CHEMICAL REPROCESSING OF NUCLEAR FUEL

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ABSTRACT

This paper describes the status of the present nuclear fuel reprocessing industry and comments on trends for the future. It also discusses the developmental work and plans for reprocessing of future reactor fuels. Improved technology is being applied not only to the main process but also to the containment of radioactive effluents. The Purex process is almost universally used for making the separations. For the light-water reactor (LWR) fuels, the chop-leach head-end has become the preferred method. For high-temperature, gas-cooled reactors (HTGRs), burning of the graphite fuel matrix appears to be the favored head-end step. This burning procedure presents a unique off-gas treatment problem which appears to be near solution. Certain differences inherent in liquid-metal fast breeder reactor (LMFBR) fuels make them more difficult to process. Because of their high content of valuable plutonium, a factor of 10 higher than that of light-water reactor fuel, there is a large economic incentive for processing at shorter decay times. This, coupled with the fact that LMFBR fuels will operate at higher power densities, 150 vs 35 kW/kg for LWR fuel, and to burnups of the order of 100,000 MWD/metric ton, creates a serious heating problem in handling the fuel. These same factors increase the amounts of volatile fission products, such as iodine, xenon, krypton, and tritium, which must be handled and contained in the plant. A comprehensive development program is being carried out in the United States of America to solve these and other problems associated with the processing of spent LMFBR fuels. Methods are being developed for the deactivation and removal of sodium. Handling techniques to provide reliable cooling of the spent fuel elements are also being developed. In the head-end, the fuel is chopped and the volatile fission products are removed by a new process, called voloxidation, which involves oxidation at 450°C. Dissolution and feed preparation for the high-plutonium-content, high-burnup fuel are also being studied. Other countries, notably France, Germany, and the USSR, have similar programs under way. In addition, France and the USSR are developing fluoride volatility processes for LMFBR fuels.

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The industry for chemical processing of spent nuclear power reactor fuels is still in its infancy. No power fuel reprocessing plant is being operated in the United States at present, and the multipurpose plants in France and England represent the major capacity in the Western world for processing such fuels. The industry is expected to grow dramatically during the next two decades in proportion to the expected worldwide growth of nuclear power.

In this paper, the Midwest Fuel Recovery Plant, owned and operated by the General Electric Company, is described as an example of a modern processing plant. This will be followed by a review of the forecasted growth of the reprocessing industry; methods for control of radioactive effluents; and, finally, management of radioactive wastes.

DESCRIPTION OF THE MIDWEST FUEL RECOVERY PLANT

The Midwest Fuel Recovery Plant¹ (MFRP) was designed for a nominal capacity of one metric ton of fuel per day. The process selected for the plant, called "Aquafluor," uses a combination of aqueous and fluoride volatility technology. In this discussion, an attempt will be made to delineate those operations which are unique to this particular plant.

Spent reactor fuel is shipped by rail or truck to the reprocessing site and unloaded into a storage basin. In the head-end section of the plant (see Fig. 1), fuel rods are withdrawn from the assemblies, singly or in groups, and extraneous hardware is removed by cutting with an abrasive saw. The fuel rods are then sheared to the desired length and fed to a continuous leacher for dissolution with nitric acid. Solid wastes from this operation (hulls, assembly scrap) are monitored and stored underwater in an underground vault. The leacher solution containing uranium, plutonium, and fission products is transferred to a "topping" tank, where fines are collected in a collar around the top of the tank while the clarified feed solution overflows to the main body. Following adjustment to chemical flowsheet conditions, the feed is transferred to the adjusted feed tank.

FIGURE 1. MIDWEST FUEL RECOVERY PLANT FLOW CHART.

MIDWEST FUEL RECOVERY PLANT FLOW CHART

Major decontamination of the plutonium, neptunium, and uranium from fission products and ionic contaminants is accomplished in a solvent extraction cycle that utilizes an extraction-scrub pulsed column and a strip column. Purex technology employing tributyl phosphate as an extractant and demineralized water as a stripping agent is used in this step. Scrubbing is accomplished with 3 M HNO_3 , and plutonium and neptunium valence adjustment is accomplished with reductants and oxidizing agents.

