LA-6442

UC-79c (Base Technology)
Reporting Date: July 1976
Issued: September 1976

MASTER

**Review of Partitioning Proposals for
Spent Nuclear Fuels**

by

David F. Bowersox

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**This work was supported by the US Energy Research and Development
Administration, Division of Nuclear Research and Applications.**

**Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$3.50 Microfiche \$2.25**

This report was prepared as an account of work sponsored
by the United States Government. Neither the United States
nor the United States Energy Research and Development Ad-
ministration, nor any of their employees, nor any of their con-
tractors, subcontractors, or their employees, makes any
warranty, express or implied, or assumes any legal liability or
responsibility for the accuracy, completeness, or usefulness of
any information, apparatus, product, or process disclosed, or
represents that its use would not infringe privately owned
rights.

REVIEW OF PARTITIONING PROPOSALS FOR SPENT NUCLEAR FUELS

by

David F. Bowersox

ABSTRACT

The initial phase of a study about recovery of valuable fission products from spent nuclear fuels has been to review various partitioning proposals. This report briefly describes the aqueous Purex process, the salt transport process, melt refining, fluoride volatility process, and gravimetric separations. All these processes appear to be possible technically, but further research will be necessary to determine which are most feasible. This review includes general recommendations for experimental research and development of several partitioning options.

I. INTRODUCTION

A program has been initiated at the Los Alamos Scientific Laboratory (LASL) to demonstrate the recovery of valuable fission products from spent nuclear fuels. The spent fuel could be used more efficiently. The actinides are extremely valuable and if the long-lived isotopes were completely removed and used or recycled, the remaining waste would be far easier to store and manage. The literature on reprocessing nuclear fuels has been studied and this report summarizes the findings. This summary does not signify a completion of the review; in fact, both the literature search and consultations with scientists active in this field should be continued. The collected information will be used to propose programs to study the parameters needed for devising viable processes. This research will be conducted at LASL at our present and proposed research facilities. Experience at LASL in studies of the metallurgy and chemistry of plutonium, uranium, and the actinides will be applicable to these new programs.

A Fuel Cycle Task Force surveyed the fuel cycle recently and reported their findings (Ref. 1). They

concluded that exploratory mining, milling, enrichment, and fabrication of uranium for nuclear fuel have been satisfactorily demonstrated and that this part of the reactor program is operable. However, even though processing of spent nuclear fuels has been studied extensively, they found that reprocessing has not been demonstrated adequately. They recognized problems in recycling because of the radioactivity of the spent fuel and the necessity for environmental protection. The safeguards problems and the questions of licensing probably cannot be overcome by private industry alone. The Task Force recommended that the Energy Research and Development Administration (ERDA) proceed with demonstration programs and, if necessary, build government facilities to demonstrate commercial fuel reprocessing.

This report briefly describes the types of reactors planned for the United States and the spent fuels to be generated in them. It then covers aqueous and pyrochemical processes and in particular, the expected partitioning problems. Finally, it recommends approaches to experimental studies of several phases of these problems.

II. PROPOSED REACTORS

The three major reactor systems now proposed to generate commercial power in the United States are the light-water reactor, the high-temperature gas-cooled reactor, and the liquid metal-cooled fast-breeder reactor. The first of these to operate commercially was the light-water reactor (LWR). The LWR is fueled with slightly enriched UO_2 sealed in Zircaloy fuel rods, and the reactor core is cooled by ordinary (light) water. The uranium, or a mixture of uranium and plutonium produced during reactor operation, could be recovered from the spent fuel and recycled into the LWR. Such recycling is not absolutely necessary as long as more uranium is available. However, recycling would lower power costs and result in a larger number of operational reactors being on line for the same amount of initial uranium. The limited supply of uranium, in fact, could be extended by about 25% by recycling spent fuel as a mixed uranium-plutonium oxide.¹ Recycling has been considered extensively and the concept is near the demonstration phase. The earliest commercial use of the mixed oxide fuel is estimated at 1981.²

In the high-temperature gas-cooled reactor (HTGR), a blanket of ^{232}Th is converted to fissile ^{233}U by an initial reactor fuel of ^{235}U . The ^{233}U is used to power the reactor in subsequent fuel cycles. This reactor would be powered by the more abundant thorium rather than by the scarcer uranium. Graphite is used extensively in the HTGR as a moderator, cladding, and reflector material so that the recycling stream will contain large amounts of carbon as well as thorium and the fission products. The HTGR is still in the design and prototype demonstration stages. Commercial operation might be feasible by 1993.³

