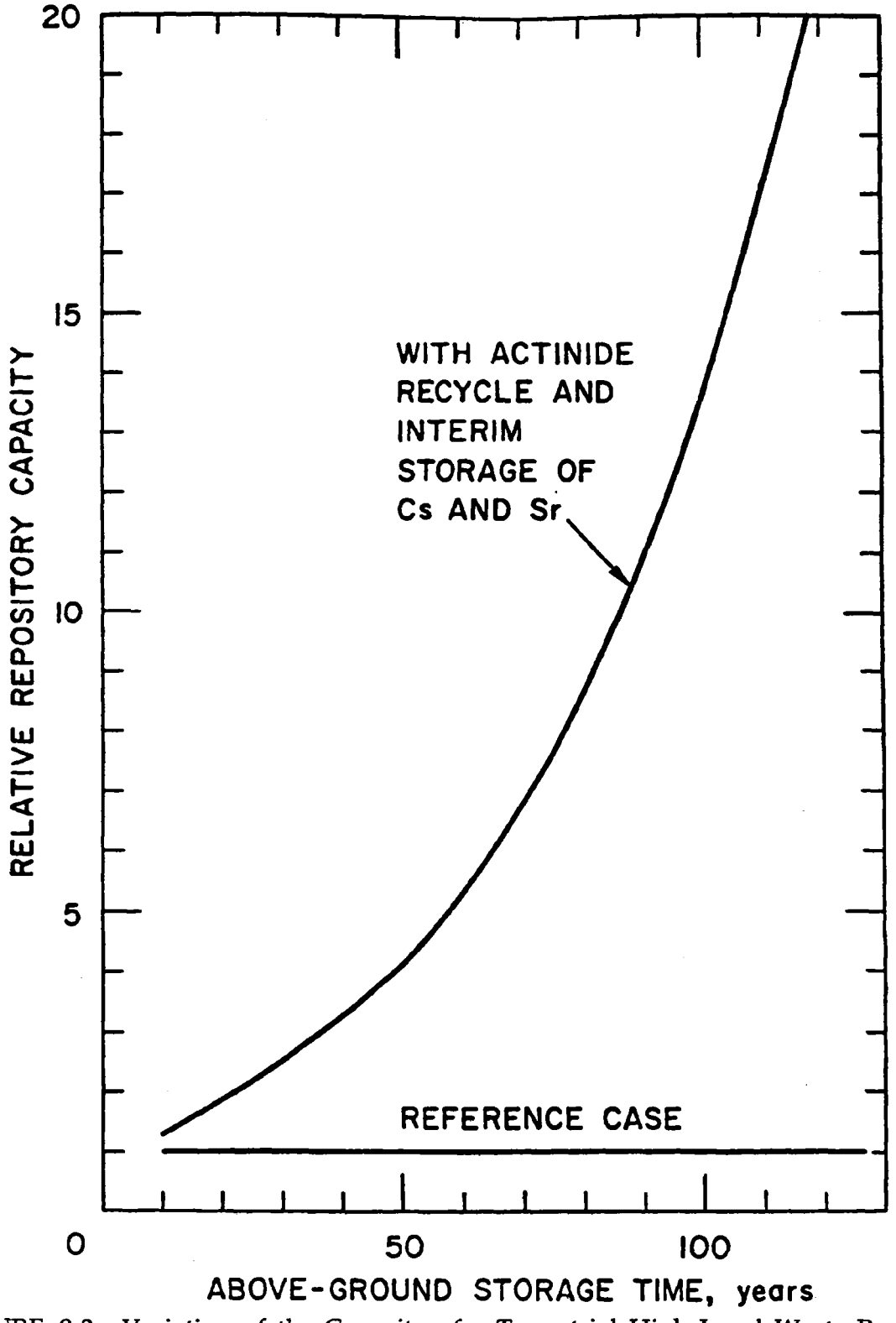

FIGURE 8-3: Variation of the Capacity of a Terrestrial High Level Waste Repository as a Function of the Duration of Prior Monitored Interim Surface Storage of Wastes, comparing cases with and without burning