The stripped aqueous solution containing plutonium, neptunium, and uranium is then pumped to an adjustment tank, where the plutonium valence is adjusted to the 4+ state to permit its isolation by ion exchange. A continuous ion-exchange column with loading, scrubbing, and stripping zones is employed for plutonium purification and isolation. The uranium and neptunium quantitatively pass through this column for subsequent separation. The plutonium-bearing solution is then evaporated, sampled, and withdrawn from the system in the conventional manner.

Following valence adjustment of the neptunium, the uranium is separated from the neptunium in a second continuous ion-exchange column. This column contains the same zones as used in the plutonium column described above. The neptunium-containing solution is then evaporated, sampled, and withdrawn as product.

In contrast to most other present-day reprocessing plants, the final uranium purification is accomplished using fluoride volatility technology. Uranyl nitrate solution that has been partially decontaminated in the cycles described above is concentrated by evaporation and fed to the uranium purification system. This system employs a fluidized-bed calciner to convert the uranyl nitrate solution to UO_2 , which is then converted to uranium hexafluoride in a second fluidized-bed system. A mechanical conveyor is used to transfer the UO_2 from the calciner to the fluorinator, where it is converted to UF_6 by reaction with fluorine. Alumina powder is used as the fluidizing and heat transfer medium in the fluorinator. The gaseous UF_6 from the fluorinator is passed through a NaF sorption trap (at 400°C) to remove ruthenium and plutonium and is then collected in cold traps. After being drained from the cold traps, the UF_6 is vaporized, passed through a MgF_2 sorption trap for removal of technetium and neptunium, and finally passed through a distillation column to remove the remaining traces of high-boiling contaminants before it is loaded into product cylinders. Excellent decontamination from fission products and other impurities can be expected from this cycle, and the UF_6 product is compatible with requirements of existing uranium enrichment plants.

The MFRP incorporates several novel features for management of radioactive wastes. All radioactive wastes retained on-site are converted to solid form and stored belowground in concrete vaults. There are no facilities for long-term storage or direct burial of radioactive materials on-site. High-level aqueous wastes are calcined in a fluidized bed of alumina to produce a solid waste that is sealed in high-integrity steel containers and stored in a water-filled lined vault. Low-level wastes from the aqueous portion of the process are concentrated and stored in the form of a salt cake in a lined concrete vault. Dry chemical wastes resulting from the anhydrous processing operations and solid wastes of low activity (cladding, fuel assembly scrap, failed equipment, etc.) are stored similarly. Gaseous wastes from the process are scrubbed with caustic, passed through a silver reactor, filtered, and discharged through a stack.

Currently, the plant is undergoing shakedown testing, and individual pieces of plant equipment are being tested to establish reliability and operability. Following this testing phase, the overall plant will be checked using natural or depleted uranium. The plant operators have participated in an extensive training program, and written AEC licensing examinations have been given; oral examinations are expected to be administered in September. Barring unforeseen difficulties, the plant should commence hot operation by late 1973.

STATUS AND PROJECTED GROWTH OF THE POWER FUEL REPROCESSING INDUSTRY

Table 1 enumerates and indicates capacities of major power fuel reprocessing plants that are known to be presently operational or in an advanced stage of design or construction. All of these plants use the basic Purex process, and most use the mechanical chop-leach head-end. A number of smaller plants, which are really pilot plants, have not been included in this listing.

TABLE 1. MAJOR OPERATING AND PLANNED PLANTS FOR REPROCESSING OF POWER FUELS^a

Name	Location	Status	Approximate Capacity (tons/year)
Nuclear Fuel Services	West Valley, N.Y.	Inactive	300
Midwest (MFRP)	Morris, Ill.	1973 startup	300
Barnwell (BNFP)	Barnwell, S.C.	1975 startup	1500
Eurochemic	Mol, Belgium	Operating	100
Rhabha	Trombay, India	Operating	100
Tarapur	Tarapur, India	1973 startup	150
Kalpakkam	Kalpakkam, India	Late 1970s startup	300
Windscale	Seascale, U.K.	Operating	2200
La Hague	La Hague, France	Operating	1200
Marcoule	Marcoule, France	Operating	450
WAK	Karlsruhe, Fed. Rep. of Germany	Operating	40
EUREX-II	Rotondella, Italy	1975 startup	600
PNC	Takai-Mura, Japan	1975 startup	200

It is seen that most of the present capacity is contributed by the large multipurpose plants in France and England, which have been partially converted to the reprocessing of power fuels from systems for processing of military materials. The first moderately-large-capacity plant built entirely for reprocessing of power fuels, the Allied-Gulf Plant at Barnwell, South Carolina, is scheduled for operation in the United States in 1975. Most of the other plants currently in operation or under construction are considered primarily as prototypes of the larger plants that will be needed in the future.