In the liquid metal-cooled fast-breeder reactor (LMFBR), more fissile material would be bred than consumed. Nonfissionable ^{238}U would be converted to fissile ^{239}Pu , producing 30 to 60 times the amount of energy available from the initial uranium. The spent fuel from these reactors would contain more actinides and other fission products than would the spent fuel from the LWR. Therefore, reprocessing and waste management of the LMFBR would be more difficult. The LMFBR is still in the conceptual stage and commercial development is not expected until 1993.⁴

III. SPENT FUEL COMPOSITIONS

The operation of a nuclear reactor produces significant quantities of radioactive materials. Some of these materials interfere with the continued efficient operation of the reactor, usually by fission product absorption of the neutrons needed to sustain the nuclear chain reaction. At some point the fuel elements must be removed and either be discarded or treated to recover the valuable components of the spent fuel. Projected compositions of spent fuel for the various reactor concepts are given in Table I.⁵ Estimates for the LWR fuel are based on the Diablo Canyon reactor using plutonium recycling material.⁶ The HTGR fuel would be from an 1160-MW(e) reactor requiring one-fourth of the core to be refueled annually.^{7,8} The composition of the spent fuel from the LMFBR is based on normalized data for the Atomics International and General Electric reactor models.⁹ The spent fuel compositions vary because of the differences in the initial reactor fuels and in the amount of burnup. Economical burnup values are based on the calculated build-up of the fission products and vary from 33 000 megawatt days per metric tonne (MWd/MT) of fuel for the LWR to 94 000 MWd/MT for the HTGR. The major changes in composition are the increases in the concentrations of fission products, actinides, and plutonium in the HTGR and LMFBR. There are also large amounts of carbon, thorium, and ^{238}U in the HTGR. The spent fuels from the HTGR and LMFBR will be far more radioactive and generate much more heat than those from the LWR.

Most aqueous processes are based on use of LWR spent fuels with extrapolations made to accommodate the more intense radioactivity and higher heat-generation rates of the later spent fuels. However, modifications to the aqueous method may not be as effective for reprocessing as conversion to nonaqueous systems.

Spent fuels probably will be processed to separate at least plutonium and uranium for recycling into the reactor. The high-level wastes (HLW) produced in this separation are defined as "those aqueous wastes resulting from the operation of the first cycle solvent extraction, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuels."⁴ The HLW normally will contain most

TABLE I
COMPOSITIONS OF SPENT REACTOR FUELS

Species	Heavy Metal kg/MT		
	LWR ^a	HTGR ^b	LMFBR ^c
UO ₂	1124	---	---
PuO ₂	11.0	---	---
Clad	271	---	---
Fission Products	32.0	98.9	33.3
Actinides	5.53	2.2	0.8
Pu	---	1.7	100
C	---	11726	---
Th	---	840	---
U	---	37.2	864
²³⁵ U (Make-up)	---	11.3	---
²³⁵ U (Recycle)	---	7.5	---
B	---	0.97	---
Li	---	0.17	---
Fe	---	0.48	---
Oxides	---	119	---
Silicon Carbide	---	45	---
Stainless Steel	---	---	1372

^a33 000 MWd/MT at a specific power of 30 MW/MT.

^b94 270 MWd/MT at a specific power of 64.6 MW/MT.

^cBlended core and blanket assembly; 33 000 MWd/MT at a specific power of 58 MW/MT.

of the reactor-produced fission products and actinides. These products generate enough heat to require substantial cooling and emit large amounts of potentially hazardous ionizing radiation. Present regulations require that the HLW be solidified within 5 yr and be shipped to a federal repository within 10 yr of generation.

One approach to managing the HLW is to divide it into fractions of different half-lives; that is, to partition the waste.⁸ Storage volumes for the long-lived radioactive residues would be reduced greatly and much of the waste could be discarded within a reasonable geological time. For example, if the actinides were removed the hazard of the remaining waste at 1000 yr would be equivalent to that in a naturally occurring body of ore. Short-lived isotopes could be used commercially or stored until relatively nontoxic. The long-lived fractions, such as the actinides, could be used commercially, placed in fuel

for transmutation, or stored for a long period. If storage is required, it would be more easily done than for the undivided high-level waste because of reductions in the mass, heat output, and penetrating radiation of most of the waste. However, rather large separation factors, sometimes as high as 10⁴, may be required for the long-lived isotopes and such high factors have not been demonstrated.¹⁰