cell and retorted to vaporize the cadmium and any occluded salt and to consolidate the product by melting. Noble metals, which do not electrotransport, fall into the cadmium pool; they eventually are removed by mechanical means such as filtration or distillation of the pool. The salt is freed of lanthanides and actinides by reduction and returned to the process; the small amount of excess salt can be classified as a non-TRU waste. At some time, sodium buildup will require that the entire salt batch be discarded. This salt, which contains fission-product cesium, strontium, and iodine, may be incorporated into a ceramic matrix to produce a non-TRU waste form. The rare earths from the reduction and the noble metal fission products are consolidated into a metal such as copper to provide a permanent disposable waste form.

The chemistry of the pyroprocess is based on the relative ease of oxidation of the elements that make up the metal fuel. This is determined by the free energies of formation of chlorides of these elements. Alkali and alkaline earth metals are readily oxidized into the salt, and less easily oxidized noble elements remain as metals. The amount of oxidant can be adjusted so that the actinides and rare earths are found both as metals and in the salt, although actinides will mostly be found as metal and rare earths will mostly be chlorides. Thus, oxidation effects most of the separation of actinides from fission products.

Separate collection of the uranium product and the mixed actinide product is possible because uranium is slightly less easily oxidized than the other actinides, and because the oxidation state is such that the salt contains a mixture of actinides. When electrotransport is used simultaneously to oxidize the metals to their chlorides at an anode and to reduce an equivalent amount of chloride to metal at a solid metal cathode, uranium is preferentially deposited and the other actinides are preferentially oxidized. The product is essentially pure uranium, contaminated with the salt.

When a crucible containing liquid cadmium is used as the cathode, uranium, plutonium, minor actinides, and some of rare earths are all stabilized as metals by interaction with the cadmium. The cadmium electrode product is a mixture of actinides with small amounts of rare earths. Thus, the recovery and recycle of the actinides occur naturally in the IFR pyroprocess.

The hard spectrum reactor characteristic of the IFR makes an ideal actinide burner. Of course, actinides in a given target element can be burned in any reactor type. However, large-scale actinide burning involving the cumulated actinides from the LWR spent fuel inventory cannot be done efficiently in the thermal spectrum reactor. Because of high capture to fission cross section ratios, substantial amounts of the actinides evolve into higher mass isotopes in the thermal spectrum reactor. This degrades reactivity of the actinide mixture. Therefore, if the reactor is fueled largely with actinides, there is a limit beyond which they will be unlikely to be placed in a thermal reactor because of reactivity poisoning. As shown in Table 8.4, after four cycle generations, the reactivity value of the actinide mixture has been reduced to only about 7% of standard enriched uranium fuel. This requires a 43.6% actinide content for the fuel to have equivalent reactivity value. By this time, less than 30% of the initial actinides have burned. Thermal reactors are not feasible as true actinide burners.

Table 8.4

ACTINIDE (Including Pu) RECYCLE IN LWR

Actinide Recycle Generation	Actinide Reactivity Worth Relative to U-235	Fraction of Loading Percent HM	Initial Actinide Remaining
1	0.45	7.1	1.00
2	0.19	16.7	0.84
3	0.12	26.2	0.78
4	0.09	35.2	0.73
5	0.07	43.6	0.71

The LWR-generated actinides (plutonium, neptunium, americium, curium, etc.) can be used efficiently in the IFR spectrum because in this spectrum they have a considerable reactivity value. Further, because of the high fission to capture cross section ratios, they tend to burn rather than transmute and an equilibrium concentration of actinide is quickly established with continuous recycling. The IFR can be designed to operate in an actinide self-sustaining mode or as a net actinide burner.

The principal high-level wastes from the IFR pyroprocess fuel cycle are the metals and salts discharged from the electrorefiner. The metal waste consists of fuel cladding and perhaps a small amount of cadmium that is not recycled. This waste will also contain the noble metal fission products, most of the alloy zirconium, and small amounts of actinides. The electrorefiner salt will contain the halide, alkali-metal, alkaline earth and rare earth fission products along with some actinides. These waste streams are then converted to forms that are acceptable for disposal, as described below.