Table 2 presents recent forecasts of the projected growth of nuclear power generating capacity and the associated requirements for reprocessing of spent fuels through the year 2000. These forecasts are the "most likely" estimates made by the Office of Planning and Analysis of the U.S. Atomic Energy Commission. The forecasted nuclear power capacity for

the United States assumes that commercial-scale recycle of plutonium to LWRs will begin in 1978 and that HRGRs and LMFBRs will be introduced in rapidly increasing numbers beginning in 1980 and 1986, respectively. The HTGRs and LMFBRs are expected to penetrate the worldwide power reactor market on approximately the same time scale as for the United States; however, significant numbers of natural-uranium-fueled and advanced gas-cooled reactors are forecasted to be built outside the United States.

TABLE 2. FORECASTS OF NUCLEAR POWER CAPACITY AND FUEL REPROCESSING PLANT LOADS^a

Year	Nuclear Power Generating Capacity [GW(e)]		Fuel Reprocessing Plant Load (tons/year)	
	U.S.	Worldwide ^a	U.S.	Worldwide ^a
1973	29	53	90	490
1975	54	100	810	1,600
1980	132	290	2,400	5,800
1985	280	640	5,500	14,000
1990	510	1200	10,000	28,000
1995	810	2100	16,000	48,000
2000	1200	3300	23,000	71,000

^aExcludes People's Republic of China.

The projected reprocessing loads were derived from the forecasted generating capacity on the basis of a seemingly realistic schedule of capacity factors, typical fuel exposure levels for the various types of reactors, and a typical postirradiation decay time of six to nine months. The forecasted reprocessing loads increase by more than a factor of 10 over the next seven years and by a factor of about 30 by 1985. These data indicate that the design of several new and large plants must begin within the next year or two if the projected reprocessing demands in 1980 are to be satisfied.

TREATMENT OF RADIOACTIVE EFFLUENTS

The presently available technology has been effective in limiting the radioactivity in effluents from fuel reprocessing plants to quantities that yield concentrations of radioactive contaminants at site boundaries well below levels that have been established by national and international agencies for continuous exposure of the public. Table 3 gives typical values for the input and discharge of significant radionuclides from a representative current-generation fuel-reprocessing plant, along with the calculated average annual exposure rate of an individual at the site boundary (0.8 km from the stack). An average whole-body dose rate of 0.8 mrem/year at the site boundary is estimated with a thyroid dose of 20.8 mrem/year. These values represent 0.16% and 1.4% of the International Commission on Radiological Protection's recommended maximum exposure to whole body and thyroid, respectively, for an individual in the general population. Krypton-85 contributes approximately 0.1 mrem/year to the whole-body dose and gives ~10 mrem/year exposure to the skin. Tritium contributes significantly to the whole-body dose at the site boundary.

TABLE 3. TYPICAL EXPOSURE RATE TO BE EXPECTED AT THE SITE BOUNDARY OF A 5-TON/DAY FUEL REPROCESSING PLANT

Nuclide	Limiting Organ	Concentration in Fuel (Ci/ton)	Plant Retention Factor	Discharge to Environment (Ci/year)	Average Annual Exposure Rate at Site Boundary (Mr/year) (% of RCG) ^a	
⁸⁵ Kr	Skin	11,000	1.0	1.6×10^7	10	0.33
³ H	Whole body	700	1.0	1×10^6	0.5	0.10
¹³¹ I	Thyroid	2	1000	3	15.0	1.0
¹²⁹ I	Thyroid	0.04	1000	0.06	5.0	0.33
⁹⁰ Sr	Bone	8×10^4	1×10^9	0.12	0.05	<0.01
^{134,137} Cs	Whole body	3×10^5	5×10^8	0.9	0.03	<0.01
Pu	Bone	2×10^5	1×10^9	0.3	0.15	0.03
Am-Cm	Bone	5×10^4	1×10^9	0.075	0.10	0.02
Total whole body		-	-	-	0.8	0.16
Total bone		-	-	-	1.1	0.22
Total thyroid		-	-	-	20.8	1.4

^aRCG - Radiation Concentration Guide.