The long-lived isotopes could solve several of our present energy problems; energy sources include ⁸⁸Sr, ¹⁴⁷Pm, ²³⁷Np, ²³⁸Pu, and ²⁴⁴Cm. For example, our first spacecraft to pass Jupiter and Saturn was powered by ²³⁸Pu. Isotopes such as ⁸⁸Sr could be used to power unmanned radar sites, and ¹³⁷Cs might replace ⁶⁰Co in radiographical applications. Significant quantities of the platinum metals will also be produced in these reactors; if recovered, these could be valuable.¹¹ Dix, in fact, has estimated that the

isotopes in spent fuels could be worth billions of dollars.¹² Rohrman believes that americium, curium, the noble metals, and the rare gases can be recovered and that the sale of these elements would lower the cost of power significantly.¹³ If no market existed for a separated isotope, it could probably be transmuted into less radioactive species by recycling through the reactor.

IV. PROCESSING

Several principles apply to all processing schemes. All avoid adding chemicals that could be particularly troublesome in later processing. Processing and storage space are kept as small as possible by minimizing required volumes. Because of the radioactivity of the spent fuels, most operation and maintenance are conducted remotely. Therefore, the equipment should be kept as simple as possible. Finally, solvents and process streams are recycled whenever feasible to keep waste volumes as low as possible.

Bartlett et al. have published a comprehensive evaluation of transuranic partitioning of high-level fuel reprocessing waste by solvent extraction and ion exchange methods.¹⁰ These authors concluded that partitioning by conventional reprocessing methods, particularly solvent extraction, is preferable to a revision of reprocessing operations. Reasons for this conclusion were not evaluated in their report. Under present and forthcoming regulations, alternative methods might prove superior to the Purex process. Conventional Purex processing may be altered to provide for partitioning, but formidable problems must be solved.^{14,15} Pyrochemical processes are also technologically feasible and may prove to be economically preferable and also result in fewer problems with operation and waste management. Therefore, not only the aqueous Purex process but also the salt transport, melt refining, and fluoride volatility processes are presented in this summary. A reference to a flotation scheme is also given. This does not cover all possible methods, for certainly other methods such as laser-enhanced processing may be developed. The processes described, however, appear to be well worth further study.

All processing of spent fuel starts with storage in order to eliminate some of the short-lived, very active fission products. Fuel in storage, by definition, is not in productive use so that short storage times

are desirable. Particularly with LMFBR fuels, the plutonium in the spent fuel represents a sizable investment. The pyrochemical procedures can be conducted remotely after short storage times. In aqueous processing, longer storage may be necessary.

The second step in the processing is either dissolution of the entire element or separation of the cladding. In the chop-leach method adopted for the Purex process, up to 1% of the fuel remains with the cladding residues. Other decladding methods also have drawbacks. For example, at higher burnups, oxide fuels often adhere to the cladding wall so that vibration does not separate all of the fuel. Dissolution of clad in anhydrous hydrochloric acid results in a highly corrosive system, and dissolution in liquid metals leads to a difficult physical separation of molten metal and oxides. However, some of these separations may prove to be quite adequate with additional scouting studies and evaluations. In the following discussions of processing methods, different decladding procedures are proposed. In most cases, these methods are interchangeable. For example, the liquid zinc dissolution proposed for the salt transport process could be used in the Purex process as well. Therefore, systematic studies of decladding should be useful regardless of which process is finally chosen.

V. AQUEOUS PROCESSES AND THE PUREX PROCESS

Probably aqueous processing using an organic solvent extraction for purification is the most familiar method for separating uranium, plutonium, and specially produced actinides from various impurities. A generalized flow sheet for such processing is given in Fig. 1. The solvent extraction step can be replaced by a number of other purification methods such as precipitation or ion exchange. Ion exchange is not used in many cases because solids that form during processing plug the columns and because of possible radiolysis of the exchange resin.

The flowsheet shown in Fig. 1, however, is typical of aqueous processing. After a storage period, the end pieces and hardware would be removed from the fuel element and the cladding would be chopped into small pieces. Separation of the element would be effected by ball-milling, vibration, or leaching of the spent fuel. The residue, which would be radioactive,

Fig. 1.
The aqueous process.

would be stored as waste. After separation, the fuel would be dissolved and other purification steps would be performed. Finally, the purified uranium and plutonium solutions would be resynthesized into fuel elements.

Bartlett et al. reported that Purex processing would be the most useful of the various aqueous methods in commercial recycling and partitioning processes.¹⁰ It is the only aqueous process discussed in this report.

