MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0145658 4

ORNL/TM-10226

ornl

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

Americium Product Solidification and Disposal

J. C. Mailen
D. O. Campbell
J. T. Bell
E. D. Collins

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-10226

Chemical Technology Division

AMERICIUM PRODUCT SOLIDIFICATION AND DISPOSAL*

J. C. Mailen
D. O. Campbell
J. T. Bell
E. D. Collins

Date of Issue — January 1987

*Research sponsored by Rockwell Hanford Operations,
Rockwell International Corporation

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under
Contract No. DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0145658 4

CONTENTS

	Page
EXECUTIVE SUMMARY	v
ABSTRACT	1
1. INTRODUCTION	1
2. CATION SORPTION AND CONCENTRATION	3
2.1 ORGANIC EXCHANGE RESINS	3
2.1.1 Past Studies	3
2.1.2 Discussion	6
2.1.3 Disposal	8
2.1.4 Waste Streams Created	8
3. INORGANIC EXCHANGERS	9
3.1 PRIOR STUDIES	9
3.2 DISCUSSION	11
3.2.1 Waste Streams	12
4. THERMAL DENITRATION	12
4.1 DENITRATION BY DOUBLE-SALT DECOMPOSITION	12
4.1.1 Prior Studies	12
4.1.2 Safety Considerations	14
4.1.3 Discussion	16
4.1.4 Waste Streams	16
4.2 DIRECT THERMAL DENITRATION WITHOUT NITRATE ADDITION	17
4.2.1 Prior Studies	17
4.2.2 Discussion	17
4.2.3 Waste Streams	18
4.3 MICROWAVE EVAPORATION AND DENITRATION	18
4.3.1 Prior Studies	18
4.3.2 Discussion	18
5. PRECIPITATION	19
5.1 OXALATE	19
5.1.1 Prior Studies	19
5.1.2 Discussion	19
5.1.3 Waste Streams	22
5.2 PEROXIDE	22
5.2.1 Prior Studies	22
5.3 HYDROXIDE	22
5.3.1 Prior Studies	22
5.3.2 Discussion	23
5.3.3 Waste Streams	23
5.4 FLUORIDE	25
5.4.1 Prior Studies	25
6. DISCUSSION	25
7. RECOMMENDATIONS	30
8. REQUIRED DEVELOPMENT	31
9. REFERENCES	31

EXECUTIVE SUMMARY

The americium product from the Transuranium Extraction (TRUEX) Processing Plant needs to be converted into a form suitable for ultimate disposal. An evaluation of the disposal based on (1) safety, (2) number of process steps, (3) demonstrated operability of the processes, (4) production of low-level alpha waste streams, and (5) simplicity of maintenance with low radiation exposures to personnel during maintenance has been made. Unfortunately, none of the possible processes is ideal for the americium product disposal. The following listing gives the evaluation of possible processes using these criteria, with the best processes having the lowest numerical values:

	Process	Safety	Steps	Operability	Waste acceptability	Maintenance	Aqueous waste
1.	Ion exchange	1	1	1	1	1	1
2.	Denitration (NH_4NO_3)	2	1	1	2	2	2
3.	Denitration (no NH_4NO_3)	1	1	2	2	3	2
4.	Oxalate precipitation	1	2	3	2	4	4
5.	Hydroxide precipitation	1	1	3	2	4	1
6.	Hydroxide precipitation (cross-flow filtration)	1	1	3	2	?	1

It is difficult to place weights on the criteria; but clearly, (1) safety, (2) operability, and (3) maintenance criteria are the most important (much required maintenance will result in significant personnel radiation exposure). The subjective conclusion of the authors is that cation exchange is the best of the currently available options. Clearly, cation exchange using inorganic ion exchange materials would be most desirable in order to eliminate safety questions in the use of the organic cation exchange resins; but inorganic exchangers with the ability to operate in acidic media are not commercially available. The potential hazards of using organic cation exchange resins are avoidable by (1) calcination or oxidation of the resins immediately after loading and (2) avoiding elution using strong nitric acid. The other options all have significant questions of operability in a glove box system largely due to the highly radioactive product and the possibility than hands-on maintenance could be necessary. The ion exchange and hydroxide precipitation options appear most likely to give a non-TRU waste — a primary objective of the process.

AMERICIUM PRODUCT SOLIDIFICATION AND DISPOSAL

J. C. Mailen, D. O. Campbell, J. T. Bell, and E. D. Collins

ABSTRACT

The americium product from the TRUEX processing plant needs to be converted into a form suitable for ultimate disposal. An evaluation of the disposal based on safety, number of process steps, demonstrated operability of the processes, production of low-level alpha waste streams, and simplicity of maintenance with low radiation exposures to personnel during maintenance, has been made. The best process is to load the americium on a cation exchange resin followed by calcination or oxidation of the resin after loading.

1. INTRODUCTION

The Transuranium Extraction (TRUEX) flowsheet contemplated for addition to the Plutonium Finishing Plant (PFP) will produce an americium product stream with the following approximate composition:

Component	(mg/L)	(mol/L)
Pu	0.017	7.0×10^{-8}
Am	3.5	1.4×10^{-5}
H^+		0.14
Zn	0.006	9.2×10^{-8}
Fe	50*	9.0×10^{-4}

*Iron content depends on how TRUEX operates; current plans are to increase the number of scrub stages from two to four (HORWITZ 1986). This will greatly decrease the iron content of the americium product stream.

The flow rate of the stream is 150 L/h, and the quantity of americium to be processed is ~12 g/d. The americium product stream is quite dilute which will decrease the efficiency of many of the possible methods for conversion of the product to a solid.

The goals of the PFP are (1) to concentrate the americium in a small volume suitable for disposal and (2) to produce an aqueous effluent which is not a Transuranium (TRU) waste.

Options for increasing the americium concentration of the product (prior to the final process which will give the solid product) are (1) evaporation (with discard of the condensate if it is a low-level waste), (2) loading on a cation exchange resin followed by elution, (3) precipitation followed by redissolution, and (4) a recycle flowsheet (BOND 1986). Evaporation or cation exchange and elution or precipitation and redissolution could increase the concentration to perhaps several grams of americium per liter and the recycle flowsheet would result in a concentration factor of about six. If evaporation or cation exchange and elution (using a strong-acid eluent) were used as a concentration step, the nitric acid content of the stream would be increased to fairly high levels (2 to ~6 M); the recycle flowsheet would result in a stream with the same nitric acid concentration of 0.15 M.

The americium in the product stream should be present as Am^{3+} ion. Although the form of the plutonium is unknown, it could be present as the Pu(IV) ion or as a hydrolyzed species with an unknown portion as polymer.

The solidification process for the americium product needs to be simple, compact, require low maintenance and be low in capital requirements. Also, the system should fit inside a glove box. Any process to be proposed should be either a demonstrated process or should be understood well enough to guarantee practicality. The product should be easily handled either due to the transfer characteristics of the product itself or by direct disposal of the product accumulation vessel. The product should also be compatible with the ultimate waste disposal requirements of the Waste Isolation Pilot Plant (WIPP). For this report, it is assumed that the product will be placed in a 55 gal drum in concrete and that the total quantity of americium in the drum will be ~100 g. Products which are powders exceeding 1 wt. % <10 μm or 15 wt. % <200 μm will need to be immobilized (WIPP specifications), possibly by blending into grout.

Candidate solidification processes to be examined in this report include (1) cation sorption and concentration; (2) thermal denitration

[direct thermal denitration], (3) addition of ammonium nitrate followed by thermal decomposition of the double salts, (4) direct denitration as used in the Consolidated Edison Uranium Solidification Project (CEUSP), (5) microwave evaporation and denitration; and (6) precipitation (oxalate, peroxide, hydroxide, fluoride, and scavenging precipitation).

Another option which should be considered is the transfer of the americium waste stream to one of the existing waste tanks; the low levels of americium and chemical constituents would not significantly change the nature of the existing alpha waste. However, it might be necessary to concentrate the waste to reduce the volume to be transported.

2. CATION SORPTION AND CONCENTRATION

2.1 ORGANIC EXCHANGE RESINS

2.1.1 Past Studies

The distribution coefficients of trivalent actinide and lanthanide elements between nitric acid (<4 M) and cation exchange resins are nearly the same (RYAN 1974). The expected distribution coefficient for Am(III), using the data (Fig. 1) for gadolinium, ytterbium, and erbium (STRELOW 1965), is $\sim 6 \times 10^3$ for Dowex 50W-X8 resin with a solution containing 0.15 M H^+.

Americium loads on 30 to 50 μm, size-classified cation exchange resin very rapidly giving a very sharp loading band (KNAUER 1986). This fact indicates that a resin bed will be loaded to nearly the equilibrium distribution value before major breakthrough occurs. Also, it is expected that loading on larger diameter macroreticular cation exchange resins would be rapid. If the latter is true, it would be possible to load an ion exchange bed to nearly the extent given by the equilibrium distribution coefficient.

