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SOLIDIFICATION OF ICPP ACTINIDE PARTITIONING SOLUTIONS

by

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ABSTRACT

An extensive literature survey has been made of possible methods of solidifying the rare earths and actinides in the solutions from the actinide partitioning columns, and several simple experiments have been run. If both actinides and lanthanides are to be solidified together, direct oxalate precipitation from mildly acid strip solution appears most promising. Oxalate will precipitate Np(IV), Pu(III or IV) and Am(III) from the $NH_2OH \cdot HNO_3$ plus dilute HNO_3 strip solution. Direct evaporation of the solution on a glass frit also appears promising if glass is the final waste form. Many inactive simulated waste glasses have been prepared and leach tested; highly durable glasses can be prepared at 1100°C. Inorganic titanate, $HTi_2O_5^-$, ion exchanger efficiently sorbs Np and Pu from neutralized strip solution but not from the acid strip solution. Titanate can be pressed to give a durable ceramic waste form.

SUMMARY

An extensive literature survey has been made of methods of solidifying the rare earths and actinides in the solutions from the actinide partitioning columns. If both actinides and lanthanides are solidified together, direct oxalate precipitation from mildly acid strip solution appears most promising. Other precipitation methods such as NH_4OH precipitation of hydroxides and ammonium diuranate, $(NH_4)_2HPO_4$, HF or HIO_3 precipitation of trivalent and tetravalent ions, or peroxide precipitation of Pu and Np are also possible solidification methods. A number of laboratory experiments were run to evaluate precipitation methods.

Another promising method tested is direct evaporation of the solution on a glass frit. Ion exchange can be used to concentrate or solidify the actinides. Tests were made of the absorption of Np and Pu on titanate, $HTi_2O_5^-$ ion exchanger; it absorbs Pu quantitatively and Np fairly well from neutralized strip solution. The ion exchanger could be pressed to give a highly durable TiO_2 ceramic waste form. A number of highly durable actinide-lanthanide waste glasses have been prepared and leach tested.

One of the safety factors of waste forms made from unseparated ICPP calcines is the large dilution of the actinides and fission products in the waste form. If actinides and lanthanides are separated, the waste forms will have a high loading of alpha active nuclides and so will be subject to high radiation and decay heat. Unless the actinides can be used beneficially or consumed in reactors, the partitioning does not seem worthwhile.

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I. INTRODUCTION

The Idaho Chemical Processing Plant, ICPP, has developed a process for separating the actinides and rare earth fission products from its high level processing waste.[1] The actinides and lanthanides are extracted with dihexyl-N, N-diethylcarbamylmethylene-phosphonate in decalin plus diisopropyl benzene, then stripped with dilute HNO_3 plus $NH_2OH \cdot HNO_3$. The composition of typical actinide separation solution is given in Table I. If actinides are separated, the major actinide free waste stream, <10 nCi/g alpha activity, will present a very minor hazard after 30.17 year ^{137}Cs and 29 year ^{90}Sr have decayed, but the highly alpha active waste stream containing the actinides will either have to be converted into a highly durable waste form for repository disposal or the lanthanides and actinides will have to be separated and the actinides used beneficially or incinerated in a reactor (best fast breeder) or, if it becomes available, a fusion reactor blanket. Thus processes have to be developed to solidify the actinide strip solution and prepare highly durable radiation stable waste forms or to partition actinides and lanthanides and solidify the actinide stream and produce pins for reactor or fusion blanket irradiation. If actinides and rare earths are separated from the present calcined waste, the calcine must be dissolved and there will probably be a small insoluble residue. The residue, expected to be mainly ZrO_2 or insoluble fluorzirconates may contain sufficient actinides, especially Pu, so that it will have to be incorporated with the solidified actinides in the final waste form.

This study includes an extensive literature survey of methods of solidifying actinides and lanthanides, results of some laboratory solidification tests, and describes the preparation and properties of a number of lanthanide-actinide waste glasses.