The flowsheet for the Purex process after fuel dissolution is given in Fig. 2. After storage and mechanical removal of the end pieces, the fuel element is separated from the cladding by a chop-leach method using nitric acid for the dissolution. The aqueous feed is treated with tributyl phosphate (TBP) in an organic diluent to separate uranium and plutonium from the fission products. The aqueous phase becomes the high-level liquid waste (HLLW). The proposed composition of this phase at the

Fig. 2.
The Purex process.

Barnwell Allied-General Nuclear Services processing plant, which is currently under construction, is given in Table II. Present plans are to solidify and store this waste.

The organic solvent is then selectively stripped of the plutonium and the uranium into separate aqueous streams. These streams are purified as necessary before synthesizing the uranium and, for mixed oxides, the plutonium into fuel.

TABLE II
COMPOSITION OF BARNWELL HLLW

Origin	Species	Conc. (moles/l)	Origin	Species	Conc. (moles/l)
Dissolution	HNO ₃	≈ 1			
Fission product	Se	0.0003	Fission product	Sn	0.00038
Fission product	Br	0.0003	Fission product	Sb	0.00016
Fission product	Rb	0.0071	Fission product	Te	0.0074
Fission product	Sr	0.0166	Fission product	Cs	0.034
Fission product	Y	0.0082	Fission product	Ba	0.022
Fission product	Zr	0.072	Fission product	La	0.0167
Fission product	Mo	0.065	Fission product	Ce	0.032
Fission product	Tc	0.016	Fission product	Pr	0.016
Fission product	Ru	0.041	Fission product	Nd	0.051
Fission product	Rh	0.0086	Fission product	Pm	0.0004
Fission product	Pd	0.025	Fission product	Sm	0.0118
Fission product	Ag	0.0013	Fission product	Eu	0.002
Fission product	Cd	0.0021	Fission product	Gd	0.0014
Fission product	In	0.00002	Fission product	Tb	0.00002
Total fission product		0.046			
Actinides	U	0.074	Impurities and corrosion products	Na	0.0077
	Np	0.0036		Fe	0.063
	Pu	0.0007		Cr	0.0068
	Am	0.0038		Ni	0.0024
	Cm	0.0002	Soluble nuclear poison	Gd	0.1007
Total actinides		0.115	TBP decomposition	PO ₄ ³⁻	0.037

*35 000 MWd/MT fuel after 150-day storage.

^aWaste is in 568 l.

The conventional Purex process must be modified extensively for efficient partitioning. If the AGNS flowsheet is adopted, plutonium and neptunium must be coextracted into TBP by stabilizing the neptunium in the hexavalent state. It would be far more effective to remove stabilized neptunium with the plutonium and uranium during the initial processing of the fuel. In either case, studies are needed to determine the stabilizer, an alternative reductant for stripping plutonium from the organic solvent so that the solvent can be recycled, and methods for recycling all solutions.¹⁴

If the precipitates formed during aging of the HLLW before partitioning contain actinides, a dissolution method must be found. After dissolution, chemical similarities of the rare earths to americium

and curium will make separations of americium and curium extremely difficult. Processes such as Talspeak have been developed for small-scale separations, but they are very complex.¹⁴⁻¹⁶ Large volumes of waste would certainly be generated with such methods and, at the low acidities required, the actinides may well precipitate. Actinide separations after rare earth removal should be fairly straightforward and could involve either solvent extraction or ion exchange.

Bartlett et al. proposed a massive program to develop a modified Purex process for effective partitioning.¹⁰ The research cost was estimated to be three million dollars, but the potential gain is far greater. Bond and Leuze were directing another study to develop partitioning for LWR wastes,¹⁴ but

this has evidently been dropped to develop a closed fuel cycle without partitioning.

The major advantages of the Purex process include the large amount of published research available and the length of time the method has been used, since the late forties, in separating uranium and plutonium from scrap and fission products. The Purex process has been used in nearly every existing major fuel processing facility and many proposals have been made for modifying it for partitioning.

However, even after 30 yr of development, the Purex process is still imperfect. The wastes from spent fuels will be far more radioactive and generate much more heat than those encountered in research and weapons operations. Problems were encountered when the process was used at the National Fuels Services Plant. Precipitates and inextractable species are formed during processing and aging.^{17,18} The decladding operation leaves plutonium and uranium in the cladding residues.¹⁹⁻²² Spent LMFBR fuels containing more than 20% plutonium dioxide may not totally dissolve in the leaching solution. The method for solidifying the HLLW stream is being developed. Therefore, the Purex process is still not fully developed.