The capacity of an ion exchange resin at equilibrium is given by:

$$W = (K_d)(V)(C)(d) \quad , \qquad (1)$$

ORNL DWG 86-854R2

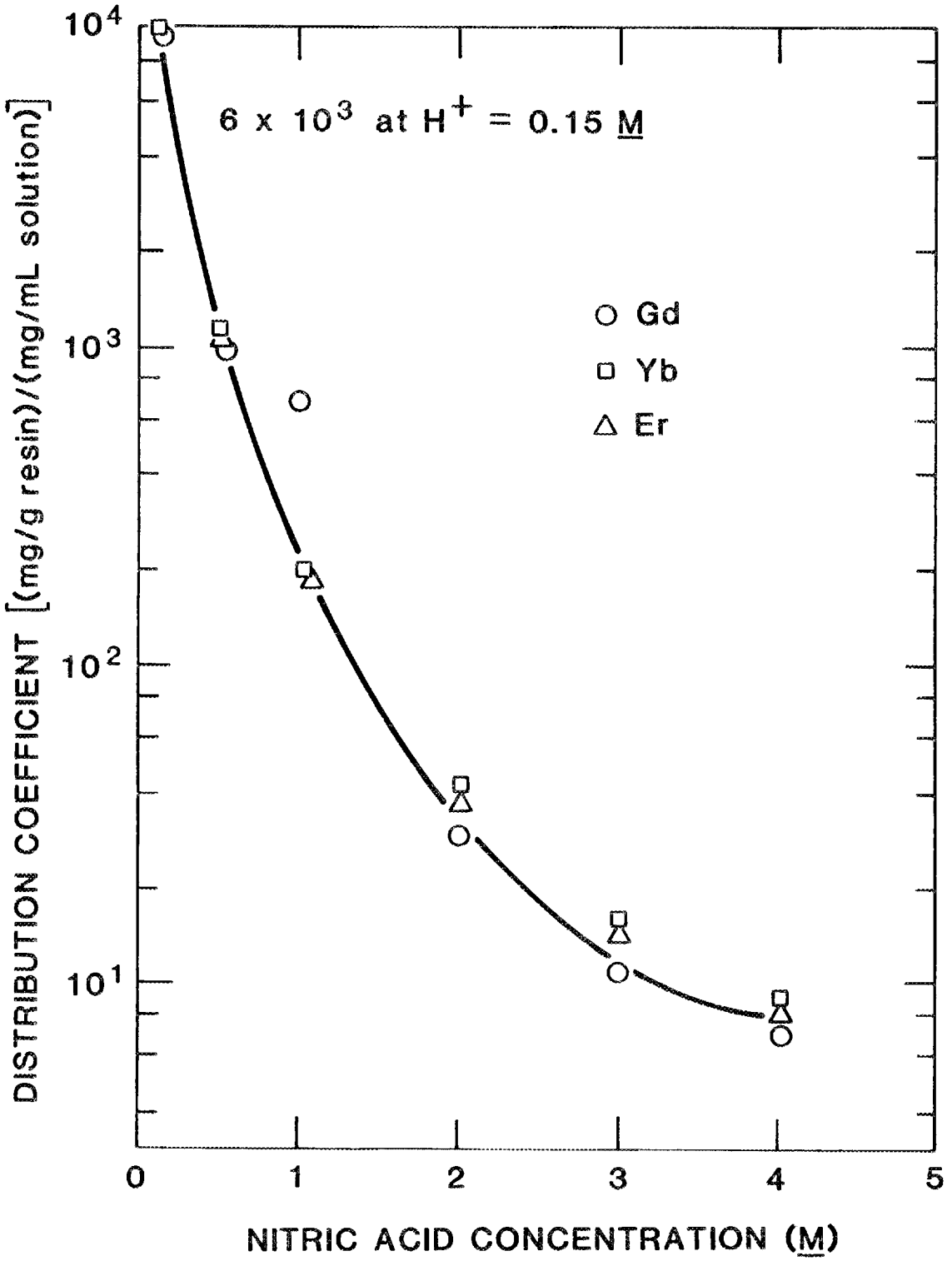

Fig. 1. Distribution coefficients of gadolinium, ytterbium, and erbium.

where W is the weight of americium adsorbed, (mg); K_d is the distribution coefficient, [(mg Am/g resin)/(mg Am/mL solution)]; V is the volume of the resin, (mL); C is the concentration of americium in the aqueous feed, (mg/mL); and d is the bulk density of the resin, (g/mL). A more readily used equation can be obtained by substituting the approximate density of the ion exchange resin (450 g/L) and conversion to more common units as follows:

$$W' = (Kd)(V')(C')(4.5 \times 10^{-4}) \ , \qquad (2)$$

where W' is the weight of americium adsorbed, (g); V' is the volume of the resin, (L); and C' is the concentration of americium in the aqueous feed, (mg/L).

At Hanford cation exchange and elution has been used to concentrate americium and plutonium from a dilute product stream (SCHULZ 1976). The feed to the process typically contained 0.1 to 1 mg/L each of Am and Pu, and the feed was diluted to 0.25 M HNO_3. The dilution factor was not given so it is assumed that it did not appreciably change the americium concentration. The distribution coefficient for americium under this condition is about 2.5×10^3 (Fig. 1). The exchange column contained 14 L of Dowex 50-X8 resin in the H^+ form in a column 15 cm in diameter and 80 cm tall. The column loaded 12 to 24 g of Am and Pu before being eluted. Using 2.5×10^3 (mg Am/g resin)/(mg Am/mL solution) as the distribution coefficient and a density of the resin of 450 g/L, the equilibrium capacity of the resin is given by:

$$W' = [1.125][V'][C'] \ . \qquad (3)$$

Thus, for solutions with americium concentrations of 0.1 to 1 mg/L, the capacities should range from 1.6 to 15.75 g of americium. The column loadings reported were as high as that predicted from these numbers; it is concluded that the columns were loaded to nearly saturation.

(WHEELWRIGHT 1980) discussed the purification and recovery of americium; as part of the system, the americium was loaded on Dowex 50-X8 cation exchange resin. It was loaded from 0.75 to 1.0 M HNO_3 onto 94 L of

resin in a column 21 cm ID and 270 cm long. The maximum loading reported was 13.8 g Am/L of resin, but the concentration of americium in the feed was not specified.

2.1.2 Discussion

The maximum capacity of the Dowex 50-X8 resin is stated to be 0.57 mol/L or ~137 g Am/L. The equilibrium content using the value of K_d of 6×10^3 would be:

$$W' = [2.7][V'][C'] \ . \tag{4}$$

For a concentration C' = 3.5 mg Am/L, this equation gives a capacity of 9.5 g/L of resin; for a concentration of 21 mg Am/L (by the recycle flowsheet), the capacity of the resin would be 57 g/L. If the lower concentration of americium is used (no recycle), 1 L of resin would be required per day since the quantity to be processed is ~12 g/d. If the higher concentration was used, a liter of resin would last about a week (the higher concentration would have to be examined to determine whether the heat or radiation would be excessive). The incentive for recycling to increase the concentration of the americium product stream does not appear to be large for this disposal method. Note that the iron in the feed would also load on the resin, unless present as Fe(II), which could use up a significant fraction of the resin capacity and thereby require more resin.

The applications for the use of organic exchange resins are shown schematically in Fig. 2. In the direct application, the resin is either burned or calcined. Ion exchange resins can also be eluted to generate concentrated feed streams for processes such as thermal denitration or precipitation.

In these applications, the americium would be loaded onto cation-exchange resin from a dilute nitric acid solution. No elution is necessary if the americium is not removed from the resin; thus no contact of the resin with strong nitric acid is necessary and any hazards of