II. ACTINIDE-LANTHANIDE SOLIDIFICATION

Methods of solidifying actinides are well developed and are extensively used in nuclear fuel fabrication. Precipitation methods are the most frequently used, especially for Pu, Am, and Cm, and are well documented.[2,3] Calcination of solutions in unstirred and stirred pot calciners, fluidized bed calciners, spray calciners, flame calciners and moving-bed calciners have been used to produce uranium oxide for nuclear fuel as well as to calcine nuclear waste solutions.[4] The chemistry of the precipitation and calcination processes is reviewed in Comprehensive Inorganic Chemistry.[5]

A. Oxalate Precipitation

The most promising method of solidifying the actinides and lanthanides in the strip solution is oxalate precipitation. Oxalate precipitation is widely used for plutonium and other actinide solidification[6] and could be used instead of solvent extraction to separate trivalent and tetravalent actinides and lanthanides from high-level waste solutions.[7] Oxalates can be precipitated from moderately acid solutions and are easily handled precipitates with adequate radiation stability. In the following discussion, the symbol An represents any actinide and Ln any lanthanides plus yttrium.

All tri and tetra valent actinides and rare earths form acid insoluble oxalates. The waste solution is first concentrated by evaporation or ion exchange to give a rare earth-actinide concentration in excess of several grams/litre and the acidity adjusted to $\leq$ 4M HNO_3. A reducing agent, such as ascorbic acid, hydroxylamine nitrate, sulfamic acid or HI is added and then excess $H_2C_2O_4$ is slowly added to the 50°C solution to give a final oxalate concentration of $\sim$0.1M. The mixture is digested at 50°C to give oxalate crystals which are easily filtered (centrifuged). The precipitate is washed in dilute HNO_3 plus $H_2C_2O_4$, dried and ignited to $Ln_2O_3+AnO_2$ at 500°C. The oxalate consists of $Np(C_2O_4)_2$ and $(Pu, Am, Cm, Ln)_2\ (C_2O_4)_3$ and, if the proper reducing agent is used, also carries U as $U(C_2O_4)_2$. The filtrate contains small amounts of unprecipitated actinides and may have to be recycled. Both excess $C_2O_4^=$ and acidity cause increased solubility of the actinides so optimum acidity must be used. The oxide from ignition of oxalate is easily handled, and will be ideal for fabricating glass or oxide ceramic waste forms. The dried oxalate or perhaps even the damp filtered oxalate could be fed directly to the glass melter.

B. Other Precipitation Methods

A simpler precipitation method, but one which gives a less easily handled precipitate, is precipitation of hydroxides and ammonium diurante with NH_4OH.[8] All oxidation states will be carried. The initial solution (fairly acid, >1M HNO_3) is heated to $\sim$50-55°C and the NH_4OH slowly added (over 30 minutes). The precipitate is digested, filtered, washed with dilute NH_4NO_3, and dried at 180-200°C. Ignition of the dry hydroxide at 850°C (in $N_2+\sim6\%\ H_2$ if Np and U are present) yields $AnO_2+Ln_2O_3$. The hydroxides are highly insoluble but the filtrate is likely to contain some colloidal sol and may have to be recycled. Washing with NH_4NO_3 minimizes peptization. Precipitation with NH_4OH has been used commercially in preparing U_3O_8-UO_2 for uranium fuel. Concentration of the solution before precipitation is probably unnecessary.

Other methods of solidifying actinides or actinide-rare earth mixture have been used:

Precipitation of Np and Pu peroxides by slowly adding 30% H_2O_2 at $\sim$15°C to a $\sim$5-50 g/L solution of Np+Pu in 3-4M HNO_3 (a little $SO_4^=$ helps). Cool to $\sim$6°C and hold for $\sim$30 minutes. Wash with 1.5M HNO_3+2% H_2O_2; filtrate must be recycled. Precipitate will be mainly Np plus Pu peroxides but will carry considerable rare earths and trivalent actinides. Ignition of peroxide yields $(Pu,Np)O_2$.

Precipitation of LnF_3, AnF_3, and AnF_4 can be used to separate trivalent and tetravalent ions from AnO_2^{++} and NpO_2^{+}. To carry U and Np, concentrate solution to 50-70% g/L, adjust to $\sim$4M HNO_3, then reduce with ascorbic acid and add 2.7 to 4M HF to give an excess of HF and digest. Filter precipitate, wash and dry at 100°C. The precipitate is UF_4, NpF_4, and trivalent fluorides of the other actinides and rare earths. Relatively little actinides will be left in the filtrate. Since the final material is a fluoride, the fabrication of the final waste form may be complicated.

Precipitation of $An(IO_3)_3$ and $An(IO_3)_4$ can also be used, add excess HIO_4 to a dilute HNO_3 solution of PuIII, Pu^{IV}, Np^{IV}. The tetravalent iodates are more insoluble than the trivalent ones. Iodates are easily ignited to oxides.