VI. THE SALT TRANSPORT PROCESS

The salt transport process, developed at Argonne National Laboratory (ANL), appears to be quite promising for small-scale, on-site fuel recycling. The general flow sheet for the process is shown in Fig. 3. After 30 day storage, the fuel elements are declad in liquid zinc at 850°C. The dissolved clad would be decanted from the spent oxide fuel, and the oxides would be treated with a molten salt and alloy mixture to remove selected fission products and reduce the oxides to metal. The metals would then be treated with molten alloys and salts for further purification and, finally, synthesized into recycled fuel.

Most of the gaseous fission products would be released into the cover gas during decladding; any krypton, xenon, iodine, and tritium remaining should be released during the reduction step. Fission products such as rubidium, cesium, strontium, beryllium, and samarium should transfer into the salt phase during reduction. An additional contact with salt could be made to improve such a transfer.

Fig. 3.
Salt transport processing.

Uranium metal, which is virtually insoluble in the selected alloy, would be formed from the oxide and precipitated whereas plutonium would remain in the alloy phase.

The alloy would be separated from the salt phase and precipitate, and fission products such as yttrium and the rare earths would be removed through a series of salt-extraction cells. In a second series of salt-extraction cells, plutonium would be separated from elements such as zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, and palladium. The purified plutonium would then be separated from the alloy by vacuum distillation.

The uranium precipitate would be dissolved in a suitable alloy and purified by transfer through a series of salt-extraction cells similar to those for plutonium purification. The purified uranium would be reprecipitated, separated, and vacuum melted into an ingot. Finally, uranium and plutonium would be oxidized to form a fuel.

The rare earths are removed from the actinides during the salt transfer process. A salt transfer cell is shown in Fig. 4. The element A, which is being purified, transfers from the initial donor alloy into the liquid salt carrier in exchange for element B, which is common to the salt and the acceptor alloy.

Fig. 4.
Salt-transport cell.

Element A is transferred through the salt into the intermediate alloy and then into the acceptor alloy, where it is exchanged with element B. The reaction series in a chloride salt may be written as

The overall reaction becomes

The alloys and salts are selected so that the extraction results in a purification of element A. Better separations are obtained with one or more alloys of intermediate composition between the donor and acceptor alloys. The rare earth elements would be retained in the salt phase and the actinides could be isolated in selected alloys during the transport process.

Steunenberg et al. showed the feasibility of the salt transport process,²³ but laboratory tests are needed to determine suitable operation conditions for effective separations. Data on solubilities and transport of actinides as functions of salt mixtures, alloy compositions, and temperature will be needed.

The advantages of this process include the small volumes of waste generated as stable solids. The uncomplicated equipment would require little space, and would be maintained remotely. The process chemicals are radiation resistant and processing

could be used effectively at a reactor site with little increase in safeguards or environmental protection requirements. Expensive, long distance transport of fuel would be eliminated. The method would separate and isolate the rare earth fission products and potentially could partition the actinides very effectively.

Disadvantages of the salt transport process include the time required to develop a demonstrated system and the need for additional bench-scale research. This type of processing, particularly in the nuclear industry, is far less familiar than Purex processing. However, pilot studies and uranium fuel reprocessing in the Second Experimental Breeder Reactor (EBR-II) indicate that this process can be applied successfully.

VII. MELT REFINING PROCESS

Melt refining is a relatively simple procedure for limited purification of metallic fuels. It has been used successfully in recycling uranium in the EBR-II.²⁴ The process could be useful for mixed oxide, carbide, or nitride fuels if a reduction step is placed after decladding. A flow sheet for the modified process is given in Fig. 5. After the decladding and reduction steps, the mixture would be maintained at high temperature for several hours with an oxide slag such as magnesite. The melt, containing most of the uranium and plutonium, would then be poured into an ingot and resynthesized into fuel. Data indicate that about two-thirds of the fission products will be separated by this technique, but that molybdenum, ruthenium, and zirconium will remain with the fuel. In fast reactors, where neutron poisoning should be minimal, this process might be satisfactory. Calculation of acceptable concentrations of fission products will be needed in evaluating this technique. Laboratory experiments will be necessary to determine the behavior of the actinides.

The fission products and uranium remaining in the slag from melt refining would be recovered by a skull reclamation process, developed at ANL,²⁵ which is similar to the salt transport process. Metallic uranium fuel for the EBR-II was recycled remotely for over 5 yr by the melt-refining process. The skull reclamation process was developed in the laboratory but was not used because EBR-II was converted to a test reactor.²⁶ The demonstrated success of the melt-refining process and its relative

Fig. 5.
Melt refining processing.

simplicity indicate that it would be a promising method for at least interim processing of spent fuels.