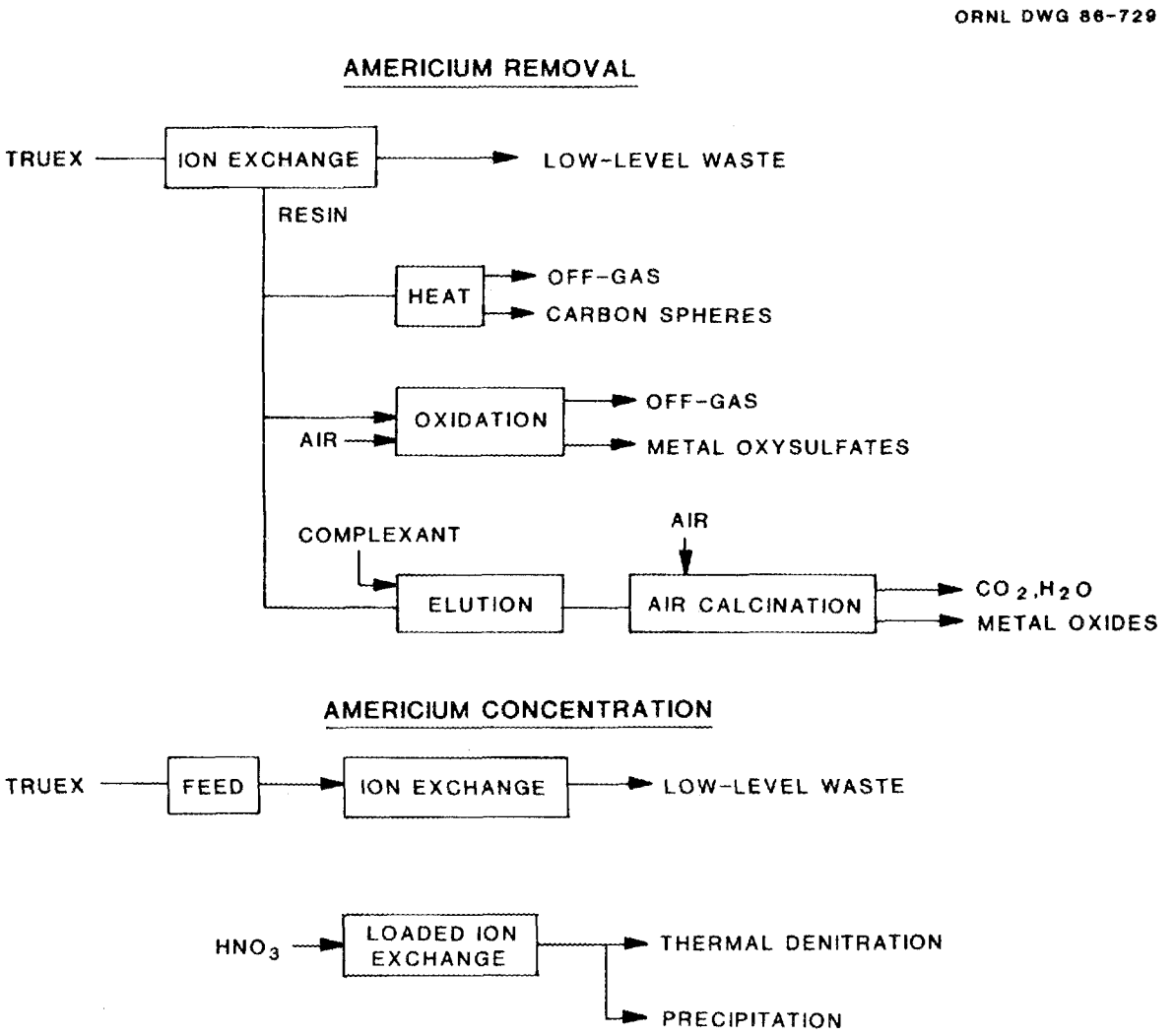

Fig. 2. Options using cation-exchange resin.

decomposition of the resin are avoided. There has never been a report of a safety hazard in systems restricted to cation-exchange resins (Dowex 50 type) and dilute nitric acid.

Schemes using ion exchange resins to concentrate the product streams for use in other solidification treatments would require the use of strong nitric acid or organic complexing agents for the elution. Strong nitric acid, as the eluent, could introduce some degree of safety hazard. It might be necessary to destroy the organic complexing agent before subsequent treatment of the concentrated americium stream.

Another option would be to load the cation exchange resin, elute the americium with an organic complexant, and evaporate and calcine the eluate in a pot calciner. The organic content could be oxidized yielding CO_2 and H_2O as the only products; no scrubber system would be required. This option is included in Fig. 2.

2.1.3 Disposal

The resin can be treated by burning to yield a granular solid (oxysulfate) containing the americium. This method is used at the Transuranium Processing Plant (TPP) for preparing americium and curium targets for the High Flux Isotope Reactor (HFIR). It can also be treated by calcination in an inert gas to yield free-flowing carbon spheres incorporating the americium. This method is said (BIGELOW 1986) to be prone to leaving a sticky organic residue which could decompose further by radiolysis. The ion-exchange resin could probably be burned in the bed container and the container discarded as waste.

2.1.4 Waste Streams Created

The off-gas from the calcination or burning step would have to be treated further due to the presence of organic compounds and SO_2. A secondary combustor plus a scrubber is one possibility, but the quantities involved would be small.

3. INORGANIC EXCHANGERS

3.1 PRIOR STUDIES

Inorganic cation exchangers which have possible application include synthetic zeolites (KANNO 1985). Zeolon 900 Na has K_ds for Eu and Tb of $\sim 10^5$ at pH values of 4 and 4.8, respectively. The K_d decreases fairly rapidly as pH decreases with the K_d for Eu falling to $\sim 3 \times 10^3$ at a pH of 3. The K_d decreases somewhat more slowly as the pH increases with the K_d for Eu falling to $\sim 10^4$ at a pH of 5 (Fig. 3). Calcining the zeolites at 1100 to 1200°C collapses the structure and results in a solid of low leachability (KANNO 1985).

(SCHULZ 1980) gives data on the sorption of americium on several solid sorbents. The titanate is stable in <0.01 M HNO_3, the zirconate in <0.5 M HNO_3 and the niobate in 0.5 M HNO_3. The distribution coefficients of americium to the inorganic adsorbents increase rapidly with increasing pH. To obtain a K_d of 6×10^3 would require pH values of 3.1, 5, and 2.7 for the titanate, zirconate, and niobate respectively. Americium was shown to have a K_d to sodium titanate from 0.6 M $NaNO_3$ of 1.1×10^4 (YING 1984). Material described as "loose granules" had a capacity of ~0.7 mmol/g; material described as "hard granules" had a capacity lower by a factor of 5 to 6. Tests with a column 1 cm in diameter, 11 cm in length, and a water flow rate of 6 to 7 bed volumes per hour for 440 h showed no problems with plugging (YING 1984). However, most materials of this type have low structural strength.

Zirconium phosphate has been tested for the sorption of americium at 75°C and pH 2 (HORWITZ 1966); the americium distribution coefficient was found to be $\sim 8 \times 10^3$. The capacities for neodymium were 0.2 and 0.12 mmol/g for PO_4/Zr ratios of 1.34 and 1.13, respectively; however, the exchange properties of zirconium phosphate for trivalent ions are said to be difficult to reproduce from batch to batch (MOISEEV 1981).

Granular, porous, high silica glasses which have been activated to produce ion exchange capability are being developed by the Vitreous State Laboratory of the Catholic University of America under the sponsorship of

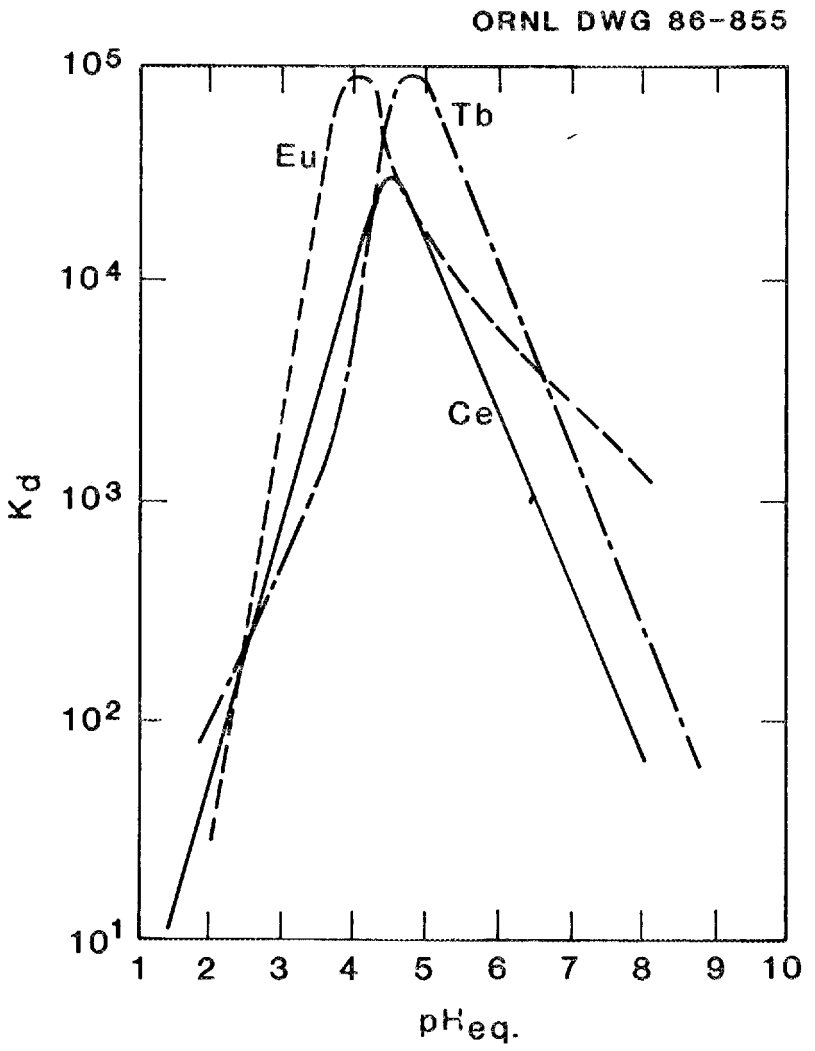

Fig. 3. Cation exchange properties of Zeolon 900 Na.

the National Patent Development Corp.; this technology is being marketed by Duratek Corp. Durasil 10 is said to be effective in the removal of a number of multivalent cations including Nd(III) and U(IV); no further details are given (MACEDO 1980).

