Proliferation Resistance of Borosilicate Glass as a Host Form for Weapons-Grade Plutonium

by

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ABSTRACT

The proliferation resistance of borosilicate glass was examined and a process was developed to extract and recover a plutonium analog (thorium) from borosilicate glass. The glass matrix examined was developed at MIT, and consisted of the ARM-1 frit (with simulated fission products) loaded with 2 wt. % thorium and 2 wt. % each of three rare earth elements (Gd, Sm, Eu), which were added for criticality control and to possibly increase the proliferation resistance of the glass matrix.

The plutonium analog was recovered from the glass by dissolving the crushed glass in a 3.8M nitric acid solution at 90°C for 2 hours, and was subsequently decontaminated using a solvent extraction process. The acid dissolution process was able to extract 88.4 ± 6.8 % of the plutonium surrogate from the glass host form. The bench top solvent extraction process was 30.2 ± 10.9 % efficient in recovering the plutonium analog as a purified product. Overall, this process was able to extract 26.7 ± 9.9 % of the plutonium analog from the glass as a purified product. This process is comparable to the PUREX process currently used to recover plutonium from spent nuclear fuel.

MCNP was used to determine the compressed critical mass of a plutonium alloy with the same composition as the product of the extraction process. For the average product composition, the compressed critical mass was 4.72 kg of material. The best and worst compositions obtained from this process were 3.30 kg and 8.24 kg, respectively. On average, one compressed critical mass could be recovered from 696 kg of borosilicate glass, assuming a 2 wt. % plutonium loading in the glass.

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1. Introduction

With the end of the cold war and the signing and implementation of the unilateral disarmament treaties, significant quantities of weapons-grade plutonium has been declared surplus in both the United States and the former Soviet Union. Due to the special nature of this material, there is a great deal of concern regarding its disposition. In the United States, the Department of Energy has created the Office of Fissile Materials Disposition to decide and implement the nation's policy on the disposition of the excess plutonium.[1] Currently, the options under consideration for the disposition of surplus plutonium are burning the plutonium in nuclear reactors, direct geological disposal of the plutonium, and immobilizing the plutonium by vitrification or embedding it in a ceramic or other material.[2]

Among the numerous solutions to the problem of the disposition of weapons-grade plutonium is to vitrify the plutonium in borosilicate glass. Recently, work has been done to determine the feasibility of this option in order to determine the "optimal" matrix for the long term disposal of the plutonium [3]. However, no work has been done to quantify how the vitrification option would effect the proliferation resistance of the weapons-grade plutonium itself.

The primary goal of this work is to determine the proliferation resistance of weapons-grade plutonium in the borosilicate glass host form developed here at MIT[4] as compared to the proliferation resistance of plutonium in other possible host forms. The other potential host forms for the weapons-grade plutonium would be monazite, Zircon[5], and spent reactor fuel.

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[1] U.S. DOE. Office of Fissile Materials Disposition: FY 95 Program Plan. p. 2. (U1)

[2] ibid. p. 6. (U1)

[3] Sylvester, Kory W. B. *A Strategy for Weapons-Grade Plutonium Disposition.* MIT. September, 1994. (S5)

[4] Borosilicate glass with rare earth elements added. Sylvester, et. al. (S5)

[5] Ewing, R. C., Lutze, et. al. "Zircon: A host-phase for the disposal of weapons plutonium." Journal of Materials Research. (E1)

In order to determine the proliferation resistance of the host forms in question, it is necessary to conduct various laboratory experiments to determine how difficult or easy it would be to extract plutonium from the various host forms. Due to the special nature of plutonium, however, it will be necessary to use thorium as an analog for the plutonium in the various host forms. Thorium is known to follow plutonium in current solvent exchange processes, and has a stable Th(IV) oxidation state which corresponds to the Pu(IV) state for plutonium. Thorium does not have as many stable oxidation states as plutonium, and thus can not be used as an analog for plutonium in REDOX (reduction-oxidation) reactions. Thus, thorium should be more difficult to extract from the host forms than plutonium would be. As such, if thorium can be recovered from the host form, then plutonium should also be recoverable.