The salt waste is treated to reduce actinide content to less than 1 ppm by contact with a Li-Cd alloy, followed by filtration to remove insoluble impurities. After this treatment, the salt contains only the fission products cesium, strontium, and iodine. Its alpha activity will be below 100 nCi/g. The salt waste will then be immobilized in a suitable matrix and dispersed in metal or sintered ceramic matrix sealed in containers.

The metallic wastes from electrorefining will be combined with the Cd-Li used in treating the salt and the excess cadmium will be removed by retorting. The residue will be dispersed and immobilized in a corrosion-resistant metal matrix such as copper. This mixture will then be sealed in corrosion-resistant containers for disposal as high-level waste.

In the IFR process, cesium and strontium are already separated in the form of the salt waste, and therefore, there is no need to have additional separation processes developed if it were deemed desirable to implement the alternative waste management discussed earlier. The salt waste packages can be stored for an appropriate period to allow the decay heat reduction before they are permanently disposed in the geologic repository.

The status of the IFR process development has reached the point where a prototype demonstration of the entire IFR fuel cycle will be conducted in conjunction with EBR-II and its refurbished Fuel Cycle Facility, beginning in late 1991.

EXTENSION OF PYROPROCESSING TO LWR SPENT FUEL

IFR pyroprocessing appears to promise improvements in long-term waste management for the IFR itself. The next question that arises naturally is whether the approach can be extended to process LWR spent fuel. And, in fact, it turns out that there is an extensive experience base at Argonne in applying pyrochemical processes to oxide fuel.

In the late 1960s, the EBR-II fuel cycle facility operated for about five years using a simple drossing process, known as melt refining. In this process the electropositive fission products were separated from the fuel by reaction with a zirconium oxide crucible. The volatile elements were released and collected on a fume trap or condensed cryogenically from the cell atmosphere.

A pyrochemical process for recovering the actinides occluded with the dross, or crucible skull, was developed and demonstrated on an engineering scale with simulated fuel. This skull reclamation process employed liquid zinc-magnesium and molten chloride salt as process solvents. Also a blanket process for recovery of plutonium from metallic uranium blankets was demonstrated on a bench scale. This process involved the selective extraction of plutonium from molten uranium into an immiscible magnesium phase.

The techniques developed to process EBR-II skulls and blankets were then extended to processing uranium oxide and mixed oxide fast reactor fuels. Rapid methods for reducing these

dense oxide fuels were demonstrated, and a liquid metal-fused salt extraction step was developed for isolating the uranium, plutonium, and fission products. This "salt transport process" was demonstrated on a laboratory scale, but funding terminated before a planned pilot plant demonstration could be completed.

The earlier pyrochemical process development efforts were discontinued because there was no clear advantage to producing a pure plutonium product stream over the traditional PUREX process. Today, however, the processing goal has changed. In traditional reprocessing based on PUREX, the goal was to produce a highly decontaminated, pure Pu product stream. However, when LWR processing is viewed as a waste management strategy, the goal is quite different. Neither a pure Pu product stream nor a high decontamination factor is required. In fact, just the opposite is desirable. The new process goals, when LWR spent fuel processing is viewed as a waste management strategy, are as follows:

- Direct extraction of all actinides (Pu, Np, Am, Cm, etc.) from the spent fuel as a single product stream.
- An actinide recovery target of 99.9%, at minimum.
- The process should be incapable of producing pure Pu product.
- The process should be incapable of achieving a high decontamination factor for fission products.
- The process should be simple enough to achieve acceptable economics.

A preliminary assessment has been made to investigate the feasibility of using pyrochemical processes for directly extracting actinides from LWR spent fuel, satisfying the new process goals discussed above. It appears that the pyrochemical processes are exactly compatible with the new process goals and two promising flowsheet options have been identified: (1) a salt transport process and (2) a magnesium extraction process. These two processes are described below.