If phosphate glasses are chosen as the final waste form, tri and tetravalent phosphates can be precipitated. Add $(NH_4)_2HPO_4$ to a weekly acid reduced solution of An^{3+} plus Ln^{3+}, then heat and digest to get more filterable crystals. The precipitate is $(Ln,An)PO_4 \cdot \frac{1}{2}H_2O$ which, when ignited at 900°C gives anhydrous $(Ln,An)PO_4$. The anhydrous $(Ln,An)PO_4$ is synthetic monazite and might be a desirable waste form as such. Monazite is resistant to alternation and is commonly found in detrital sands. $PuPO_4$ is very insoluble, solubility product equals 4.3×10^{-25} (ionic strength 0.5). The tetravalent phosphates like PuP_2O_7 from ignited $Pu(HPO_4)_2 \cdot nH_2O$ and NpP_2O_7 are even less soluble.

C. Direct Evaporation

The most direct approach is to concentrate the strip solutions by evaporation, then either spray calcine the concentrated nitrate solution to oxide and use the oxide to produce the final waste form or add the concentrated solution plus any actinide containing undissolved calcine to the solid glass frit or other materials added to make the final waste form, and dry and melt or sinter the mixture. Since the rare earth and actinide nitrates easily decompose to nonvolatile oxides, one would not expect any loss of activity due to volatilization although dust might be entrained in the off-gas. The major hazard of direct evaporation is the possible reaction of nitric acid with residual organic compounds in the solution. The scrub solution that removes the dust from the off-gases could be recycled by adding it to the original solution being evaporated.

D. Ion Exchange

An alternative solution concentration scheme is absorption onto either an organic or an inorganic ion exchange bed from the solution.[9] If an organic resin is used, the actinides and lanthanides could be eluted as a more concentrated solution and the resin reused. If an inorganic resin, like hydrated TiO_2 or ZrO_2, is used, the bed could be used until the actinides and lanthanides started to break through, then the ion exchange medium with absorbed actinides and lanthanides ignited to a highly insoluble TiO_2 or ZrO_2 ceramic which would be the final waste form.[10] The organic ion exchange resins add no mass to the waste, but the resin will be slowly degraded by radiolysis and will ultimately have to be destroyed, probably by wet ashing or ignition, and the ash added to the waste. Simultaneous ion exchange concentration of such chemically diverse species as AnO_2^{++}, AnO_2^{+}, An^{4+}, and An^{3+} plus Ln^{3+} could be difficult. Ion exchange with organic resin can easily separate AnO_2^{++}, AnO_2^{+}, An^{4+}, and An^{3+} plus Ln^{3+}. Ion exchange concentration is most attractive if the higher valent actinides are to be partitioned from the trivalent ions. Ion exchange separations of An^{3+} from Ln^{3+} have been developed but are very difficult.[11] Solidification by absorption on zirconate or titanate ion exchange materials will require that the solution be neutralized. The zirconate ion exchange material could be fabricated from zirconium waste such as cladding hulls.[12]

E. Laboratory Experiments

A number of precipitation methods have been tested in the laboratory. Rare earth oxalates, precipitated from 1M HNO_3 by adding a slight excess of $H_2C_2O_4$, after digestion give crystalline precipitates, $Ln_2(C_2O_4)_3 \cdot 9H_2O$ or $Ln_2(C_2O_4)_3 \cdot 10H_2O$, which are easily filtered or centrifuged. The oxalates are easily ignited to give an easily handled oxide powder. Am(III) and Pu(III or IV) are also quantitatively precipitated from solution and give easily handled crystalline precipitates. A number of experiments were made on the carrying of Np, Pu, and Am on the rare earth oxalates precipitated from 1N HNO_3+0.2M $NH_2OH \cdot HCl$ by adding an excess of $H_2C_2O_4$, see Table II for solution composition and Table III for results. Americium and plutonium are quantitatively carried while Np, probably as $Np(C_2O_4)_2 \cdot 6H_2O$, is less completely carried. Oxalate precipitation will remove Am and Pu and Np if a reducing agent is present. If necessary, the filtrate could be recycled to reduce losses. The oxalate in the filtrate is destroyed if the solution is calcined.

Cold tests have been made on the precipitation of rare earths plus Th and U by adding $(NH_4)_2HPO_4$ or NH_4OH to simulated strip solution. The phosphate precipitates are gelatinous and hard to handle and digestion does not improve them. The pH of the solution must be carefully controlled to obtain complete precipitation. Both UO_2^{++} and rare earths are quantitatively precipitated by adding excess NH_4OH to the dilute, ∿1N, acid solution. The precipitate, ammonium diuranate plus rare earth hydroxides, is bulky and gelatinous and hard to handle. Neither precipitant is as promising as oxalate.