First, a literature search was conducted in order to determine the processes that can be used to extract the thorium from the host forms. Some of these processes were then be used in the laboratory to determine at least the following parameters for the borosilicate glass host form:

1) The overall yield of thorium from the separation process,
2) The level of technical sophistication required to accomplish the specified processing steps,
3) The minimum time required to recover an amount equivalent to a weapon from a typical log of the host form,
4) The equipment needed for the separation process,
5) The potential for scaling up to a large production facility

Once a method for recovering weapons-usable plutonium from the borosilicate glass host form was determined, an examination of the relative proliferation resistance (the resistance to recovery of WGPu from the host form, at least) of the three primary vitrification options was performed.

This thesis is outlined as follows: Chapter 2 provides the background information on the politics of plutonium and the disposition option available, and the technical background on the extraction options for various waste forms, various decontamination processes, the production of plutonium metal, and its use in nuclear weapons; Chapter 3 provides a summary of the experimental work done to determine a process for recovering a plutonium surrogate from borosilicate glass; Chapter 4 details the analysis of the extraction process developed to determine the usefulness of the material recovered, based on MCNP calculations of the compressed critical mass of the recovered material; and Chapter 5 provides an overall summary of this work, as well as a discussion of the results, including an evaluation of borosilicate glass, relative to the spent fuel standard as well as other potential host forms.

2. Background

Before an evaluation of the proliferation resistance of borosilicate glass as a host form for weapons-grade plutonium can be attempted, it is necessary to understand a few things about the politics of the disposition of WGPu. Also, it may prove helpful to examine how plutonium might be extracted from various host forms, as well as how it can be purified and fabricated for use in a nuclear device. This chapter will provide a summary of the political background surrounding the disposition of WGPu. It will also detail a number of extraction, decontamination, and reduction processes could be used by a would-be proliferator to recover the WGPu from various host forms.

2.1 Plutonium

Since it's discovery, plutonium has become one of the most important elements know to man. Not only can plutonium be used as a fuel for nuclear power reactors, but it can also be used to build nuclear weapons.

The Pu-239 isotope is the most important isotope, and is produced by the capture of a neutron by U-238, followed by a series of two beta decays. Higher isotopes of plutonium are produced by neutron capture in Pu-239. The quality of the plutonium for use as a weapon (and in a reactor) is determined by the build-up of these higher isotopes.

2.2 Political background -- *"the Plutonium Problem"*

As a result of dismantling the nuclear arsenals of the Untied States and the former Soviet Union, significant quantities of weapons-usable fissile materials have become surplus to national defense needs. "These stocks of fissile materials pose significant dangers to national and international security. The dangers exist not only in the potential proliferation of nuclear weapons but also in the potential for environmental, safety, and health consequences if surplus fissile materials are not properly managed."[1] It is estimated that some 60 metric tons (MT) of weapons-grade plutonium (WGPu) will be removed from dismantled nuclear weapons in the United States, and

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[1] U.S. DOE. "OFMD: FY 95 Program Plan". p 1. (U1)

another 70 MT from the weapons of the former Soviet Union.[2] "The Department of Energy has recently stated publicly that 'up to approximately 50 metric tons of plutonium will (or may) become available by about 2005 ... [for] civilian (unclassified) purposes,' from both weapons and other sources."[3]

2.2.1 NAS Report on the Disposition of Plutonium

In 1992, the National Academy of Sciences' Committee on International Security and Arms Control was asked by the Bush administration for a full-scale study of the management and disposition of excess weapons plutonium. The academy recommended that the United States and Russia "pursue long-term disposition options that:

> (a) Minimize the time during which the plutonium is stored in forms readily usable for nuclear weapons;
> (b) preserve material safeguards and security during the disposition process...
> (c) result in a form from which the plutonium would be as difficult to recover for weapons use as the larger and growing quantity of plutonium in commercial spent fuel (<u>the spent fuel standard</u>); and
> (d) meet high standards of protection for public and worker health and for the environment."[4]

The most promising alternatives for the disposition of excess weapons plutonium for achieving these aims are fabrication and use as fuel, without reprocessing, in existing or modified nuclear reactors; or vitrification in combination with high level waste.[5] The disposition options proposed by the NAS were "designed to meet three key security objectives:

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[2] Miller, M. "Disposal of Weapons Plutonium". Lecture. MIT. April 25, 1995. (M2)