VIII. FLUORIDE VOLATILITY PROCESS

The flowsheet for the fluoride volatility process is given in Fig. 6. Because the equipment must withstand fluorine and its compounds, the cladding can be volatilized in anhydrous hydrochloric acid. The spent fuel would then be treated with fluorine gas or an interhalogen fluoride at 300°C in a fluidized bed to volatilize uranium hexafluoride and most of the other volatile fluorides such as ruthenium, niobium, antimony, molybdenum, neptunium and tellurium. Fluorine would then be used to volatilize plutonium hexafluoride at 550°C. The nonvolatile fluorides, that is, those elements in Groups I, II, III, and IV of the Periodic Table, would remain in the solid fluidized bed. Ruthenium-niobium pentafluoride

Fig. 6.
Fluoride volatility process.

would be trapped in partial condensers and transferred into a bed of sodium fluoride. Thus, most of the wastes would be in solid form. Off-gases such as xenon, krypton, iodine pentafluoride, tritium, fluorine, and oxygen would be trapped and compressed.

The plutonium hexafluoride would be separated from uranium hexafluoride and the remaining fission products by thermal decomposition. The uranium hexafluoride would then be distilled and the purified uranium and plutonium fluorides would be converted to mixed oxide fuel.

There has been extensive study of uranium hexafluoride and fluoride volatility in the program associated with gaseous diffusion for enrichment of the ^{233}U isotopes.²⁶ Fluoride volatility processes have been used in the commercial refining of uranium at the Allied Chemical Plant at Metropolis, IL, and in development of methods for processing several types of irradiated fuels. There have been basic and pilot scale preparation and transport of plutonium hexafluoride.²⁷ Fluid-bed calcination of radioactive waste solution has been conducted at Idaho National Engineering Laboratory. Laboratory studies of the fluorination of simulated oxide fuels at ANL showed that fluorination and subsequent separation of uranium and plutonium from spent fuels is feasible.²⁸

The uncertainty in using the fluoride volatility process is primarily over the high levels of radioactivity in the high-plutonium fuels of the LMFBR. The process for decladding by anhydrous hydrochloric acid should be developed, and the handling of the solids in a processing plant of this nature needs refinement. Checks are needed to ensure that plutonium losses to the fluidized bed are low. The behavior and separation of the actinides must also be determined.

Major advantages of the process include the number of studies and applications mentioned, and the relative simplicity of the equipment and of the process itself. Disadvantages include the extreme corrosiveness of fluorine and its compounds and the intense radioactivity of the fluoride products.

IX. GRAVIMETRIC SEPARATIONS

Another method for separating fission products would be by using the differences in densities of the oxides, as shown in Table III.²⁹ After decladding, the spent fuel would be subject to further oxidation and then placed in a ferrofluidic medium such as that proposed by Khalafalla and Reimers.^{30,31} The density of this fluid, they claim, can be magnetically adjusted from 1 to 50 g/cm³. Such separations, if feasi-

TABLE III

DENSITIES OF SELECTED OXIDES

Oxide	Density (g/cm ³)
UO ₂	10.96
U ₃ O ₈	8.30
PuO ₂	11.48
NpO ₂	11.11
CmO	---
AmO ₂	11.68
PtO ₂	10.2
MoO ₂	6.47
ZrO ₂	5.6
RuO ₂	6.97
PdO	8.70
ReO ₂	11.4
RhO ₂	8.2
RuO ₂	6.97
Ce ₂ O ₃	6.86
Cs ₂ O ₃	4.25

ble, would be extremely useful in spent fuel processing.

Khalafalla and Reimers separated nonferrous metals from residues of incinerated urban refuse by density differences.^{31,32} A colloidal suspension of magnetite in kerosene was placed between the poles of a magnet, and, by adjusting the density of the suspension, the solid refuse particles were separated into light and heavy components.

This method would be simple and could be operated remotely. Any study would necessarily start with a thorough examination of the results of Khalafalla and Reimers. Extensive developmental work would be necessary.

X. RECOMMENDATIONS AND SUMMARY

Although the Purex process has been used for scrap recovery and small-scale actinide separations, it should not be adopted for partitioning without proof that it is indeed the best available method. As the heat content and radioactivity of the spent fuels become larger, problems in the Purex scheme become critical. Even at the Nuclear Fuel Services Plant problems were encountered in processing spent uranium oxide fuels. The successful processing

of uranium fuel in the EBR-II shows that pyroprocessing can be accomplished. The pilot plant studies of the skull reclamation process²⁶ also indicate that the salt transport process can be adapted to a commercial scale plant. The fluoride volatility process also has significant potential advantages.