Some cold tests have been made to test the direct evaporation of simulated strip solution containing rare earths, $UO_2(NO_3)_2$ and $Th(NO_3)_4$ on a Savannah River Laboratory glass frit 21, see Table V.[15] Because of its simplicity, direct evaporation appears very promising if a glass is the final waste form. Additional tests will be needed to ensure that the reaction of the HNO_3 and $NH_2OH \cdot HNO_3$ during evaporation does not cause trouble on a production scale.

Some tracer tests have been made to determine the absorption of Np and Pu on titanate ion exchanger. Because the $HTi_2O_5^-$ is soluble in acid, the solution used was simulated NH_4OH neutralized strip solution. Plutonium is extremely strongly absorbed while Np is less well absorbed, see Table IV. Neither Np or Pu are eluted with distilled water, but 1N HNO_3 elutes considerable Np and degrades the $HTi_2O_5^-$, see Table IV. Since the $HTi_2O_5^-$ can be pressed to give a highly durable TiO_2 ceramic waste form,[10] the titanate ion exchanger is a promising solidification material, but the neutralization step plus handling the resulting $NaNO_3$ or destroying NH_4NO_3 are complicating factors. Absorption on $HTi_2O_5^-$ could be used to remove the small amounts of actinides left in the neutralized filtrates from the precipitations. The slightly basic NH_4OH filtrate from a hydroxide precipitation might be decontaminated by the ion exchanger so that it could be discarded as inactive waste.

TABLE I. EXPECTED COMPOSITION OF ACTINIDE STRIP SOLUTION

Component	Concentration
HNO_3	0.24 M
Hydroxylamine Nitrate	0.05 M
U	0.36 mg/L
Np	trace
Pu	7.2 mg/L
Am	0.12 mg/L
Cm	0.0024 mg/L
Rare Earths	360 mg/L
Other Fission Products	trace

TABLE II. COMPOSITION OF SYNTHETIC ACTINIDE STRIP SOLUTION

Component	Concentration
HNO_3	0.24 M
Hydroxylamine Nitrate	0.05 M
Rare Earths (as Lanthanum)	360 mg/L

TABLE III. PERCENT Am, Pu, Np REMOVED BY OXALATE PRECIPITATION

Run No.	Am	Pu	Np
1	99.80	99.67	98.6
2	99.81	99.78	-
3	99.79	99.40	-
4	-	98.8	-
5	-	99.59	-
6	-	99.56	-

TABLE IV. ABSORPTION OF Np and Pu ON TITANATE ION EXCHANGER FROM NEUTRALIZED ACTINIDE STRIP SOLUTION

		Percent Eluted
Neptunium		
	a. 9 mL 1M NH_4NO_3+$NH_2OH\cdot HCl$ plus 6 mL H_2O wash	0.20
	b. 13 mL H_2O wash	0.004
	c. 10 mL 1M HNO_3	7.1
Plutonium		
	a. 5 mL 0.2M NH_4NO_3+$NH_2OH\cdot HCl$ plus 7 mL H_2O wash	0.001
	b. 12 mL H_2O wash	0.004

TABLE V. COMPOSITION OF FRITS FOR ACTINIDE GLASSES

	Weight Percent						
	127	127 Ti-Mg	127 Ti-Ba	335	SRL-21	FRG-98	UKM-9
SiO_2	70.4	64.3	59.7	45.3	52.5	55.2	54.3
B_2O_3	8.6	8.4	7.8	16.6	10.0	14.9	29.4
Na_2O	12.7	10.5	9.8	6.1	18.5	15.0	10.9
Li_2O	6.2	5.1	4.7	5.9	4.0	7.3	5.4
TiO_2	-	8.9	8.2	12.7	10.0	4.6	-
CaO	-	-	-	8.9	5.0	3.0	-
MgO	-	2.8	-	-	-	-	-
BaO	-	-	9.7	-	-	-	-
CuO	2.1	-	-	4.5	-	-	-