The assumed retention factor of 1000 for ^{129}I as well as ^{131}I may be an order of magnitude more or less than that experienced by operating plants. In addition to the retention factor for iodine, other factors significantly affecting the thyroid exposure to individuals at the site boundary are the method of discharge and the land use in the vicinity of the plant site. As indicated in Table 3, all releases of radioactivity are well below accepted limits; thyroid exposure from iodine releases is probably the most significant.

The effects of krypton and tritium releases on the world population throughout the next few decades are expected to be minimal. It has been estimated that the total discharge of tritium and krypton from the projected nuclear power economy through the year 2000 will produce worldwide exposure rates equal to about 1% of the natural radiation background. The continuing research and development that is directed toward reduction of the discharge of radioactive materials from LWR fuel reprocessing plants is being performed primarily to determine the limits of practicality that may be employed in minimizing radiation exposures. For the case of the LMFBR fuel, the successful completion of this development work is necessary if the desirable reduction of cooling times to less than 180 days is to be realized.

OFF-GAS FLOWSHEET FOR IMPROVED FISSION PRODUCT CONTROL

In order to attain significant improvements in the retention of the volatile fission products, attention must be given to containment and to the reduction of gaseous and liquid effluent flow rates.⁴ Reduction of net effluent flows to 1% or less of current practice appears necessary for the practical operation of high-efficiency removal systems.

One approach to the control of the volatile fission products in a fuel reprocessing plant is shown schematically in Fig. 2. Tritium may be volatilized and trapped before the fuel is contacted with aqueous solutions in the dissolver, thus avoiding dilution of the tritium by the plant water inventory. This can be accomplished by heating the fuel, after shearing, in a small stream of oxygen. We have called this step "voloxidation." Krypton is released during shearing, voloxidation, and dissolution and can be recovered from the relatively small volume of off-gas. Most of the iodine remaining after voloxidation can be vaporized from the dissolver solution and recovered from the off-gas by the primary iodine removal system. This is desirable since it prevents the bulk of the iodine from contacting the solvent in the solvent extraction systems and thereby forming organic iodide complexes that are much more difficult to remove from gas streams than elemental iodine.

FIGURE 2. FUEL REPROCESSING PLANT-EFFLUENT CONTROL FLOWSHEET.

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FUEL REPROCESSING PLANT-EFFLUENT CONTROL FLOWSHEET

The primary iodine removal equipment on the dissolver off-gas stream should provide decontamination capabilities of the order of 10^3 so that the concentration of iodine in the effluent is less than that of the off-gas from downstream processing steps. The effluent from the primary system is combined with the off-gas from the remainder of the process equipment and cells and then passed through a secondary off-gas treatment system. Here the off-gas is treated for further removal of iodine as well as particulates and semivolatile components. For an advanced plant with a very high degree of fission product retention, most of the treated effluent from the secondary off-gas system would be recycled for process use, leaving a relatively small stream to be treated further before it is discharged to the environment. Liquid effluents are treated similarly; a major portion of the purified water is recycled to the process and a minimal stream is decontaminated further and collected as aqueous waste or evaporated and discharged up the stack.

Processes for controlling and removing each of the volatile fission products from process streams have been under development at the Oak Ridge National Laboratory for a number of years. Some of the more attractive systems applicable to the process steps illustrated in the flow-sheet (Fig. 2) are described in detail here.

SYSTEMS FOR CONTROLLING VOLATILE FISSION PRODUCTS

Iodine control systems

Overall containment of iodine in a reprocessing plant requires an understanding and control of iodine in each of the process steps as well as the ability to effectively remove iodine from liquid and gaseous effluent streams. This total control becomes increasingly important as retention factor requirements increase. The approach to iodine control illustrated in Fig. 2 includes volatilization of the bulk of the iodine from the dissolver solution and subsequent trapping of the iodine from the off-gas. All plant effluent streams, both liquid and gaseous, are treated further to remove trace quantities of iodine which escape or bypass the primary system. Several systems for evolving and trapping of iodine are in various stages of development.