Whether the development task for one process will be greater than for others is unclear. The technological problems associated with pyrochemical processes are not insurmountable. It would appear reasonable to initiate studies of alternate processing. Such programs could well lead to simplified processing, partitioning, and waste management at far less overall cost than presently projected. Although proponents of the Purex process now claim that it is the classical, conventional method for reprocessing, it was not always the accepted method. Just as the Purex process replaced other, less desirable methods, so one of the pyrochemical processes could well become the conventional method after extensive research and development.

Pyrochemical processing of spent reactor fuels is technologically feasible and studies of such processes would fit into the capabilities and the areas of interest at LASL. Areas in which studies could be developed include the processes reviewed in this summary; that is, salt transport, melt refining, and fluoride volatility processing. Programs of research should be proposed using any one (or more than one in combination) of these methods to develop a workable plan for recycling oxide, carbide, and other fuels for both the LWR and the LMFBF and for separating the actinides from the waste streams. In fact, detailed proposals for study of the salt transport process are being written.

The limited time before spent fuel from the LWR must be processed, probably at the Barnwell plant by the Purex process, means that some form of aqueous processing will be used for several years. However, as more reactors are on line and as more fuel must be recycled, the use of pyrochemical processes could replace the present method. By the time LMFBF fuels must be reprocessed, pyrochemical processes that are economically and technologically superior to the Purex process for both LWR and LMFBF fuels should be in use.

Spent fuels must be separated from the cladding in all these processes, and the chop-leach treatment proposed for AGNS does not dissolve all the fuel. Although residues containing plutonium and

uranium could be treated with a nitric-hydrofluoric acid leach, or by a fluoride volatility process, a second corrosive processing stream would result. Additional studies of separation by chemical means, by liquid metals, and by mechanical treatments are needed for all processes. Such studies could be made at LASL.

Personnel at LASL should become familiar with many of the programs now being conducted on reprocessing. The Sandia Solidification Project at Sandia Laboratory, Albuquerque, for example, is a different approach to waste solidification through use of an inorganic ion exchange resin. Research at the Idaho National Engineering Laboratory and Battelle Northwest Laboratory indicates that bidentate compounds can be used to separate americium and other trivalent actinides from many wastes. Studies of reprocessing and waste management in Europe should also be of interest. The potential in laser separations should also be continuously evaluated.

These recommendations will be developed into an on-going program. The task of finding the best method for reprocessing nuclear wastes will be challenging. The value could, however, be very great in lowering the cost of power, using the actinides and other fission products, and in simplifying the tasks of waste management.

REFERENCES

1. T. R. Clark, E. E. Kintner, F. K. Pittman, and W. R. Voigt, Jr., "Nuclear Fuel Cycle," Energy Research and Development Administration report ERDA-33 (March 1975).
2. J. O. Blomeke, "Radioactive Wastes from the LWR Fuel Cycle," presented at Third Annual Conference on Nuclear Power and Environmental Assessment, Berkeley, CA, (September 1975).
3. J. O. Blomeke, C. W. Kee, and J. P. Nichols, "Projections of Radioactive Wastes to be Generated by the U.S. Nuclear Power Industry," Oak Ridge National Laboratory report ORNL-TM-3965 (February 1974).
4. D. E. Deonigi, Battelle Northwest Laboratories, unpublished data, May 1972.