III. ACTINIDE-LANTHANIDE FINAL WASTE FORMS

A. Borosilicate Glass Preparation

Unless inorganic ion exchangers are used to solidify the actinides, the most promising final waste form is a borosilicate glass. The ∿98% lanthanide oxide plus ∿2% actinide oxide mixture from ignited oxalates, hydroxides or evaporation of nitrate solutions will be added, along with any undissolved calcine, to the glass frit and melted to form a glass. No loss of actinides by volatility is expected during melting. A number of glasses have been prepared using three parts by weight of various glass frits, see Table V, and one part simulated actinide calcine containing 50% ZrO_2 representing undissolved calcine plus 49% La_2O_3, CeO_2 and Nd_2O_3 and 0.5% each of UO_2 and ThO_2. Frit 127 was developed at ICPP for vitrifying zirconia calcine[13] and frit 335 is a promising frit for vitrifying alumina calcine.[14] Frits 127 Ti-Mg and 127 Ti-Ba can vitrify mixed ZrO_2 and Al_2O_3 calcines at 1100°C.[14] Savannah River Laboratory frit SRL-21,[15] and a German frit FRG-98[16] and a British frit UKM-9[17] were also used. All the frits gave glasses that melted and could be cast at 1100°C; frit 127 glass was the most viscous.

B. Leach Testing

Both cast cylinders ∿1.26 cm diameter by 1.4 cm high, and ground -16+30 mesh glasses were leach tested in static distilled water and in a Soxhlet apparatus. The leach tests are based on various proposed standardized tests.[18-22] The leachant is contained in polypropylene or teflon bottles for static tests below boiling while the high temperature tests are run in a stainless steel autoclave. Solid pieces are suspended in the leachant by a stainless steel or polypropylene holder, while ground glass is contained in fine mesh stainless steel baskets. The Soxhlet extractors used for the dynamic leach tests on both solid pieces and ground glass are made from Pyrex glass or fused silica; the sample thimbles are bathed in steam to keep the water temperature at boiling.

For static leaching of ground glass and autoclave leaching, 150 mL of leachant are used, while for static leaching of solid pieces below 100°C, a volume (cm^3) of leachant equal to ten times the sample surface area (cm^2) is usually used as recommended by the standard tests. The effect of varying the ratio of the volume of leachant to the area of sample has been investigated.

At the conclusion of the test, the pH of the leachate is measured then the container rinsed with dilute HCl or HNO_3, the rinse added to the leachate, and aliquots taken for activation analysis and spectrochemical analysis. Suspended solids, e.g., silica gel, are mixed with the leachate and analyzed while any solid that sticks to the container is discarded. The aliquots for instrumental activation analysis are evaporated nearly to dryness in teflon evaporating dishes, then dried in small polyethylene cups for irradiation. The dried leachate samples along with small samples of the original glass are irradiated for six hours in a pneumatic rabbit facility at $\sim 8\times10^{12}$ n/cm²/sec. After decay of about five days to allow 15 hr ^{24}Na to decay to the level of other activation products, the samples are counted with a calibrated Ge(Li) gamma spectrometer and the gamma activities calculated and corrected for decay by computer. A cobalt-aluminum alloy flux monitor is irradiated with the samples so corrections can be made for variations in neutron flux.

The elemental leach rates are calculated from the fraction leached as determined from the gamma activities. Fraction leached equals the corrected gamma activity in the leachate per mg sample leached divided by the corrected gamma activity in the glass per mg. The elemental leach rate in $g/cm^2/day$ is then determined by dividing the fraction leached by the specific area, cm^2/g of the sample and the days leached.

The results of the leach tests are summarized in Tables VI and VII. Leach rates are in static distilled water except those with Sox after the temperature which are in a Soxhlet apparatus. The actinide glasses prepared from frit 127 were the most durable and those from the modified 127 frits also quite durable. Frit 335 gave a somewhat more durable glass than the equally fusible Savannah River and European frits. The leach rates in static distilled water at 95°C were much lower than the 95°C rates in a Soxhlet apparatus. The ground glass shows a much lower leach rate than cylinders when expressed in $g/cm^2/day$. Leach tests show that highly durable actinide waste glasses can be fabricated from the separated actinide-lanthanide fraction. Pu, Am, and Cm would be expected to have leach rates about the same as Th or rare earths; Np would be likely to show a higher leach rate, perhaps like U or even weight loss, especially if the leachant is saturated with air.