Iodine evolution from aqueous streams. - In general, 98 to 99% of the iodine present in a typical dissolver solution can be volatilized by gas or steam stripping in the presence of excess NO_2 . Elimination of all condensation and reflux is essential. For reasons not completely understood, but most probably the presence of stable organic iodides, further removal of iodine activity is difficult, even if stable iodine carrier is added to restore the initial ($\sim 10^{-5} M$) iodine concentration. Various methods for promoting isotopic exchange between the added carrier and the residual activity are being investigated, and enhanced evolution of iodine (perhaps 99.9% removal) appears practical.

Off-gas scrubbing with concentrated nitric acid. - An aqueous scrubbing system employing nitric acid at concentrations in the range of 17 to 20 M is effective for removing both elemental iodine and organic iodides from gas streams. All iodine forms are oxidized to the 5+ valence state by the concentrated nitric acid and can be removed from the bottoms stream of an evaporator as dense I_2O_5 solids. Laboratory data indicate that iodine retention factors in excess of 10^4 are attainable in scrubbing equipment operating at normal liquid and gaseous throughputs. This system is particularly attractive for the primary iodine removal systems where kilogram quantities of iodine must be removed in a form suitable for permanent storage of the ^{131}I component. A flow-sheet for the concentrated-acid removal systems for iodine is shown in Fig. 3.

FIGURE 3. PRIMARY IODINE REMOVAL: IODEX.

Off-gas scrubbing with mercuric nitrate--nitric acid. -- With the addition of 0.2 to 0.4 *M* mercuric nitrate to nitric acid in the concentration range of 10 to 14 *M*, efficient scrubbing of both iodine and organic iodides can be obtained. The iodine is removed as mercuric iodate and can either be disposed of in this form or converted to sodium iodide and the mercury recycled to the scrub system. The mercuric nitrate scrub system has similar advantages and applications to the concentrated nitric acid system but is poisoned by small concentrations of aromatic compounds in the treated gas.

Solid sorbents for iodine removal from gas streams. -- Charcoal has long been used to effectively remove both elemental iodine and methyl iodide from clean, dry gas streams, but the application of charcoal beds to the removal of iodine from actual chemical processing plant off-gas streams has often proved ineffective due to the sensitivity of charcoal to poisoning by water vapor, trace organic vapors, and other contaminants.

One of the most attractive solid sorbents investigated for removal of iodine compounds from gas streams is Linde 13X Molecular Sieve which has been partially converted to silver zeolite. This material has a removal capability equal to, and possibly better than, charcoal for most iodine forms. In addition, it is noncombustible and appears to be less affected by organic contaminants in the off-gas stream. Methyl iodide decontamination factors approaching 10^4 can be obtained at gas velocities of 5 to 15 m/min for 5-cm-thick beds of silver zeolite. The most favorable operating temperature for silver zeolite beds is in the range of 100 to 200°C.

Although much superior to charcoal with respect to poisoning by water and organic vapors, other contaminants, specifically halides and sulfur compounds, quickly poison silver-containing beds if they are present in significant quantities.

PRIMARY IODINE REMOVAL
IODEX

Solid sorbents for iodine removal from aqueous streams. — The removal of iodine from aqueous streams is required in a plant before the water is discharged to the environment. Several macroreticular resins are effective for removing trace quantities of iodine from acid streams that have HNO_3 concentrations ranging from 0.01 to 4 M. Different resins must be used as the concentration varies from the low to the high side of this range. Charcoal is also effective for removing iodine from aqueous streams containing $<0.01 \text{ M HNO}_3$.

Evolution and removal of krypton-85

As was the case with tritium, a significant fraction of the krypton escapes from ruptured fuel rods during mechanical handling and disassembly, thus requiring removal of krypton from the mechanical handling cell off-gas. Krypton and xenon are volatilized during shearing and voloxidation to the extent of 30 to 90%; the remainder is evolved when the fuel is dissolved. Thus, as indicated in Fig. 2, the logical location for krypton removal equipment is on the combined off-gas streams from the dissolver and tritium removal equipment. Effective krypton removal can be accomplished at any point downstream of the dissolver, but effective and economic control of krypton depends on a relatively low off-gas flow rate.

A number of systems for removing krypton from off-gas streams have been demonstrated. Two of the most promising are: cryogenic absorption in liquid nitrogen followed by fractional distillation, and scrubbing with a fluorocarbon solvent. Based on results of work at Jülich and the Oak Ridge National Laboratory, scrubbing with liquid CO_2 also appears to be a promising process, particularly for treating the off-gas from the burning of HTGR fuels.