Salt Transport Process

The schematics of the salt transport process is shown in Fig. 8-4. In the salt transport process, LWR fuel oxides are reduced to metal in a liquid metal-fused salt system. The oxide fuel reacts with calcium to form CaO, which dissolves in the $CaCl_2$-based salt. The reduced metals dissolve, or, if solubility is exceeded, precipitate in the immiscible liquid metal phase, a copper-magnesium-calcium solution. This reduction system operates at 800°C. Uranium, which is the bulk of the reduction product, precipitates in the metal phase. The concentrations of plutonium and other actinides are below their solubility limits in the Cu-Mg liquid and accumulate in the liquid metal phase. Alkali, alkaline earth, and iodine fission products remain in the salt phase, while rare earth and noble metal fission products accumulate in the Cu-Mg alloy.

After the reduction, the salt phase is treated in an electrolytic cell where the CaO in the $CaCl_2$-CaO solution is reduced at a carbon electrode. The carbon electrode is consumed to form gaseous CO/CO_2 (a waste product). The calcium metal produced is dissolved in a liquid copper-magnesium cathode and is used in the next reduction operation.

The spent reduction salt must be recycled to avoid the generation of excessive waste. Calcium was selected as the reductant because it can be regenerated from the CaO in the reductant salt by an electrolytic reduction process. The chemical feasibility of electrolytic reduction has been demonstrated, but engineering development of this process has not been pursued. Removal of CaO from the reduction salt should permit continued use of the reduction salt until limits are reached from the heat generation resulting from buildup of strontium and cesium. Consequently, the salt waste will only be a small dragout stream to limit these elements.