TABLE VI. DISTILLED WATER LEACH RATES OF ACTINIDE GLASS CYLINDERS

					g/cm^2/day											
Frit	Time days	Temp ^{o}C	Sp. Area cm^2/g	Weight Loss	Na	Zr	Ba	La	Ce	Hf	Th	U	B	Ca	Li	Si
127 Q	28	70	1.61	4.2E-7	2.0E-6	-	-	4.8E-9	-	-	-	1.6E-7				
	28	95	1.69	8.2E-6	1.5E-5	-	-	6.5E-8	-	-	-	5.1E-7				
	14	95 Sox	1.58	5.7E-5	8.6E-5	-	-	3.3E-6	-	-	-	2.3E-6	9.7E-5	-	7.5E-5	2.1E-4
	3	250	1.59	2.3E-3	2.6E-3	-	-	5.4E-7	-	-	-	8.9E-4	2.7E-3	-	1.8E-3	1.6E-3
127 Ti-Mg Q	28	70	1.58	2.7E-6	5.7E-6	-	-	4.3E-9	-	-	-	6.1E-8				
	28	95	1.59	2.2E-5	2.8E-5	-	-	4.0E-7	4.0E-7	-	-	7.9E-7				
	14	95 Sox	1.62	4.5E-5	8.6E-5	-	-	4.0E-6	3.3E-6	-	-	5.6E-6	7.2E-5	-	6.7E-5	2.7E-4
	3	250	1.66	1.9E-3	3.1E-3	-	-	2.4E-6	-	-	-	3.0E-4	3.7E-3	-	2.4E-3	2.1E-3
127 Ti-Ba Q	28	70	1.59	1.1E-6	4.7E-6	-	1.5E-6	5.0E-9	-	-	-	6.8E-8				
	28	95	1.44	1.0E-5	2.0E-5	-	5.4E-6	5.6E-8	4.2E-8	-	-	1.3E-7				
	14	95 Sox	1.61	8.6E-5	-	-	-	-	-	-	-	-				
	3	250	1.59	1.2E-4	8.9E-4	-	7.3E-6	5.7E-7	5.5E-7	-	-	4.1E-5	2.8E-4	-	7.7E-4	5.5E-4
335	28	70	1.54	6.9E-6	2.2E-5	-	-	9.2E-8	4.0E-8	-	-	1.6E-7				
	28	95	1.52	1.1E-5	3.8E-5	-	-	2.1E-8	-	-	-	1.2E-7				
	14	95 Sox	1.58	2.0E-4	5.1E-4	-	-	1.1E-7	-	-	-	1.6E-6	4.1E-4	2.3E-4	6.2E-4	1.7E-4
	3	250	1.70	2.2E-4	8.1E-4	-	-	2.5E-7	-	-	-	1.4E-5	8.1E-4	5.2E-5	5.2E-4	4.8E-4
SRL-21 Q	7	70	1.59	1.7E-5	9.0E-5	9.3E-6	-	1.5E-6	1.2E-6	-	-	2.0E-5				
	21*	70		a	3.0E-5	-	-	2.2E-8	2.0E-8	-	-	1.9E-7				
	3	95 Sox	1.64	2.7E-4	2.2E-4	-	-	2.3E-7	-	-	2.0E-7	6.3E-7				
	11*	95 Sox		a	3.8E-4	6.5E-6	-	2.2E-6	1.5E-6	3.5E-6	1.4E-6	3.2E-6				
N	3	250	1.83	3.0E-3	6.1E-3	2.8E-4	-	6.8E-6	-	-	-	7.5E-4				
FRG-98 Q	28	70	1.79	1.1E-5	2.8E-5	2.6E-6	-	1.4E-5	7.8E-6	-	2.1E-6	4.8E-6				
	3	95 Sox	1.72	4.3E-4	1.1E-3	-	-	6.9E-7	-	-	-	8.0E-6				
	11*	95 Sox		a	5.2E-4	3.1E-5	-	3.9E-5	2.6E-5	2.7E-5	3.2E-5	3.9E-5				
	3	250	1.67	4.4E-3	8.4E-3	7.8E-4	-	2.9E-5	-	-	-	2.6E-3				
N	7	70	1.66	2.6E-5	4.6E-5	-	-	9.4E-8	3.4E-7	-	-	3.3E-6				
	21*	70		a	7.6E-5	-	-	1.0E-5	9.4E-6	9.6E-6	8.4E-6	1.4E-5				
	3	95 Sox	1.65	5.0E-4	4.4E-4	4.5E-6	-	6.5E-7	-	-	-	4.8E-6				
	11*	95 Sox		a	1.4E-3	9.0E-5	-	1.2E-4	7.9E-5	5.7E-5	6.2E-5	1.4E-4				
UKM-9 Q	7	70	1.75	2.8E-4	4.9E-4	1.0E-5	-	1.4E-6	2.9E-6	-	-	3.1E-5				
	21*	70		a	3.8E-4	4.1E-5	-	5.9E-5	4.9E-5	2.6E-5	3.5E-5	1.2E-4				
	3	95 Sox	1.95	1.2E-3	1.7E-3	1.6E-5	-	2.4E-6	2.9E-6	2.9E-6	1.0E-6	2.7E-5				
	11*	95 Sox		a	1.7E-3	4.6E-5	-	4.3E-5	3.4E-5	8.5E-6	2.3E-5	6.9E-5				
N	7	70	1.80	2.2E-4	1.3E-4	3.8E-6	-	3.8E-7	-	-	-	7.8E-6				
	21*	70		a	3.0E-4	2.0E-5	-	2.4E-5	1.6E-5	1.1E-5	1.1E-5	6.5E-5				
	3	95 Sox	1.65	9.2E-4	1.4E-3	1.9E-5	-	1.2E-6	2.1E-6	2.8E-6	-	2.3E-5				
	11*	95 Sox		a	1.2E-3	2.9E-5	-	2.3E-5	1.8E-5	7.6E-6	2.3E-5	5.2E-5				