Cryogenic absorption in liquid nitrogen. — Absorption of krypton and xenon in liquid nitrogen, followed by fractional distillation to concentrate the krypton-xenon fraction, is an effective method for removing krypton from an off-gas stream and concentrating it for storage. This system, like cryogenic adsorption on charcoal, requires that the feed gas be purified of contaminants such as H_2O , O_2 , CO_2 , nitrogen oxides, and organics. A potential explosion hazard exists from the build-up of organic materials or radiation-produced ozone in the system. It is felt that these problems can be satisfactorily dealt with, and cryogenic distillation is considered to be one of the two most promising processes for krypton-xenon recovery. Such a system has been in operation for several years at the Idaho Chemical Processing Plant. Systems are presently being marketed commercially for removing krypton-xenon from reactor off-gas streams.

Selective absorption in fluorocarbons. — Absorption and separation of krypton from air streams by scrubbing with a fluorocarbon solvent has been demonstrated on a pilot-plant scale at the Oak Ridge Gaseous Diffusion Plant. This system operates in the temperature range of -50 to -5°C and thus avoids the potential hazards associated with operating at liquid nitrogen temperatures. The system is also less sensitive to contaminants such as organics, CO_2 , and nitrogen oxides. Water must be removed effectively, however, to prevent formation of ice in the system. This process system is shown schematically in Fig. 4.

FIGURE 4. KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM.

Absorption in liquid CO_2 . - Krypton can be absorbed in liquid CO_2 at -30°C and 20 atm pressure and effectively concentrated for storage. Such a system is under development at Karlsruhe and the Oak Ridge National Laboratory for removing krypton and xenon from the off-gases from burning graphite fuels. In this application, the primary constituent in the off-gas is CO_2 . Gas pretreatment is similar to that for the fluorocarbon scrub systems requiring water removal.

Tritium evolution and removal

One promising method for control of tritium in a fuel reprocessing plant depends on evolving the tritium from the fuel prior to dissolution and then effectively trapping the evolved tritium from a relatively small off-gas stream. The quantity of tritium escaping from failed fuel rods during mechanical handling and disassembly operations may be significant in comparison to tritium retention requirements and thus require the off-gas from the mechanical handling cell to be treated for tritium removal. Shearing of the fuel elements will most certainly release tritium in significant quantities and necessitate treatment of the shear off-gas.

The process step, voloxidation, in which the sheared fuel is heated in air to $\sim 450^\circ\text{C}$ for 2 to 4 hr, effectively volatilizes tritium from the fuel. Results of rather extensive laboratory and hot-cell experiments with the voloxidation systems show that the residual tritium is in the range of 0.1% of that produced in the fuel. If the combined off-gas from the mechanical handling cell, the shear, and the voloxidation step can be limited to a few tens of cfm, removal of tritium as tritiated water will become a straightforward process using common desiccants such as molecular sieves. A low off-gas flow rate is important because it reduces equipment size and complexity and serves to limit the volume of tritiated water that must be permanently stored. For example, the water content of a $0.3\text{-m}^3/\text{min}$ air stream saturated at 22°C is approximately 8 liters/day.

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KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
SCHEMATIC FLOW DIAGRAM

Virtually complete recycle of water within the plant may also provide a practical method for minimizing the release of tritium. For effective retention the ratio of the volume of plant water to its release rate must be large as compared to the mean life for radioactive decay of tritium of approximately 18 years. This may provide a preferred concept in future plants if very tight containment and nearly complete removal of tritiated water from off-gas streams can be proven to be practical.