New inorganic exchangers which show promise include stannic selenophosphate (NABI 1981) and cerium (IV) phosphosilicate (VARSHNEY 1981). These materials appear to be easy to make by methods similar to the preparation of silica gel. The capacities for mono- and di-valent cations are ~1 and ~0.7 mmol/g for the stannic selenophosphate and the ceric phosphosilicate, respectively. Both materials are stable in 1 to 2 M HNO_3, but distribution coefficients from 0.1 M HNO_3 are only ~100. With more dilute acid, the distribution coefficients increase to ~1000 in 0.01 M and to very high values from water. Cerium (IV) phosphosilicate prepared at ORNL (PRUETT 1986) contained a mixture of particle sizes from fairly fine particles up to particles of about 2 mm and the physical strength of this preparation is quite high. The capacities of the materials with various particle sizes have not yet been determined.

3.2 DISCUSSION

The efficient use of any of these inorganic ion exchangers would require adjustment of the pH of the americium product stream prior to loading on the exchanger. A minimum acceptable K_d would probably be ~1000 which would give a saturation loading of ~3.5 g americium per kg of sorbent.

The thermal and radiation stability of inorganic exchangers allows easy preparation of the bed for storage; the bed could be simply dried and then capped. They can be vitrified simply by heating, although the temperatures required may be high. Synthetic zeolites would need a temperature of ~1500°C for complete melting. One option would be to introduce additives to the bed after loading, which would lower the glass-forming temperature. A commercial technique has been demonstrated which produces a glass of material from zeolites by heating to 1050°C. This glass is said to be three orders of magnitude less leachable than the best

cements and it is equivalent to the leachability of borosilicate glass which is used for vitrification of high-level waste (SUTTER 1983).

The only commercially available inorganic ion exchange materials which could be used for americium removal are the synthetic zeolites and perhaps Durasil 10 or a similar synthetic glass. Adjustment of the pH to values desirable for the zeolite adsorbents (~3 to 5) would cause difficulties due to precipitation of the iron component of the americium product stream and interfere with its efficient collection by the zeolite. The precipitated iron would carry most of the americium (see Sect. 5.3.1). While some of the experimental inorganic cation exchangers can operate at pH values as low as 2, those materials are not commercially available and cannot be recommended without considerable development.

3.2.1 Waste Streams

No significant waste streams would be created by the use of the inorganic ion exchange materials.

4. THERMAL DENITRATION

Thermal denitration includes a variety of processes which convert the dilute americium solution into an oxide solid. Those to be discussed here are (1) denitration by double-salt decomposition, (2) direct thermal denitration, and (3) microwave evaporation and denitration. The first two methods are illustrated schematically in Fig. 4.

4.1 DENITRATION BY DOUBLE-SALT DECOMPOSITION

4.1.1 Prior Studies

Direct thermal denitration has been used for many years to produce oxides of uranium and plutonium. A mastic stage is produced which makes continuous operation difficult. The addition of ammonium nitrate to the solution to be denitrated forms double salts with the metal nitrates (HAAS 1982). The thermal decomposition of the double salts proceeds smoothly without a mastic stage and results in finely powdered oxides.

ORNL DWG 86-730

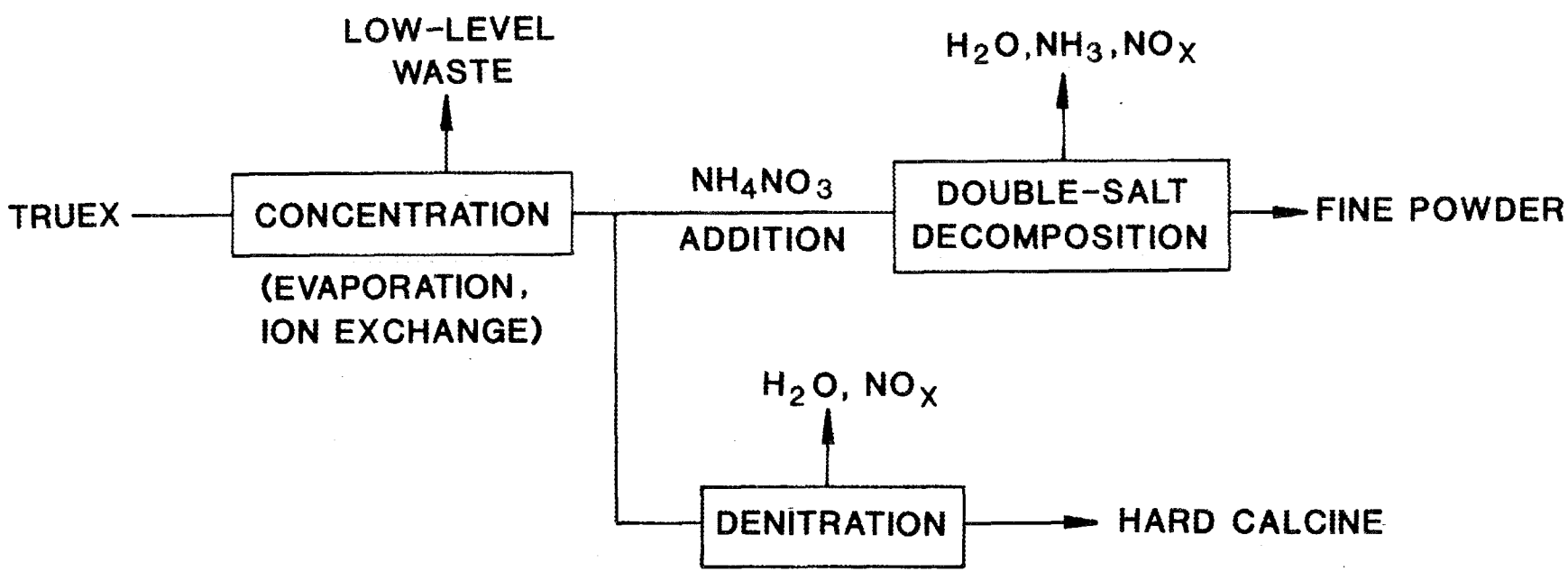

Fig. 4. Options for denitration.

The normal operation of the denitrator (ammonium nitrate present) is to feed the solution to a rotary calciner where the aqueous phase is flashed off and the ammonium nitrate complexes with the metal salts are thermally decomposed. The ammonium nitrate decomposes into (1) nitrogen oxides, (2) ammonia, and (3) water which are carried into a partial condenser by a countercurrent flow of air. The partial condenser acts as a scrubber to remove entrained dust and returns it to the rotary calciner. It is also possible to perform the denitration, as a batch or continuous operation, in a pot-calciner.

Thermal denitration of cerium nitrate using ammonium nitrate has been successfully tested in a pot calciner (HAAS 1982); americium is expected to behave similarly to Ce(III). Since the americium product stream will contain more iron than americium, the denitration behavior of iron nitrate would probably control the reactions; thermal decomposition of the double salt containing iron nitrate has not been examined.

Thermal denitration of a uranium-plutonium solution was tested in a small rotary calciner (Fig. 5) in a glove box (MAILEN 1982). That system produced about 15 g of product per hour. The powder produced was relatively difficult to transfer due to poor flowability.

4.1.2 Safety Considerations

The decomposition of ammonium nitrate within the calciner cannot result in an explosion if the gas phase is continuously swept from the decomposition vessel. Studies of the explosive decomposition of ammonium nitrate show that the explosion is initiated by a detonation of the gas phase consisting of a reaction of NH_3 with NO_2. If the system is confined and a pressure of 0.6 MPa (6 atm) or greater is generated by this gas phase explosion, the solid ammonium nitrate can explode. This information is summarized in (MELLOR 1964). Although the bulk of the ammonium nitrate is decomposed to yield N_2O, an innocuous gas, a small amount of ammonia is formed. This situation could lead to complications due to an accumulation of ammonium nitrate in off gas lines or in aqueous waste streams.