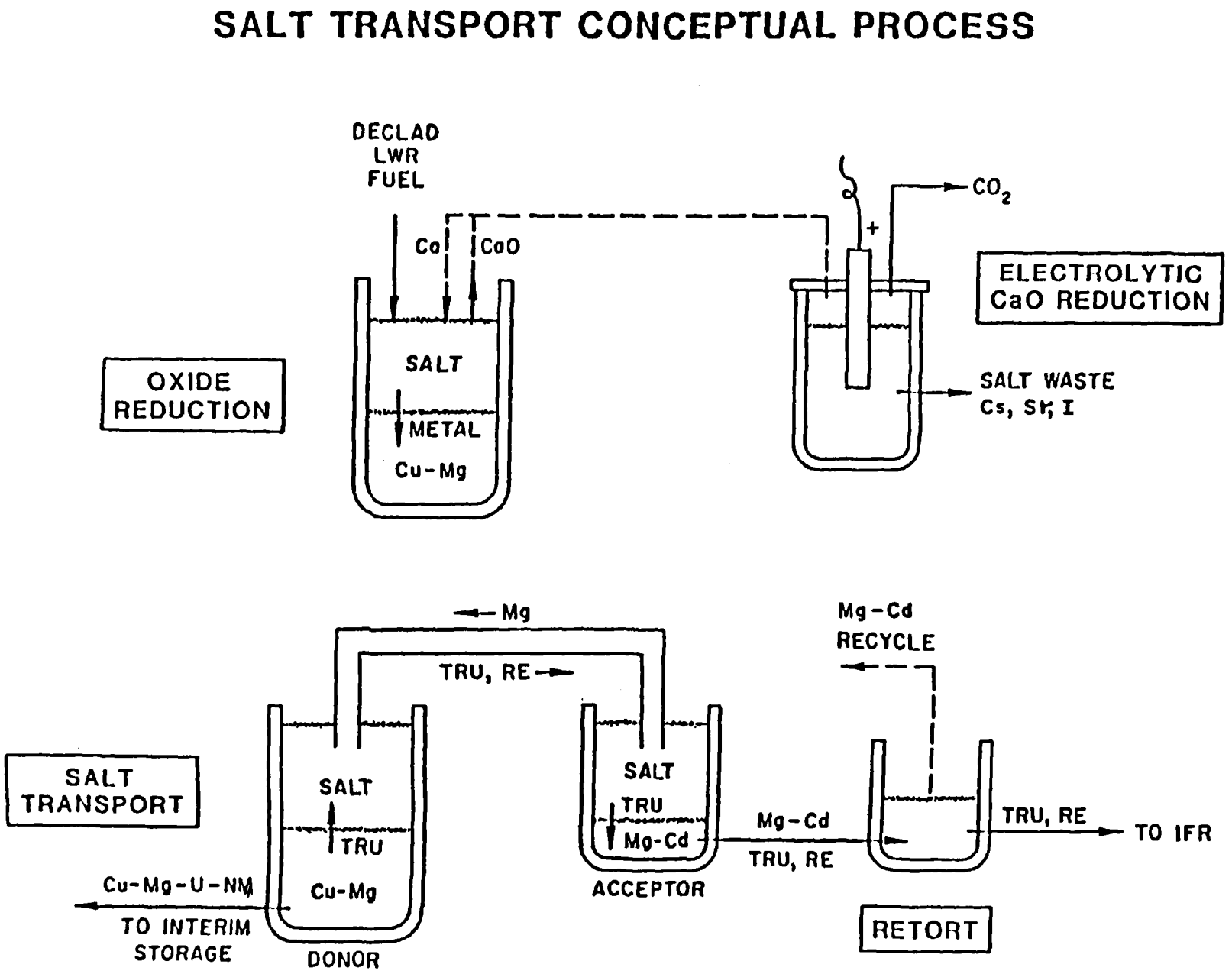

FIGURE 8-4: Schematic Diagrams of the Salt Transport-Based Pyro-Metallurgical Spent Fuel Process

The metal phase left in the reduction vessel after the removal of the salt phase is processed by the salt transport step. Transport salt is brought into contact with the metal phase (now called the donor alloy for the salt transport step). Chemical equilibrium is established in which plutonium, neptunium, americium, and curium tend to displace magnesium (from $MgCl_2$) in the salt and form their respective chlorides. The magnesium dissolves in the Cu-Mg alloy. This transport salt is then contacted with an "acceptor" alloy (Zn-Mg or Cd-Mg). In the chemical equilibration in this contact, the magnesium from the alloy reduces plutonium, neptunium, americium and curium from the salt. The $MgCl_2$ formed becomes part of the salt and the reduced actinides dissolve in the acceptor alloy. Conditions can be arranged to control (within limits) the amount of uranium that is transported along with the plutonium and higher actinides. The net result of this salt transport step is an equivalent exchange of magnesium for actinides. Magnesium moves from the acceptor alloy to the donor alloy and the actinides move from the donor alloy to the acceptor alloy. Rare earth fission products also tend to transport to the acceptor alloy. Noble metal fission products stay in the donor alloy along with the bulk uranium. The salt must be cycled several times between the donor and acceptor alloys to achieve the desired 99.9% recovery of the actinides. There is no significant waste created by this salt transport step.

The two products of the salt transport step are the donor and acceptor alloys. The Cu-Mg donor alloy with accumulated solid uranium can be recycled to accumulate more uranium. After a buildup of uranium from a number of batch cycles, the magnesium can be retorted off for recycling and the copper-uranium-noble metal cast into an ingot suitable for storing until the uranium is to be reused. The acceptor product from the plutonium salt transport step will be retorted to remove the volatile matrix alloy, which is recycled to make the acceptor alloy for the next batch. The actinide-rich heavy metal product from the retorting, which will also contain the rare earth fission products, can be charged directly to an IFR electrorefiner.

Magnesium Extraction Process

The key steps in the magnesium extraction process are: (1) reduction of the LWR fuel oxides, (2) extraction of actinides and rare earths from the uranium-iron alloy into magnesium, (3) recovery of the actinides from the liquid magnesium extract by retorting the magnesium, and (4) regeneration of the salt and calcium reductant to minimize waste volumes as described previously. A process flowsheet is presented as Fig. 8-5.