*Continued Leach
^{a}Weight loss rate

28 d at 70^{o} or 14 d Soxhlet

Q-Air quenched glass
N-Annealed glass

TABLE VII. DISTILLED WATER LEACH RATES OF GROUND ACTINIDE GLASS

-16+30 mesh, 38.5 cm^2/g, $g/cm^2/day$

Frit	Time days	Temp ^oC	Weight Loss	Na	Zr	Ba	La	Ce	Hf	Th	U
SRL-21 Q	7	70	2.6E-6	1.0E-5	-	-	1.5E-8	1.6E-8	-	1.1E-8	6.8E-8
	21*	70	a	6.9E-6	-	-	5.2E-8	3.5E-8	4.2E-8	4.2E-8	1.9E-7
	3	95 Sox	7.4E-5	1.2E-4	2.3E-6	-	7.0E-8	-	-	-	6.7E-7
	11*	95 Sox	a	7.2E-5	-	-	1.3E-8	-	-	-	2.2E-7
N	7	70	3.1E-6	1.1E-5	-	-	1.7E-8	1.8E-8	1.0E-8	8.2E-9	1.4E-7
	21*	70	a	7.6E-6	8.7E-8	-	3.4E-8	1.9E-8	-	1.6E-8	2.6E-7
	3	95 Sox	6.8E-5	1.2E-4	-	-	9.4E-8	1.8E-7	-	1.1E-7	2.6E-7
	11*	95 Sox	a	8.8E-5	-	-	5.8E-9	-	-	-	1.8E-7
FRG-98 Q	7	70	1.2E-5	4.1E-5	6.2E-7	1.8E-6	7.8E-8	1.3E-7	-	2.0E-8	1.2E-6
	21*	70	a	2.9E-5	6.3E-7	-	7.7E-8	-	6.8E-8	6.7E-8	1.7E-6
	1	95 Sox	4.6E-5	1.2E-4	-	-	8.1E-7	-	7.8E-7	-	-
N	7	70	1.3E-5	5.2E-5	1.2E-6	2.9E-6	1.6E-7	2.1E-7	5.3E-8	5.5E-8	2.3E-6
	21*	70	a	3.0E-5	8.8E-7	-	9.5E-8	-	-	6.0E-8	2.5E-6
UKM-9 Q	7	70	4.6E-5	8.8E-5	9.4E-7	-	8.5E-8	-	3.3E-8	4.2E-8	3.4E-6
	21*	70	a	3.7E-5	4.6E-7	-	5.3E-8	1.1E-7	1.3E-7	5.4E-8	3.1E-6
	1	95 Sox	4.3E-5	9.7E-5	-	-	8.4E-7	-	8.1E-7	-	-
N	7	70	4.5E-5	7.6E-5	1.3E-6	-	4.1E-8	-	-	-	4.2E-6
	3	95 Sox	3.6E-4	3.0E-4	4.6E-6	-	6.0E-7	7.4E-7	1.6E-7	1.5E-7	1.9E-6
	11*	95 Sox	a	3.6E-4	-	-	1.5E-6	-	5.7E-7	8.7E-7	3.8E-5

*Continuing Leach
[a] Weight loss rate for 28 d at 70° or 14 d at Soxhlet
Q-Air quenched
N-Annealed at 500°C