[3] NAS report. *Management and Disposition of Excess Weapons Plutonium.* 1994. p 40. (N1)

[4] ibid. p 2. (N1)

[5] ibid. p 2. (N1)

(1) to minimize the risk that either weapons or fissile materials could be obtained by unauthorized parties;
(2) to minimize the risk that weapons or fissile materials could be reintroduced into the arsenals from which they came... ; and
(3) to strengthen the national and international arms control mechanisms and incentives to ensure continued arms reductions and prevent the spread of nuclear weapons."[6]

2.2.2 U.S. Effort: Office of Fissile Materials Disposition

On January 24, 1994, U.S. Department of Energy (DOE) Secretary Hazel O'Leary created the Office of Fissile Materials Disposition and charged it with the control and disposition of surplus fissile materials and with improving the coordination of efforts within the DOE concerning these materials.[7] The primary focus of the Office of Fissile Materials Disposition (OFMD) is to examine "options for placing plutonium...in a form or condition that is substantially and inherently more difficult to use in a weapons and [to] achieve this objective in an environmentally safe, secure and verifiable manner."[8]

Currently, the OFMD is examining several broad alternatives for the disposition of surplus plutonium that either meet or exceed the spent fuel standard proposed by the National Academy of Sciences. The alternatives for the disposition of surplus WGPu that are currently under review by the OFMD that meet the spent fuel standard are (1) burn the WGPu as mixed oxide fuel in nuclear reactors; (2) immobilize the surplus WGPu by vitrification or embedding it in a ceramic, with the possible addition of radioactive high-level waste; and (3) dispose of the material directly in a geological repository.[9] The OFMD is also examining accelerator-based conversion of the plutonium

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[6] NAS report. *Management and Disposition of Excess Weapons Plutonium*. 1994. p 3. (N1)
[7] U.S. DOE. "OFMD: FY 95 Program Plan". p 2. (U1)
[8] ibid. p 2. (U1)
[9] ibid.". p 6. (U1)

(transmutation) and deep burn reactor technology that would fission most of the WGPu as options that would exceed the spent fuel standard.[10]

Currently, the Office of Fissile Materials is developing a set of criteria for evaluating the disposition options for surplus WGPu. These criteria will be used as the basis for comparing specific options for materials disposition. "The factors to be considered in the screening criteria are as follows: Resistance to theft or diversion in processing and storage; Resistance to retrieval, extraction and reuse; Technical viability; Environmental Safety and Health compliance; Cost effectiveness; Timeliness; Cooperation with Russia and other countries; Public and institutional acceptance; [and] additional benefits."[11]

2.3 Vitrification Host Forms

One of the primary options under consideration for the disposition of WGPu is to immobilize the plutonium by vitrification or embedding it in a ceramic, either alone or with some added radioactive material (which could be high-level nuclear waste, cesium, or some other radioisotope), which would eventually be disposed of in a geologic repository. Three of the possible host forms for the plutonium are borosilicate glass, zircon, and monazite.

2.3.1 Borosilicate Glass

After decades of research, glass has become the material of choice of every major country currently involved with immobilizing and isolating high-level radioactive waste (HLW). The main features of borosilicate glass that contribute to the acceptability of immobilizing HLW as borosilicate glass waste forms are its excellent technical performance (good flexibility, high chemical durability, good mechanical integrity, and high radiation and thermal stability) and the ease of processing that borosilicate glass affords. These properties also make the incorporation of plutonium into borosilicate glass an option for the disposition of surplus WGPu.[12]

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[10] U.S. DOE. "OFMD: FY 95 Program Plan". p 7. (U1)

[11] U.S. DOE. "OFMD: FY 95 Program Plan". pp. 5-6. (U1)

[12] McKibben, et. al. *Vitrification of Excess Plutonium.* Westinghouse Savannah River Co. May 1993. p 3. (M1)

Vitrification options utilizing borosilicate glass as a product matrix provide a high degree of nuclear safety, with the plutonium immobilized in an inert matrix of high chemical durability and enhanced nuclear criticality resistance, and would serve to meet the primary objective of rendering the surplus WGPu resistant to diversion and short-term re-assembly into destructive configurations by a host nation, non-weapons state, or terrorist group.[13] Vitrification options in which the surplus WGPu is vitrified along with radioactive HLW satisfy the NAS' spent fuel standard for the disposition of plutonium, as "the task of extracting the plutonium from the glass logs would be roughly comparable in difficulty to extraction of plutonium from spent fuel bundles. Moreover, experience with separating materials from such glass is far less widely disseminated than experience with spent fuel reprocessing."[14]