The initial step in this process, following removal of the fuel from the cladding, is the reduction of the spent LWR oxide. As for the salt transport process, calcium metal is used as the reductant. The oxide is dispersed in a $CaCl_2$-CaF_2 salt, which is added to the reduction vessel along with the reductant and a uranium-iron eutectic alloy (melting point <800°C). This alloy, which has a composition close to the iron rich liquidus, acts as a receiver for the metals reduced from the oxide fuel. The CaO is soluble in the salt. After the oxide reduction is completed, the salt is transferred to a separate vessel where the CaO is electrolytically reduced to metal for calcium recycle along with salt to the reduction step. This is similar to the calcium-recovery step described above for the salt transport process. The liquid uranium-iron alloy, now with a composition close to the uranium-rich liquidus and containing the reduced metals, is transferred to the magnesium extraction vessel. The magnesium extraction is based on the unique property that the actinide elements and rare earths are soluble in molten magnesium, whereas uranium, iron, and most of the noble metal fission products are not. The two immiscible liquid metals (U-Fe/Mg) are then separated. The separated magnesium phase is distilled leaving a residue of actinide and rare earth elements, which becomes feed stock for the IFR electrorefiner or fuel element casting furnace. The magnesium is recycled to the extraction step. A portion of the uranium-iron alloy is enriched in iron and returned to the reduction vessel. The majority of this alloy is cast into suitable shapes for storage. It is assumed that the uranium will be recovered from this alloy for use in future reactors, probably by electrorefining.