IV. DISCUSSION

If actinides are partitioned and then incorporated into highly durable glass or ceramic final waste forms, waste forms will be produced which have a much higher specific alpha activity and radioactive heating than the final waste forms prepared from the present calcines. Table VIII lists the specific activity of some long cooled alumina and zirconia calcines,[23] expected activity of present calcine, and calculated activity[24,25] of future calcine assuming very high fuel burnup and the same ratio of fuel to zirconium and process chemicals as in the present calcines. If the unseparated calcine is vitrified or made into a ceramic, the radioactive decay heating and radiation damage to the waste form will be much less than that of vitrified commercial waste.[26] Glass has been shown to be stable at much higher levels of radiation than waste forms produced from our normal calcines will be exposed to.[27] However, waste forms made from partitioned actinide-lanthanide fractions will have a very high alpha activity and heat production rate.

Actinide-lanthanide separation fractions from future fuel could easily contain 1-2% ^{238}Pu and the waste forms could have a total alpha decay of $\sim 3\times10^{19}$d/cm^3 during the first few hundred years, an amount greater than commercial waste forms will receive in 10^6 years. Thus before actinides are separated, the radiation stability of the waste forms must be carefully evaluated. The alpha decay of ^{238}Pu will also produce heat, 0.56 w/g ^{238}Pu or $\sim$10 w/kg waste form. Additional heat production will arise from 284 d ^{144}Ce and 2.6 yr ^{147}Pm when the decay time is less than $\sim$10 years. Actually, if the separated actinides are to be disposed of as waste, it appears best not to separate actinides but use the unseparated waste to form the final waste forms. Handling the high specific activity separated actinide-lanthanide fraction will be difficult, and if large amounts are handled criticality must be carefully considered.

Actinide partitioning, however, could be valuable if the separated actinides are used beneficially. The high enrichment ^{238}Pu that could be separated from future ICPP reprocessed fuels would be valuable as a radionuclide heat or power source. The ^{237}Np might also be worth separating since low nvt irradiation of ^{237}Np will yield very pure ^{238}Pu for use in pace makers or other small radionuclide power sources which must have a very low radiation field. The actinide fraction could also be incorporated with the Pu fuel of a fast breeder and incinerated. The ^{238}Pu and Np and Am in the fuel would help denature the Pu for weapons use.

TABLE VIII. ACTIVITY OF TYPICAL ICPP CALCINES

	μCi/g			
	Alumina Calcine	Zirconia Calcine		
		Present		Future
Decay	16 yr	13 yr	3 yr	2 yr
5.27 yr ^{60}Co	3.4	2.3	8.9	-
29 yr ^{90}Sr	5100	2300	5600	8800
64 d ^{95}Zr	-	-	73	620
2.13x10^{5} yr ^{99}Tc	1.1	0.40	0.78	1.3
368 d ^{106}Ru	-	-	190	1000
2.06 yr ^{134}Cs	78	30	940	-
30.17 yr ^{137}Cs	6000	1900	6600	9000
284 d ^{144}Ce	-	-	1100	5400
2.62 yr ^{147}Pm	460	380	8900	23000
8.2 yr ^{154}Eu	28	37	96	-
2.14x10^{6} yr ^{237}Np	0.0036	0.0008	0.010	0.021
87.7 yr ^{238}Pu	1.71	17	24	75
2.41x10^{4} yr ^{239}Pu	0.17	0.22	0.10	0.16
6540 yr ^{240}Pu	0.068	0.21	0.091	0.17
14.7 yr ^{241}Pu	2.0	27	14	33
3.76x10^{5} yr ^{242}Pu	-	0.0005	0.0002	.0005
432 yr ^{241}Am	0.34	0.85	0.51	0.14

V. CONCLUSION

Possible methods of solidifying the actinide-lanthanide partitioning solutions have been studied. Precipitation of mixed oxalates from the ∿1N HNO_3 plus $NH_2OH \cdot HNO_3$ solution appears most promising. Direct evaporation with glass frit also is promising if a glass waste form is to be fabricated. Inorganic $HTi_2O_5^-$ ion exchanger could be used to absorb Np and Pu from the neutralized strip solution and the ion exchanger hot pressed to give a highly durable ceramic. A number of simulated actinide-lanthanide waste glasses have been prepared and leach tested; some are very durable.

From the overall waste handling standpoint, actinide partitioning does not appear to be advantageous because of the hazards of handling the ^{238}Pu in the waste and the high radiation damage and heat production of the waste forms. If separated actinides can be used beneficially, or are incinerated in a fast breeder where they serve as fuel, the separation might be advantageous.

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