WASTE MANAGEMENT

For nearly 20 years, emphasis on the management of nuclear fuel reprocessing wastes in the United States has centered on the development of processes for converting the high-level solvent extraction raffinates to stable solid forms and on demonstrations of the suitability of natural salt formations for permanent disposal of these solidified materials. In the course of this work, four waste solidification processes have been developed and tested successfully with high levels of radioactivity, and extensive laboratory and field demonstrations have tended to confirm the acceptability of salt as an appropriate repository. In 1970, the U.S. Atomic Energy Commission announced plans to establish a demonstration waste repository in a salt mine near Lyons, Kansas; however, subsequent investigations revealed geologic problems (attributable to man's recent activities there) which made that particular site less desirable. As a consequence, it has become necessary to institute a search for an alternate site in salt where further studies and demonstrations of its suitability can be performed on a pilot scale. Meantime, the U.S. Atomic Energy Commission has undertaken a rather detailed review of the waste management options that are available and has announced the intention to construct surface storage facilities for high-level solidified wastes to serve until a completely acceptable method for their permanent disposal can be fully demonstrated. The details and status of much of this work were reported at a recent symposium⁵ and will not be repeated here. Instead, some observations are presented with regard to the potential benefits to waste management to be derived from the separation of certain key constituents, and the results of recent projections of the reprocessing wastes to be generated in the United States over the remainder of this century are given.

The role of chemical separations

On the basis of the duration of the long-term hazard, there is potential merit in the use of separations processes that will greatly reduce the losses of uranium and plutonium to the high-level waste and, in addition, separate the high-level waste into fission product and actinide fractions. Although the required separations processes have not yet been developed, it appears that secondary treatment processes can be developed that will permit overall recovery of perhaps 99.999% of the uranium, 99.995% of the plutonium, 99.95% of the neptunium, and 99.9% of the americium and curium. Also, approximately 99.9% of the fission product iodine, containing the long-lived ¹²⁹I, will probably be separated, on the basis of its high relative volatility, from the high-level wastes during reprocessing.

Figure 5 illustrates the possible merits of these separations by comparing the hazard indexes* of the wastes from conventional processing of fuel from a typical light-water power reactor with those

*The hazard index is defined as the volume of water that could be contaminated to the Radiation Concentration Guide⁶ (RCG) value by one volume of waste or other radioactive material.

resulting from the postulated secondary treatment. For reference, the figure also shows the hazard indexes that may be associated with the mineral pitchblende and a uranium ore containing 0.2% U_3O_8 (which is typical of the large deposits that occur in the Colorado Plateau). The hazard index of the waste from conventional reprocessing decreases rapidly over the first 1000 years, due to the decay of ^{90}Sr and ^{137}Cs , but remains greater than that of pitchblende for periods exceeding one million years. The waste resulting from secondary treatment, however, has a hazard index that falls within the range of naturally occurring radioactive materials after only several hundred years, a time span for which it is possible to make reliable extrapolations of the effects of geologic, climatic, and other natural phenomena. It appears reasonable that this type of waste could be buried (and effectively diluted with nonradioactive species by a factor of 1000 or more) in natural geologic formations with negligible risk to the health and safety of future generations.

FIGURE 5. EFFECT OF AGE AND METHOD OF TREATMENT ON THE HAZARD INDEX OF HIGH-LEVEL WASTES FROM LWRs.

While the indicated separations of actinides and fission products appear to be feasible, it is apparent that a large development program would be required to reduce these concepts to practice. Separation processes that are used currently, which utilize solvent extraction and ion exchange for recovery of small quantities of certain valuable actinides (^{244}Cm , ^{252}Cf , etc.) from specially irradiated materials, have given americium, curium, and neptunium recoveries in the range of 90 to 99% and plutonium recoveries of about 99.5%. Since these processes were originally intended for recovery of the actinides and not for alleviation of the high-level waste problem, little or no effort was made to achieve higher recoveries or to regulate the amounts and types of chemical reagents for optimum waste handling.

In order to evaluate the practicality of such a waste management system, a comprehensive development program is needed to (1) solve problems that are obvious from past experience, (2) increase the removal of these actinides to the desired level, (3) determine the most

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WASTE FROM CONVENTIONAL REPROCESSING
ON THE ACTIVITY OF WASTE FROM LWR'S

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desirable method to integrate the needed process cycles into one overall system, (4) choose chemical processes and reagents that minimize high-level waste problems, and (5) determine the composition of intermediate-level waste streams that will be generated and subsequently find ways to recycle these streams.

As an adjunct to the waste management scheme that utilizes chemical separations, the iodine and actinides removed by secondary waste treatment conceivably could be recycled perpetually to the nuclear reactors that produce them for neutron-induced transmutation to other species. The waste resulting from long-term recycle has a slightly higher hazard index than the waste without recycle but is still well within the range of the hazard index of naturally occurring radioactive species (Fig. 5).