ORNL-PHOTO 4330-80

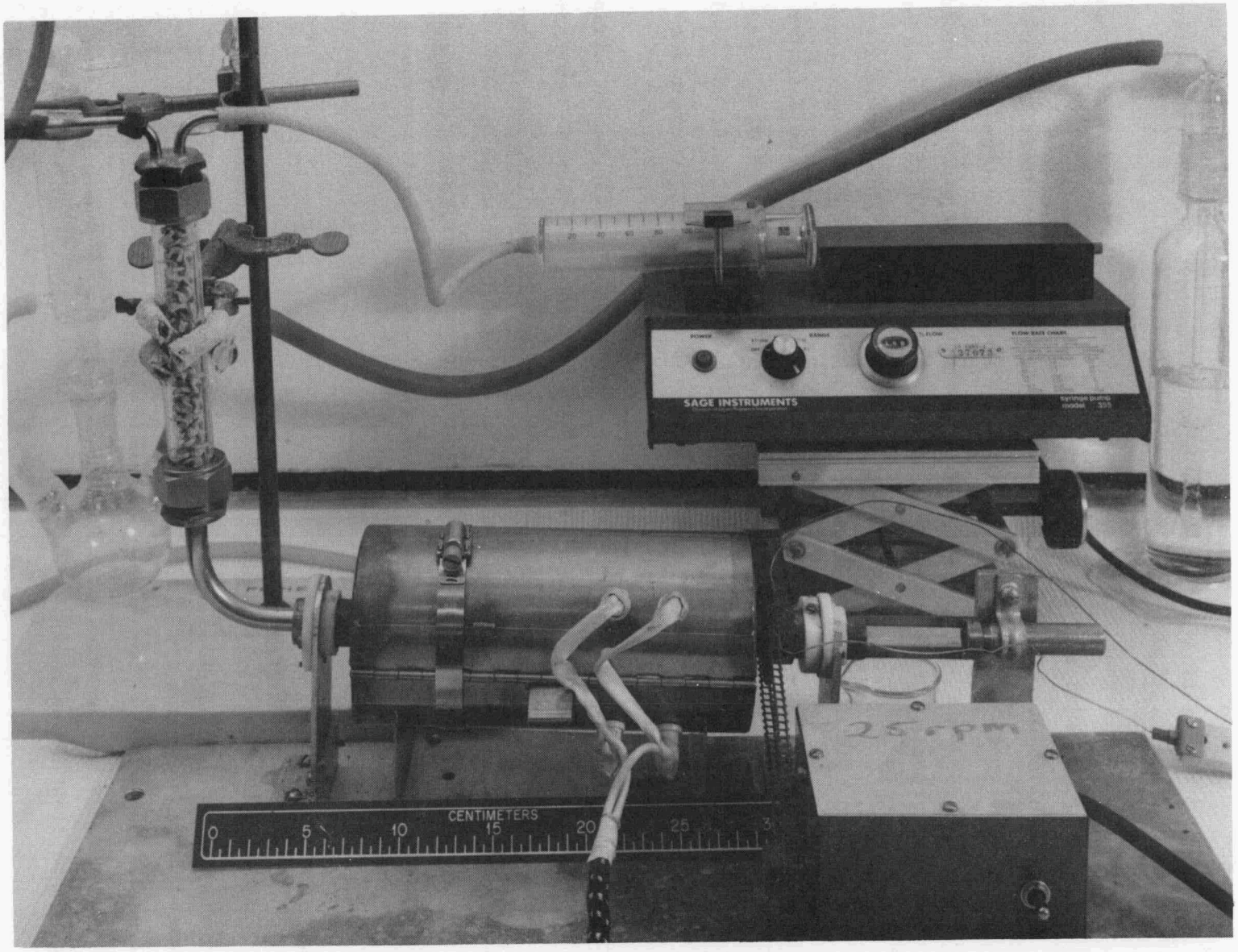

Fig. 5. Miniature rotary calciner and off-gas system.

4.1.3 Discussion

The americium product stream is probably much too dilute for any of the thermal denitration processes to be used directly. A preevaporation would greatly decrease the size of the equipment required within the glove box. An alternative concentration method would use cation exchange and elution to produce the feed to the denitrator; this method would require elution of the americium from the resin with moderately concentrated nitric acid or an organic complexing agent. [If an organic complexing agent is used for elution, the solution to be decomposed would no longer contain significant nitrate and the solids could be oxidized or added directly to grout (if the organic complexant is acceptable in the waste).] Most studies of denitration have used near-saturated solutions to minimize the amount of heat required for evaporation and the quantity of off-gas to be handled in the denitrator. Large quantities of off-gas would be expected to increase the problems of powder entrainment and would require a large and carefully operated partial condenser to recover the entrained powder. A concentration factor of 10^4 would be required to attain the americium plus iron concentrations equivalent to concentrations commonly used in thermal denitration. The equipment for thermal denitration could be quite simple except for the problems of handling the evaporated water. A pot calciner in which the powder product would be accumulated, followed by discard of the entire pot calciner would appear to be the best approach since this would eliminate handling the powder product.

4.1.4 Waste Streams

Preevaporation of the americium product stream would generate a condensate waste stream; with care, this condensate can be a low-alpha waste. The off-gases from the calciner would include nitrogen oxides, ammonia, and water. That stream could be condensed and should also be a low-alpha waste. Recycle possibilities should consider the disposal or decomposition of the ammonium nitrate.

4.2 DIRECT THERMAL DENITRATION WITHOUT AMMONIUM NITRATE ADDITION

4.2.1 Prior Studies

The Consolidated Edison Uranium Solidification Project (CEUSP) (WYMER 1985) has successfully converted ~1000 kg of uranium (containing ^{233}U) to a solid product using thermal denitration methods. The starting solutions contained cadmium and gadolinium as neutron poisons. In that process, the solution was evaporated using formaldehyde for excess HNO_3 destruction and then it was denitrated to produce a final solution which had a uranium concentration of 340 g/L and a free acid concentration of ~0.1 M HNO_3. This concentrated solution was then dripped onto a heated surface in the storage can, thereby evaporating the liquid, decomposing the nitrate, driving off the vapors and gases, and leaving the residual oxide solid. A temperature profile from 300 to 800°C was used which assured that the can was filled without major voids. The solidification cans were used as the final storage vessels. Formic acid or sugar, rather than formaldehyde, are currently recommended for the denitration step (McGINNIS 1986).

4.2.2 Discussion

The "pot calcination" approach appears to be more straightforward than the thermal denitration process using ammonium nitrate. It eliminates the potential hazards of the use of ammonium nitrate and has been well demonstrated. The acid destruction step in CEUSP was necessary to prevent precipitation of metal salts which would be caused by the high nitrate levels. Acid destruction is a relatively difficult operation and would not be recommended for treatment of the americium product stream. It is likely that iron nitrate would not precipitate during the concentration step. Ferric nitrate nonahydrate has a melting point of 47.2°C and a density of 1.684. These facts indicate a solubility of ferric nitrate (expressed as the unhydrated nitrate salt) of ~1000 g/L, which is probably high enough to prevent precipitation at the concentrations required for efficient denitration. The cadmium content of the CEUSP feed was found to be beneficial in the solidification step because it created a foam layer

which alleviated spattering of the uranyl nitrate during thermal decomposition. The CEUSP type of operation contains significant operational questions and would need demonstration for use with the americium stream. Personnel are currently available in the ORNL Chemical Technology Pilot Plant Section who are knowledgeable in the design of this type of equipment (McGINNIS 1986). A preevaporation step or other concentration steps should be performed to decrease the size of the glove box equipment. A concentration factor of $\sim 10^4$ would be required to attain the americium plus iron concentrations equivalent to concentrations commonly used in thermal denitration. As discussed earlier, the major component in the americium product stream is likely to be the iron.

4.2.3 Waste Streams

The feed concentration portion of this system would generate a liquid condensate stream (or the effluent from an ion-exchange concentration system), which probably could be discarded or recycled to the process if necessary. The stream would probably be a low-level alpha waste. Off-gas streams would contain NO_x, H_2O, and CO_2.

4.3 MICROWAVE EVAPORATION AND DENITRATION

4.3.1 Prior Studies

The Japanese (JAPAN 1979, 1982a, 1982b) have developed a method using microwaves to denitrate uranium and plutonium nitrates. Kilograms of product have been produced, and the resultant powders are said to be suitable for pellet fabrication. The system uses solutions containing ~250 g/L of heavy metals in 4 M HNO_3. The microwave powers used are 8, 12, and 16 kW for a batch of 7 L of solution.

4.3.2 Discussion

This process cannot currently be recommended for conversion of the americium process stream. This method is relatively unknown and much more development would be required along with more glove-box space than simpler thermal methods. If thermal denitration methods are to be pursued, it

could be useful to obtain further information about microwave methods. It appears that other countries (besides Japan) are seriously examining the process.

5. PRECIPITATION

5.1 OXALATE

5.1.1 Prior Studies

The solubility of americium oxalate in nitric acid has been measured (BURNEY 1967) and a portion of these data are reproduced in Fig. 6. The minimum solubility in low acid occurs at about 0.08 M free oxalic acid and this minimum for 0.15 M nitric acid is ~1 mg Am/L.

5.1.2 Discussion

Precipitation of americium oxalate from the americium product stream containing 3 mg Am/L, without adding a carrier, is unattractive. About one-third of the americium would be soluble and the precipitate would likely be so fine that entrainment would be a significant problem. The recycle system would greatly increase the fraction of the americium in the precipitate. Even then, precipitation would require handling a very fine precipitate; [Pu(III) gives a fine oxalate precipitate (LERCH 1984)]. If a major concentration of the americium product stream was made, direct oxalate precipitation would be much more attractive. Another option would be to collect the unprecipitated americium in the effluent from the precipitation on a small ion-exchange column for periodic recycle to the precipitator. Iron (present as oxalate complexes) would not load on the ion-exchange resin and would go to low level waste. The above options are illustrated in Fig. 7.