Vitreous substances (substances in the glassy state) may be said to represent a distinct state of matter, which would be included among the broader and more general classification of amorphous materials (solids lacking crystal structure).[15] The most characteristic behavior of glasses is that they have no heat of fusion. As the temperature rises, a glass eventually softens and acquires more fluidity, and when a glassy liquid is cooled, the rigid, elastic condition of ordinary glass is reached without any sudden change.[16] " For the most part, glasses are solutions of silica and other oxides, produced by fusion, capable of cooling to ordinary temperatures without crystallizing, and retaining when cold the general properties of under-cooled liquids."[17]

In work at MIT, Sylvester (S5) experimented with a borosilicate glass host form for WGPu disposition, based on the Advanced Reference Material frit (ARM-1), with the addition of thorium and select rare earth elements (europium, gadolinium, and samarium). ARM-1 is a borosilicate glass that

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[13] McKibben, et. al. *Vitrification of Excess Plutonium.* Westinghouse Savannah River Co. May 1993. p24. (M1)

[14] NAS report. *Management and Disposition of Excess Weapons Plutonium.* 1994. p 188. (N1)

[15] Scholes, Samuel R. Modern Glass Practice. p 1. (S2)

[16] ibid. p 2. (S2)

[17] ibid. p 4. (S2)

contains simulated fission products, representative of HLW. Thorium was added as an analog for plutonium, and the rare earth elements were added for criticality control as well as increased proliferation resistance.[18] The addition of 2% by mass thorium oxide (ThO_2) and 6% by mass rare earth oxides (2% Eu_2O_3, 2% Sm_2O_3, and 2% Gd_2O_3) to the ARM-1 glass "caused no visible damage to the glass (i.e. gross devitrification)."[19] The thorium loading is less than the solubility limit of thorium in ARM-1 glass (which is less than 10%)[20], and was chosen based on criticality and proliferation resistance concerns.

The glass was prepared using the following procedure. First, measured amounts of europium, gadolinium, samarium, and thorium nitrate were mixed in with the ARM-1 frit and heated at 1150°C in a furnace until melted. The melt was then poured into a graphite mold and allowed to cool before being annealed, again in the furnace, at 500°C.[21] The composition of the ARM-1 frit is shown in table 2.1.

The nominal composition of the borosilicate glass matrix used for these experiments is given in appendix A1. These nominal values were calculated from the ARM-1 composition (table 2-1) by assuming that the 2 wt. % target values for the thorium and rare earth oxides were met. (Laboratory notes would indicate that the composition of the glass, in regards to the added thorium and rare earths, was fairly close to the target 2 wt. %, provided that no material was lost during the fabrication process)

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[18] Sylvester, Kory W. B. *A Strategy for Weapons-Grade Plutonium Disposition.* Masters Thesis. MIT. Sept. 1995. pp. 37-51. (S5)

[19] ibid. p 62. (S5)

[20] ibid. p 63. (S5)

[21] ibid. p 47. (S5)

Table 2.1: Pure ARM-1 Composition[22]

Table 2.1: This table contains the composition of the ARM-1 frit. The compositions are given in weight percents (wt. %) for each compound. The ARM-1 frit (Advanced Resource Material) was developed to simulate fission product waste vitrified in borosilicate glass.

Component	Fraction
SiO_2	46.50%
Al_2O_3	5.59%
CaO	2.23%
TiO_2	3.21%
Na_2O	9.67%
B_2O_3	11.30%
Nd_2O_3	5.96%
Li_2O	5.08%
ZnO	1.46%
P_2O_5	0.65%
ZrO_2	1.80%
BaO	0.66%
MoO_3	1.67%
CeO_2	1.51%
Cs_2O	1.16%
SrO	0.45%

2.3.2 Monazite

The mineral monazite is a mixed lanthanide orthophosphate containing significant amounts of the actinide ions, thorium and uranium. Some deposits of monazite contain over 15 weight percent (wt. %) uranium oxide and over 14 wt. % thorium oxide.[23] This suggests that "the lanthanide orthophosphates could also incorporate heavier actinides that do not normally occur in nature but are produced in nuclear reactors," such as plutonium.