Studies have indicated that this type of transmutation of iodine and actinides is theoretically possible.⁷ With recycle to reactors, the ^{129}I could be transmuted at an acceptably high rate to a stable isotope of xenon, while the actinides would be transmuted to fission products. Preliminary estimates indicate that such recycling would not appreciably degrade the neutron economy of power reactors. It would, however, increase the cost of the nuclear fuel cycle by requiring the use of additional separations processes and heavily shielded and remote operation of the plants for fabricating fuel elements from the recycled material.

Projected accumulation of fuel reprocessing wastes

Projections of the radioactive wastes from fuel reprocessing are useful in the planning and design of methods and facilities that will be needed for their future management and for the assessment of potential environmental effects. To estimate the future magnitude of waste management operations, reprocessing flowsheets were constructed, assuming present and near-future technology; then, eight types of radioactive wastes were defined on the basis of their packaging, shipping, and possible disposal requirements. Annual rates of generation, shipments, and accumulations of each type of waste through the end of this century were based on a recent forecast of nuclear power in the United States,⁸ and on fuel mass-flow data developed for ^{235}U - and Pu-enriched LWRs, an HTGR, and two LMFBRs, using the systems analysis code ORSAC.⁹ Nuclear characteristics of the fuels and wastes were computed using ORIGEN.⁹

Our projections for the year 2000 are presented in Table 4, where the wastes are grouped into four major categories. The indicated possible dispositions are based principally on the duration of the containment that will be needed. These wastes that contain more than about 10 μCi of long-lived alpha (actinide element) activity per kilogram are more hazardous than naturally occurring deposits, and it is assumed they will be stored in salt mines.

High-level solidified wastes contain most of the fission products as well as significant amounts of actinide isotopes.

Alpha-beta-gamma wastes are distinguished from high-level wastes by lower heat-generation rates and reduced requirements for biological shielding. The fuel cladding may contain up to 0.1% of the actinides originally in the spent fuel.

Alpha solid wastes contain plutonium and other long-lived alpha emitters but have low thermal power and can be handled by direct contact after they are suitably packaged. Fuel preparation and fabrication plants will generate a volume of alpha wastes about ten times greater than is shown in Table 2 for reprocessing plants.

TABLE 4. FUEL REPROCESSING WASTES PROJECTED FOR THE YEAR 2000 IN THE UNITED STATES OF AMERICA

Category of Waste	Annual Generation		Annual Shipments	Accumulated		Possible Disposition
	Volume (m ³)	Activity (MCi)		Volume (m ³)	Activity (MCi)	
High-level solidified	1,300	16,000	260 ^{a, b}	13,300	151,000	Salt (600 hectares committed)
Alpha-beta-gamma						
Cladding hulls	1,980	1.4 ^c	540 ^{b, d}	21,200	35 ^c	Salt (50 hectares used)
Misc. solids	24,700	2.6 ^c	11,600 ^e	150,000	20 ^c	Salt (240 hectares used)
Alpha solids	8,300	8.8 ^c	300 ^b	83,300	49 ^c	Salt (11 hectares used)
Beta-gamma						
Tritiated solids	130	14	10 ^e	850	95	Salt (<1 hectare used)
Noble gas	59 ^f	210	180 ^{d, e}	710	1,700	Surface vaults (2800 m ³)
Iodine	<1	0.001	10 ^e	28	0.01	Salt
Misc. solids	48,300	0.01	3,600 ^e	500,000	0.09	Surface burial (140 hectares used)

^aShipped 10 years after reprocessing.

^bRail shipments are assumed.

^cActivity of only actinide elements is included.

^dShipped 1 year after reprocessing.

^eTruck shipments are assumed.

^fPressurized at 160 atm in 50-liter gas cylinders.

Beta-gamma wastes consist of concentrates of isotopes that will be generated in the decontamination of plant effluent streams prior to their recycle or release, plus miscellaneous solid refuse from plant operations. It is assumed that fission products tritium and iodine will be separated in concentrated forms and made into stable, solid materials suitable for long-term storage, whereas the noble gases will be packaged, shipped, and stored in gaseous form.

These projections portend a future waste management problem of impressive size and complexity; nevertheless, it is believed that the challenge can be successfully resolved if presently planned investigative programs and demonstrations are allowed to proceed without undue delay.

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