Another approach to the precipitation of americium oxalate would be to add another cation such as cerium or calcium, then coprecipitate the mixture. It has been shown that micro concentrations of Am(III) coprecipitate quantitatively with lanthanum and calcium (SCHULZ 1976). Precipitation with a carrier would require demonstration to determine completeness

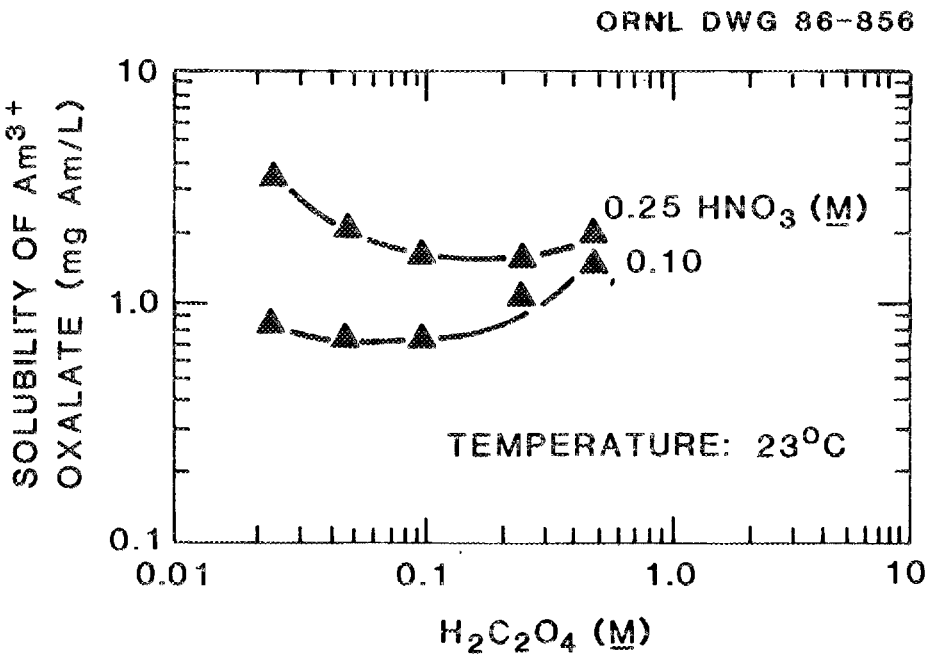

Fig. 6. Solubility of Am(III) oxalate.

ORNL DWG 86-732

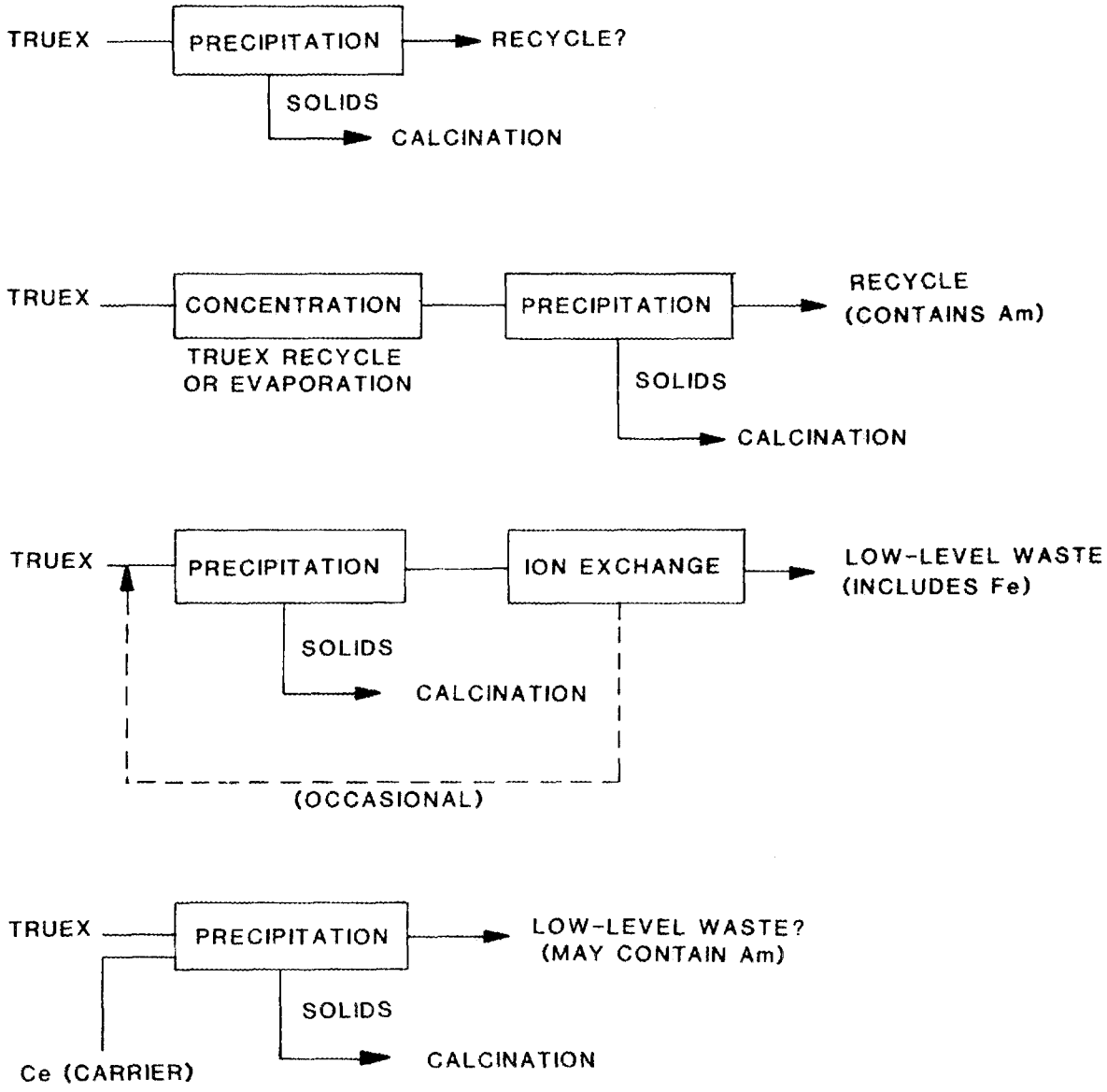

Fig. 7. Oxalate precipitation options.

of americium removal and characteristics of the precipitate. This option is also illustrated in Fig. 7.

5.1.3 Waste Streams

Phil Horwitz has stated that the supernate from an oxalate precipitation can be readily recycled to the TRUEX process, but whether the recycle of this large a volume of solution is practical or desirable should be examined. Any remaining oxalate would be beneficial to the process (HORWITZ 1986).

5.2 PEROXIDE

5.2.1 Prior Studies

Americium precipitation as the peroxide is not practical due to the large solubility of americium in peroxide solution. In fact, plutonium is often separated from americium by precipitation of plutonium peroxide. Additionally, the Fe (present in the Am product stream) is a catalyst for the decomposition of peroxide, and could lead to explosive decomposition of dry peroxides.

5.3 HYDROXIDE

5.3.1 Prior Studies

Americium hydroxide precipitation has been used to recover americium at the Rocky Flats Plant. However, the precipitate formed when KOH is added to a solution is rather difficult to filter. A better, more crystalline precipitate can be obtained by a method based on slow decomposition of urea which releases hydroxyl ions slowly (SCHULZ 1976b).

A promising more recent development (GUTMAN 1986) produces an ultrafine precipitate which adsorbs the impurities from the solution. The precipitate is then concentrated in a slurry by an ultrafiltration membrane and cross-flow filtration. In this technique, the solution and precipitate are passed, in turbulent flow, through an array of hollow tubular membrane elements. The clarified solution passes through the membrane, and the solids are kept in suspension and do not clog the membrane because

of the turbulent flow. Membrane tubes are available in various ceramics, carbon, and stainless steel. Of particular interest is the reported use of ferric hydroxide as the scavenging precipitate; the americium stream could be ideally suited for such a technique. The addition of titanium salts to the solution prior to precipitation is reported to improve the removal of actinides and presumably of americium (CAMPBELL 1986). The solids could then be separated from the concentrated slurry by any standard method such as settling, centrifugation, or filtration (if desired), or mixed directly with grout. These options are illustrated in Fig. 8.

5.3.2 Discussion

The solubility of trivalent actinide hydroxides has been estimated (ALLARD 1982) as a function of pH. The minimum solubility occurs at a pH of ~10 and is ~0.02 μM. Since the initial concentration of americium is ~14 μM, this indicates that >99.8% of the americium can be precipitated as the hydroxide. Addition of a carrier, such as cerium, to yield more material would be possible, but probably not necessary. Coprecipitation of the iron content of the americium product stream would probably be equally effective. Recovery of the precipitate for storage would need consideration. One alternative, cross-flow filtration, has been demonstrated for concentrating radioactive slurries at a pilot scale (Ryan 1986).

The scavenging precipitation with cross-flow filtration described above appears to have the advantage of yielding a concentrated slurry which should be easier to handle than the dilute slurry which would be generated by simple hydroxide precipitation. This slurry would be suitable for direct mixing with grout ingredients and casting into suitable disposal containers. Alternatively, the slurry could also be evaporated to give a dry product.