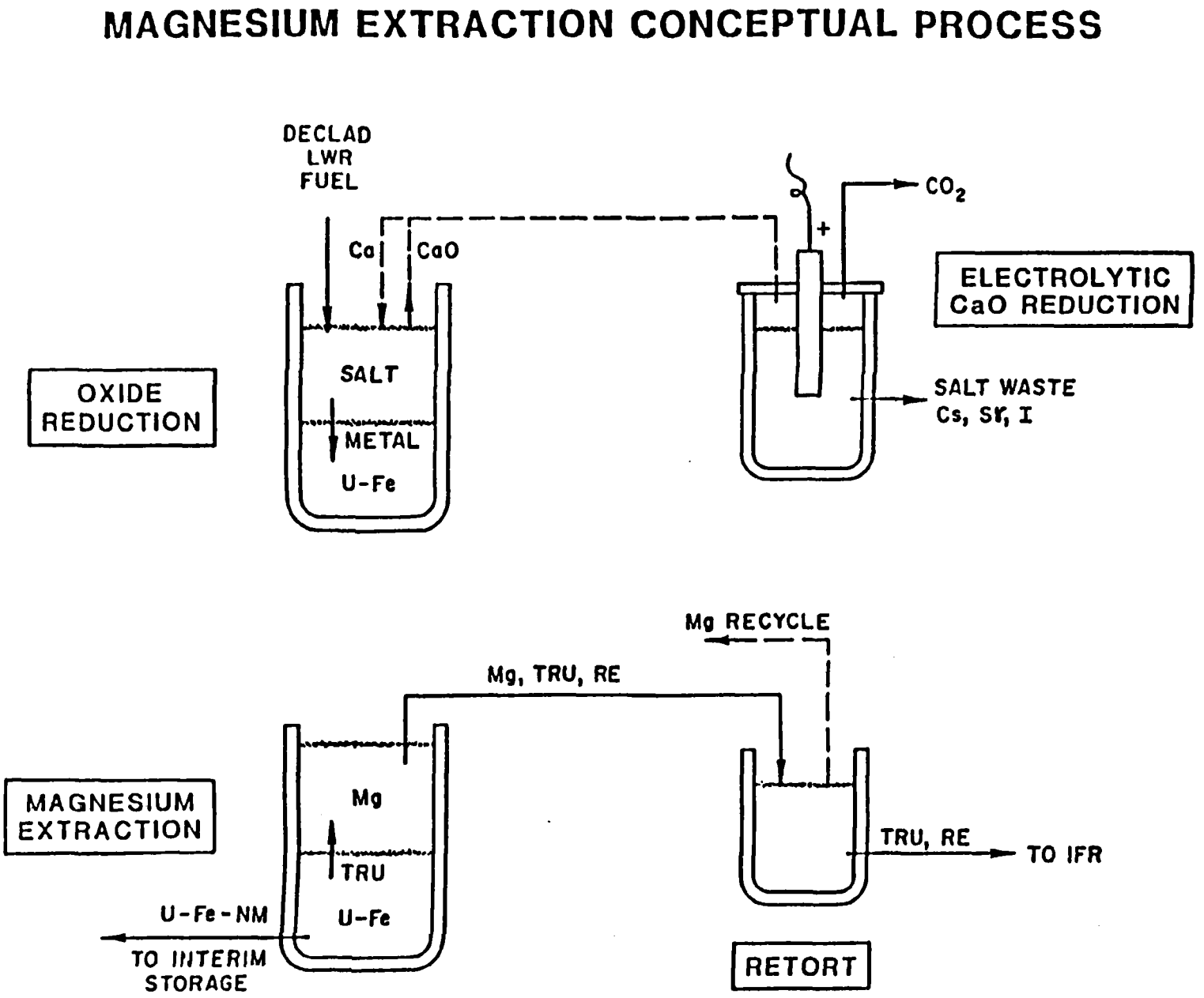

FIGURE 8-5: Schematic Diagrams of the Magnesium Extraction-Based Pyro-Metallurgical Spent Fuel Process

The two pyrochemical flowsheets described above fit naturally to the LWR actinide extraction application and should provide significant advantages over the traditional PUREX-based processes.

First, potentially all actinide elements are extracted in a single product stream, along with most rare earth fission products. A pure plutonium product is not possible. The product is highly radioactive and is not much more attractive than the original spent fuel as far as the diversion risk is concerned. The process as such therefore provides some nonproliferation protection.

Second, in these processes uranium remains as metal ingots with some noble fission product contamination. In this form the uranium can be easily stored for later recovery and use in the IFRs. The actinide extraction processes deal with only 1 or 2% of the total heavy metal. This small mass flow and the few process steps involved lead to compact equipment systems and small facility size, and portend favorable economics.

However, from the perspective of a U.S. utility, there is no immediate economic incentive in actinide recycling. With a 1 mill/kWh fee, the title to the spent fuel will be transferred to DOE for ultimate disposal. Initially, processing for actinide recycle will only add incremental cost. Thus the cost has to be kept to a minimum for the actinide recycle to be viable.

If actinide extraction is based on the traditional PUREX-based technology, it appears that even $1000/kgHM processing cost is likely to be optimistic. But even this translates to 4.3 mills/kWh incremental cost to the LWRs. Accounting adjustments such as transferring this cost increment to the future LMRs is no solution because in the end utilities will operate both the LWRs and LMRs.

It is economically essential to develop a simple process that can extract actinides directly from the spent fuel. However, to be fair, the economic cost/benefit analysis for actinide recycle must be done for the entire system including the effects on the long term repository requirements.

DEVELOPMENT NEEDS

An IFR economy can be justified and established without calling upon justification from LWR actinide recycle. However, LWR/IFR synergistic fuel cycles do provide advantages, and without the IFR fuel cycle, actinide recycling of the LWR spent fuel does not seem practical.

Specific policy decisions regarding LWR/IFR synergistic fuel cycle implementation are not possible at this time. The first repository is needed in any event. The present repository development program must continue and the IFR development program can proceed in parallel. IFR development and its associated actinide recycle technology must not be placed in the path of the repository program.

At the same time a good R&D program can be established now. It will provide the technical facts necessary to assess the practicality of actinide recycle and will be in time to allow timely policy decisions.

The IFR-based development program should have three major tasks:

- The program should begin on a practical LWR actinide extraction process, first developed, and then demonstrated.
- The presently planned IFR fuel cycle demonstration should be completed expeditiously as possible.
- Then an IFR demonstration project, including both the reactor plant and fuel cycle facility, should be put in place.

All three tasks must be completed successfully before the LWR/IFR synergistic fuel cycle can be implemented.

REFERENCES

1. Croff, A.G., J.O. Blomeke and B.C. Finney, "Actinide Partitioning-Transmutation Program" Final Report. I. Overall Assessment, ORNL-5566 (1980).

2. "Permissible Dose for Internal Radiation", International Commission on Radiological Protection (ICRP) Publication 2, (1959).

3. "Limits for Intakes of Radionuclides by Workers," International Commission on Radiological Protection (ICRP) Publication 30 (1979); Publication 30, Part 2 (1980).

4. Ibid., 1988.