5. L. V. Colby, R. C. Dahlberg, and S. Jaye, "HTGR Fuel and Fuel Cycle Summary Description," General Atomic Laboratory report GA-10233 (May 1971).
6. Keith E. Asmussen, Gulf General Atomics, unpublished data, August 1972.
7. T. D. Wolsko, Argonne National Laboratory, unpublished data, November 1969.
8. "Siting of Fuel Reprocessing Plants and Waste Management Facilities," Oak Ridge National Laboratory report ORNL-4451 (July 1970).
9. U.S. Atomic Energy Commission, "High-Level Radioactive Waste Management Alternatives," WASH-1297 (May 1974).
10. J. W. Bartlett, L. A. Bray, L. L. Burger, R. E. Burns, and J. L. Ryan, "Feasibility Evaluation and R&D Program Plan for Transuranic Partitioning of High Level Fuel Reprocessing Waste," Battelle Northwest Laboratories report BNWL-1776 (1973).
11. L. L. Clark, F. P. Roberts, J. C. Sheppard, and K. D. Kaser, "A Market Analysis of Fission Product Rh, Pd, Re, and Tc," Battelle Northwest Laboratories report BNWL-1690 (February 1973).
12. G. P. Dix, "The Beneficial Utilization of Nuclear Waste Products," presented at Second Annual Waste Management Symposium, Tucson, AR, March 25, 1976.
13. C. A. Rohrman, "Values in Spent Fuel from Power Reactors," Battelle Northwest Laboratories report BNWL-25 (May 1968).
14. W. E. Bond and R. E. Leuze, "Feasibility of the Partitioning of Commercial High-Level Wastes Generated in Spent Nuclear Fuel Reprocessing," Annual Progress Report for FY-1974, Oak Ridge National Laboratory report ORNL-5012 (January 1975).
15. W. E. Bond, H. C. Clairborne, and R. E. Lueze, "Methods for Removal of Actinides from High-Level Wastes," Nucl. Technol. 24, 362 (1974).
16. Z. Kolarik, G. Koch, H. H. Kuesel, and J. Fritsch, "Separation of Americium and Curium from Highly Radioactive Waste Solution," Karlsruhe Laboratory report KFK-1553 (1972).
17. W. Ochsenfeld, H. Schneider, and S. Theiss, "Aqueous Reprocessing of Fast Breeder Fuel Elements. Common Extraction and Separation of Macroquantities of Plutonium and Uranium in the Purex Process," United States-Euratom Fast Reactor Exchange Program report EURFNR-888 (October 1970).
18. R. E. Burns, J. N. Hartley, D. H. Lester, F. P. Roberts, J. L. Swanson, and E. J. Wheelwright, "Technical and Economic Feasibility of Partitioning Hanford Purex Process Acid Waste," Battelle Northwest Laboratories report BNWL-1907 (May 1975).
19. W. Baehr and T. Dippel, "On the Dissolution of PuO₂-Containing Breeder Fuels in Nitric Acid for Aqueous Reprocessing by the Purex Method," Karlsruhe Laboratory report KFK-673, EUR-3704d (1967).
20. J. H. Goode, "Hot-Cell Dissolution of Highly Irradiated 20% PuO₂-80% UO₂ Fast Reactor Fuel Specimens," Oak Ridge National Laboratory report ORNL-3754 (October 1966).
21. W. E. Unger, "Aqueous Fuel Reprocessing Quarterly Report for Period Ending September 30, 1973," Oak Ridge National Laboratory report ORNL-TM-4394 (February 1974) pp. 13-20.
22. W. E. Unger, "Aqueous Fuel Reprocessing Quarterly Report for Period Ending December 31, 1973," Oak Ridge National Laboratory report ORNL-TM-4488 (June 1974) pp. 9-18.
23. R. K. Steunenberg, R. D. Pierce, and I. Johnson, "Status of the Salt Transport Process for Fast Breeder Reactor Fuels," Nucl. Metall. 15, 325 (1969).
24. D. C. Hampson, R. M. Fryer, and J. W. Rizzie, "Melt Refining of EBR-II Fuels," Nucl. Metall. 15, 57 (1969).

25. I. O. Winsch, R. D. Pierce, G. J. Bernstein, W. E. Miller, and L. Burris, Jr., "ERB-II Skull Reclamation Procedure," Nucl. Metall. 15, 297 (1969).
26. N. M. Levitz, E. L. Carls, D. Grosvenor, G. J. Vogel, and I. Knudsen, "Engineering-Scale Fluoride Volatility Studies on Plutonium-Bearing Fuel Materials," Nucl. Metall. 15, 211 (1969).
27. M. A. Thompson, R. S. Marshall, and R. L. Standifer, "Pilot Plant Experience on Volatile Fluoride Reprocessing of Plutonium," Nucl. Metall. 15, 163 (1969).
28. M. J. Steindler, L. J. Anastasia, L. E. Trevorow and A. A. Chilenskas, "Laboratory Development of Fluoride Volatility Process for Oxidic Nuclear Fuels," Nucl. Metall. 15, 177 (1969).
29. L. J. Mullins, Los Alamos Scientific Laboratory, personal communication, October 1975.
30. S. E. Khalafalla and G. W. Reimers, "Magneto-Gravimetric Separation of Nonmagnetic Solids," Trans. AIME 254, 193 (1973).
31. S. E. Khalafalla and G. W. Reimers, "Separating Nonferrous Metals in Incinerator Residue Using Magnetic Fluids," Sep. Sci. 8, 161 (1973).