5.3.3 Waste Streams

A disadvantage of this treatment is the generation of additional salt waste. The scavenging precipitation with cross-flow filtration

ORNL DWG 86-731

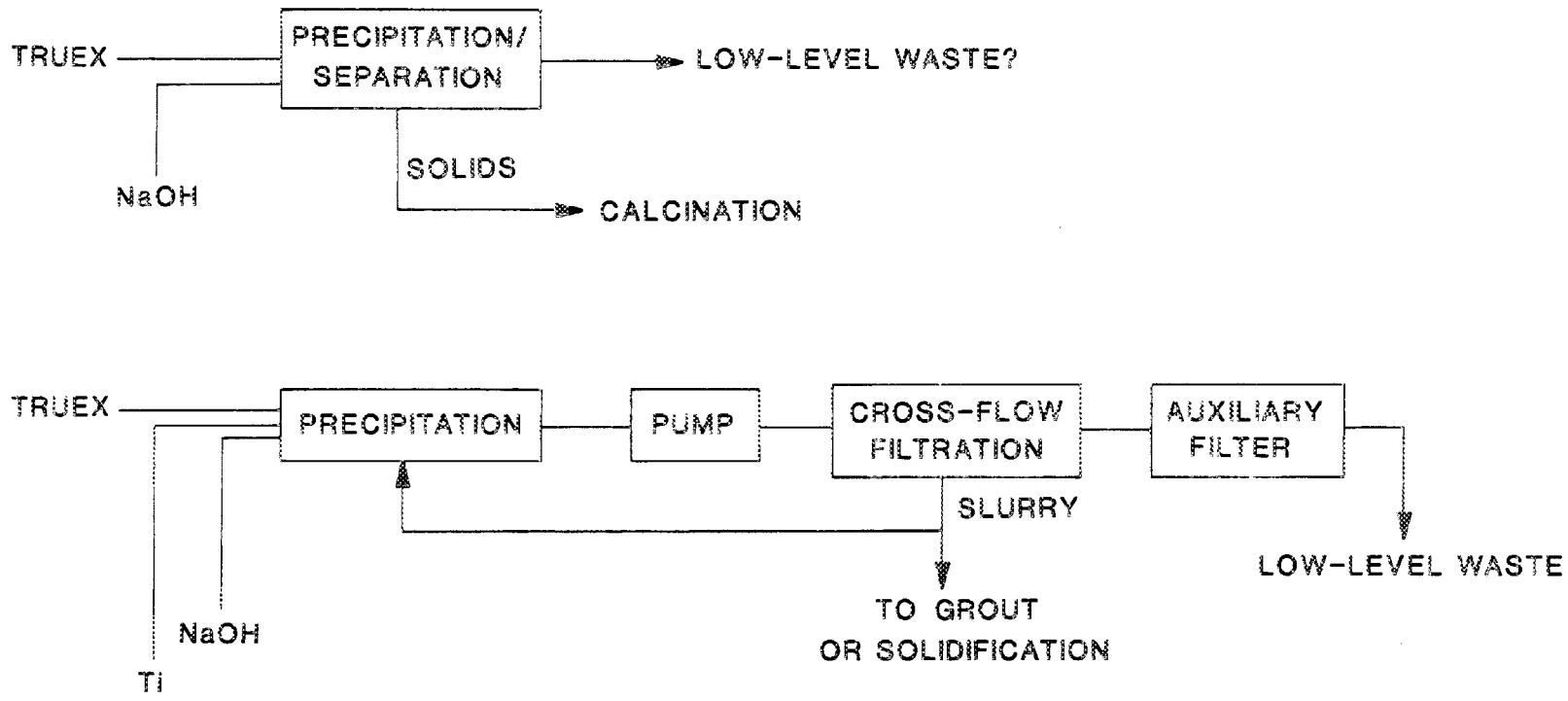

Fig. 8. Hydroxide precipitation options.

method would need testing to determine whether the quantity of americium in the filtrate would be high enough to classify the stream as an alpha waste. An additional filtration treatment could be used to further reduce the alpha content of the waste stream.

5.4 FLUORIDE

5.4.1 Prior Studies

Precipitation of americium fluoride has been used to recover americium from acid solutions (SCHULZ 1976c). The problems of introduction of fluoride into the process plant should eliminate this method from consideration.

6. DISCUSSION

The americium product from the TRUEX processing plant needs to be converted into a form suitable for ultimate disposal. An evaluation of the disposal based on (1) safety, (2) number of process steps, (3) demonstrated operability of the processes, (4) production of low-level waste streams, and (5) simplicity of maintenance with low radiation exposures to personnel during maintenance has been made. Unfortunately, none of the possible processes is ideal for the americium product disposal. The following listing gives an evaluation of the possible processes, using these criteria, with the best processes having the lowest numerical values:

Process	Safety	Steps	Operability	Waste acceptability	Maintenance	Aqueous waste
Ion exchange	1	1	1	1	1	1
Denitration (NH_4NO_3)	2	1	1	2	2	2
Denitration (no NH_4NO_3)	1	1	2	2	3	2
Oxalate precipitation	1	2	3	2	4	4
Hydroxide precipitation	1	1	3	2	4	1
Hydroxide precipitation (cross-flow filtration)	1	1	3	2	?	1

The pertinent aspects of each process in regard to the listed criteria are as follows:

Ion Exchange:

1. Acceptability - Organic cation exchange resin should be acceptable for loading americium from dilute nitric acid. The resin should be burned or calcined immediately after loading.

2. Precautions - The americium should not be allowed to remain on the resin for an extended period of time and should not be eluted using strong nitric acid.

3. Advantages - The americium can be effectively loaded from the dilute americium product stream without prior concentration or adjustment of the acidity of the stream. The equipment is very compact and simple to operate. Both the loading and calcination or oxidation of cation exchange resin loaded with trivalent actinides has been demonstrated at the Transuranium Processing Plant at Oak Ridge. If calcined, the waste would be particulate and large enough in particle size for direct shipment to the Waste Isolation Processing Plant (WIPP). If

oxidized, the waste would be granular and might need to be immobilized by addition of grout, etc. No potential for ion exchange bed plugging should exist. Both the calcined and oxidized products are granular and should not create any dust problems. No other requirements for nonroutine maintenance are apparent. The aqueous waste from the process should be non-TRU.

4. Disadvantages - Product must be calcined or burned before it can be sent to WIPP; burned resin may require immobilization depending on the size distribution of the granular product.

Denitration with NH_4NO_3:

1. Acceptability - Denitration aided by the formation of ammonium nitrate complexes is acceptable if it can be guaranteed that the decomposition off-gas will not be confined since that can lead to explosive reactions. Possible accumulation of small amounts of ammonium nitrate from the process should be examined.

2. Precautions - The decomposition gas should be swept out of the decomposition vessel continuously.

3. Advantages - Direct conversion of nitrate solution to a powdered oxide product.

4. Disadvantages - There are problems in handling ammonium nitrate and its decomposition gases. Also, small amounts of ammonium nitrate will be formed in the off-gas steam. Concentration of the americium product stream would be required. A powder is generated which must be immobilized before shipment to WIPP. The method has not been tested with an iron-americium feed. Since the product is a fine powder, it is possible that nonroutine maintenance could include periodic cleanup of dust; this procedure could result in excessive personnel exposure to radiation. Complete removal of the entrained powder from the off gas may be difficult which could result in a TRU aqueous waste.

Denitration without NH_4NO_3:

1. Acceptability - Direct denitration is acceptable, but it has not been demonstrated with iron-americium feed and could be difficult to operate.

2. Precautions - None.

3. Advantages - There is direct conversion of nitrate solution to a sintered product, and the sintered product may be suitable for direct shipment to WIPP. No particular hazards can be seen.

4. Disadvantages - This method requires preconcentration of the americium product stream which may have spattering problems. The possible spattering problems could result in requirements for nonroutine cleanup of spattered material which could result in personnel exposure. Complete removal of entrained powder from the off gas may be difficult possibly resulting in a TRU aqueous waste.

Oxalate precipitation:

1. Acceptability - This method may not be acceptable due to incomplete removal of americium (americium oxalate is relatively soluble), and adequate removal by scavenging precipitation must be demonstrated.

2. Precautions - None.

3. Advantages - This is well-developed technology which may not require preconcentration of the americium product stream.

4. Disadvantages - The scavenging precipitation is not tested, and production of a non-alpha aqueous waste is not guaranteed. There will likely be a requirement for a secondary effluent treatment (polishing step) for removal of the last traces of americium. The powdered product will require immobilization, and filtration will be required. Also, significant development will be required. The powdered product could result in a need for nonroutine powder cleanup and hence personnel exposure. The filtration step could result in non-routine maintenance and personnel exposure.

Hydroxide precipitation:

1. Acceptability - The method may be acceptable if the precipitate can be handled, but many hydroxide precipitates are gelatinous and difficult to filter.

2. Precautions - None.

3. Advantages - The iron hydroxide will act as a carrier for the americium hydroxide and should result in complete removal of the americium; the waste should be non-alpha if all precipitate can be removed. The solubility of americium hydroxide is very low; a non-TRU aqueous waste should be possible.

4. Disadvantages - The handling properties of a hydroxide precipitate are not established. Filtration, perhaps of a gelatinous precipitate, will be required, and the calcined precipitate may require immobilization. Therefore, significant development will be required. The filtration step could result in nonroutine maintenance and consequently personnel exposure.

Hydroxide precipitation with cross-flow filtration:

1. Acceptability - This method probably requires too much development and is too complex for this use.

2. Precautions - None.

3. Advantages - This procedure reduces the difficulties of handling fine precipitates; it also results in better removal of americium by adsorption on fine iron hydroxide (iron already present in the americium product stream).

4. Disadvantages - Development is required, and it is probably too complex for this use. It requires a recirculating system (to the cross-flow filter) with high flow rates and some pressurization. This complex system is prone to requirements for nonroutine maintenance and personnel exposure.

7. RECOMMENDATIONS

The above characteristics of the various promising systems indicate that no one system is without drawbacks. The only system which is known to be readily operable in a glove box is the one using cation exchange resin. This system would not be prone to significant problems during normal operations. Restriction of the cation-exchange resin to (1) loading from dilute nitric acid followed by (2) calcination or oxidation will eliminate explosion hazards. Most other systems could conceivably result in plugging of filters or other difficulties which would require significant maintenance which would be difficult to accomplish without gamma radiation personnel exposures due to the large quantities of americium involved. The simplicity of the cation exchange system and its advanced state of development make it the most desirable system we have considered. The best option using cation exchange resin would stabilize the product by calcination or oxidation of the resin.

Choosing a second choice from among the other options is difficult due to the significant potential problems. Other feasible options which require two or more process steps and sets of equipment (a disadvantage) are (1) thermal denitration which requires a concentration step, (2) hydroxide precipitation which requires precipitation and filtration steps, and (3) cation exchange followed by elution of the americium using an organic complexant. In the last case, the americium could be solidified by calcination or oxidation of the eluate or possibly by loading on an inorganic exchanger.

Precipitation of the oxalate is given a lower desirability since the filtrate will likely not be a low-alpha waste due to the large solubility of americium oxalate. The hydroxide has a much lower solubility and, particularly with iron hydroxide acting as a carrier, should allow production of a low-alpha filtrate.

The scavenging precipitation of americium and iron followed by crossflow filtration, while interesting, is likely too complex for such a small quantity of material. It would also require pumping large flows of solution, under pressure, for an extended period of time.

It is realized that regulatory requirements, including those of WIPP, may dictate the choice of methods to handle americium rather than the technical considerations discussed here.

8. REQUIRED DEVELOPMENT

One man-year of R&D should be sufficient to establish the feasibility of the thermal, precipitation methods, and the option which uses an organic complexant to elute the americium from cation-exchange resin followed by calcination or oxidation. Additional time could be required to completely develop some of the methods (primarily the hydroxide precipitation with cross-flow filtration and thermal denitration methods).

9. REFERENCES

CAMPBELL 1986. D. O. Campbell, personal communication to J. C. Mailen, June 1986.

GUTMAN 1986. R. G. Gutman, A. D. Turner, and E. W. Hooper, "Improved Processes for the Treatment of Liquid Radioactive Wastes," paper presented at ENC-4 International ENS/ANS Conference and FORATOM IX-9th Foratom Congress, Geneva, Switzerland, June 1-6, 1986.

HAAS 1982. P. A. Haas, Oak Ridge National Laboratory, personal communication to J. C. Mailen, March 1982.

HORWITZ 1986. Phil Horwitz, Argonne National Laboratory, personal communication to J. C. Mailen, Oak Ridge National Laboratory, April 1, 1986.

HORWITZ 1966. E. P. Horwitz, "The Sorption of Certain Transplutonium Ions on Amorphous Zirconium Phosphate," J. Inorg. Nucl. Chem. 28, 1469-78 (1966).

JAPAN 1979. Power Reactor & Nuclear Fuel Development Corp. (Japan), "Co-conversion R&D," paper prepared for the Third Technical Meeting on the Tokai Reprocessing Facility under the Joint Communique, Tokyo, October 3-5, 1979.

JAPAN 1982a. Japanese Patent 8234497 A2, February 24, 1982, assigned to Toshiba Corporation.

JAPAN 1982b. Japanese Patent 8234498 A2, February 24, 1982, assigned to Toshiba Corporation.

KANNO 1985. T. Kanno and H. Mimura, "Ion-Exchange Properties of Zeolites and their Application to Processing of High-Level Liquid Waste," pp. 237-47 in Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle, Proceedings of a Technical Committee Meeting on Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle Organized by the International Atomic Energy Agency and held in Vienna, 12-15 June 1984, IAEA-TECDOC-337 (1985).

KNAUER 1986. J. B. Knauer, Jr., Oak Ridge National Laboratory, personal communication to J. C. Mailen, May 1986.

MACEDO 1980. P. B. Macedo, H. G. Sutter, A. Barkatt, and W. Keene, "Application of Durasil 10 to Three Mile Island Clean-up," preprint of paper dated Dec. 22, 1980.

MAILEN 1982. J. C. Mailen, D. J. Pruett, and D. R. McTaggart, Direct Thermal Denitration to Prepare Mixed Oxides for Nuclear Fuel Fabrication, ORNL/TM-8197, June 1982.

McGINNIS 1986. C. P. McGinnis, Oak Ridge National Laboratory, personal communication to J. C. Mailen, May 20, 1986.

MELLOR 1964. Mellor's Treatise on Inorganic and Theoretical Chemistry, Vol. VIII, Suppl. I, Nitrogen (Part 1), p. 543, (1964).

MOISEEV 1981. V. E. Moiseev, R. V. Kuz'mina, and Y. V. Egorov, "Effect of Synthesis Conditions on Ion-Exchange Properties of Zirconium Phosphate," Radiokhimiya 23, 774-77 (625-28 in English trans.) (1981).

NABI 1981. S. A. Nabi, A. R. Siddiqi and R. A. K. Rao, "Synthesis, Ion Exchange Properties and Applications of Thermally Stable Stannic Selenophosphate: Comparison with Other Tin(IV) Based Ion Exchangers," J. Liq. Chrom. 4, 1225-44 (1981).

PRUETT 1986. D. J. Pruett, Oak Ridge National Laboratory, personal communication to J. C. Mailen, June 26, 1986.

RYAN 1974. J. L. Ryan, Ion Exchange, p. 373, Gmelins Handbuch der Anorganischen Chemie, Band 21, Transurane, Teil D2, G. Koch (Ed.), Verlag Chemie, G.M.b.H., Weinheim, Germany, 1974.

RYAN 1986. J. P. Ryan, Savannah River Laboratory, personal communication to J. C. Mailen, July 1986.

SCHULZ 1976. W. W. Schulz, The Chemistry of Americium, p. 245, TID-26971 (1976).

STRELOW 1965. F. W. E. Strelow, R. Rethemeyer, and C. J. C. Bothma, "Ion Exchange Selectivity Scales for Cations in Nitric Acid and Sulfuric Acid Media with a Sulfonated Polystyrene Resin," Anal. Chem. 37, 106 (1965).

SUTTER 1983. H. G. Sutter (NPS Waste Technol.), C. J. Simmons and P. B. Macedo (Catholic Univ.), "A New Waste Form for Ion-Exchangers," 160, ANS Trans. 45, Proceedings of 1983 ANS Winter Meeting San Francisco, Calif., October 30-November 3, 1983.

VARSHNEY 1981. K. G. Varshney and A. Premadas, "Silica-Based Double Salts as Cation-Exchangers -I Synthesis and Analytical Applications of Cerium(IV) Phosphosilicate," J. Liq. Chrom. 4, 1245-59 (1981).

WHEELWRIGHT 1980. E. J. Wheelwright, "Kilogram-Scale Purification of Americium by Ion Exchange," Sep. Sci. and Tech. 15, 783 (1980).

WYMER 1985. R. G. Wymer, et al., Chemical Technology Division Progress Report for the Period April 1, 1983, to March 31, 1985, pp. 92-99, ORNL-6153, October 1985.

YING 1985. Y. Ying, L. Meiqiong, F. Xiannua, "Treatment of Liquid Wastes Containing Actinides and Fission Products Using Sodium Titanate as an Ion Exchanger," pp. 223-36, in Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle, Proceedings of a Technical Committee Meeting on Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle Organized by the International Atomic Energy Agency and held in Vienna, 12-15 June 1984, IAEA-TECDOC-337 (1985).

INTERNAL DISTRIBUTION

1-5. J. T. Bell
6. W. D. Bond
7-11. D. O. Campbell
12-16. E. D. Collins
17. R. K. Genung
18. W. S. Groenier
19. J. R. Hightower
20. E. K. Johnson
21-25. J. C. Mailen
26. W. W. Pitts
27. C. D. Scott
28. F. M. Scheitlin
29. M. G. Stewart
30. V. C. A. Vaughen
31. R. G. Wymer
32. Central Research Library
33. ORNL-Y-12 Technical Library (Doc. Ref. Sect.)
34-35. Laboratory Records
36. Laboratory Records — RC
37. ORNL Patent Section

EXTERNAL DISTRIBUTION

38-40. E. P. Horwitz, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439
41-43. L. Burris, Jr., Director, Chemical Engineering Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439
44-46. W. W. Schulz, Rockwell International, Hanford Operations, P.O. Box 800, Richland, WA 99352
47-49. C. W. Manry, Rockwell International, Hanford Operations, P.O. Box 800, Richland, WA 99352
50-79. Technical Information Center, Oak Ridge, TN 37831