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[22] the composition of the ARM-1 frit was provided by Pacific National Labs and is given in Sylvester, *A Strategy for Weapons-Grade Plutonium Disposition.* p 88. (S5)

[23] Lutze, Ewing. Radioactive Waste Forms for the Future. 1988. p. 497. (L1)

"Synthetic monazite appears to be a promising storage medium for many types of high-level nuclear wastes particularly for those wastes that are rich in actinides," such as the proposed mixture of surplus WGPu and high-level nuclear waste. Synthetic monazites can be easily prepared, and have been shown to be able to incorporate simulated nuclear wastes at significant waste loadings (up to 20 wt. % simulated defense waste or about 10 wt. % simulated LWR wastes).[24] The monazite matrix provides an incredibly chemically resistant host matrix[25] for the disposition of WGPu.

Synthetic monazite has been prepared from the following starting formulation, using a procedure described in <u>Waste Forms of the Future</u> (L1)[26]. The initial mixture of 8 grams lanthanum oxide (La_2O_3), 2 grams simulated SRW waste (composition given below in table 2.2), and 0.3 grams of thorium oxide (ThO_2), was dissolved in 150 ml of 50 % nitric acid in water. The solution was heated to 150°C, and ammonium phosphate [$(NH_4)_2PO_4$] was added. Following dissolution of the constituents, 450 grams of urea was added and the resulting solution heated to 250°C. Following the complete evaporation of the liquids, the resulting powder was calcined at 600°C. A stearic acid binder (1-2 wt. %) was added to the calcined powder, and the mixture was cold-pressed with a pressure of 1 to 2 kbar. The pellets were then sintered in air at 900°C for 48 hours.

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[24] ibid. p. 558. (L1)

[25] ibid. p 498. (L1)

[26] the synthetic monazite production procedure taken from Lutze, W., and Ewing, R. C. <u>Radioactive Waste Forms for the Future</u>. 1988. p. 518. (L1)

Table 2.2 - Simulated SRW Waste Composition[27]

Table 2.2: This table contains the composition of the simulated SRW waste, used in the production of synthetic monazite.

Component	Fraction
$Fe(NO_3)_3*9H_2O$	67.5%
$Al(NO_3)_3*9H_2O$	19.2%
Mn	2.3%
CaO	1.0%
$Ni(NO_3)_2*6H_2O$	6.4%
Na_2CO_3	3.2%
Na_2SO_4	0.4%

2.3.3 Zircon

Another proposed host form for surplus WGPu is synthetic Zircon. "Zircon is an extremely durable phase which may be used as a [plutonium]-host for the disposal of weapons plutonium. The long-term durability is confirmed from natural occurrences in diverse and extreme geologic environments over geologic time.[28] Zircon occurs in nature with uranium and thorium concentrations up to 5000 ppm, and is an extremely durable mineral.[29] "Zircon with 9.2 at. % plutonium substituting for [zirconium] has been synthesized, this is equal to a waste loading of 10 wt. % plutonium."[30] Also, several processing options for manufacturing the synthetic Zircon have been demonstrated on a laboratory scale.[31]

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[27] Lutze, W., and Ewing, R. C. Radioactive Waste Forms for the Future. 1988. p. 518. (L1)

[28] Ewing, R. C., et. al. "Zircon: A host-phase for the disposal of weapons plutonium". Journal of Materials Research. Feb. 1995. p. 245. (E1)

[29] ibid. p. 243. (E1)

[30] ibid. p. 243. (E1)

[31] ibid. p. 245. (E1)

2.4 Extraction Techniques

In order for a would-be proliferator (host nation, non-weapon state, or sub-national threat (terrorist group)) to recover the plutonium for use in a nuclear weapon, they must first extract the plutonium from the host form into solution. This section will examine techniques that could possibly be used to extract the plutonium from various host forms

2.4.1 Borosilicate Glass

One of the primary reasons that glass waste forms are being considered as host forms for the disposition of surplus WGPu is that glasses (particularly borosilicate glass) are fairly chemically resistant. Not only does this mean that a glass host form will be more resistant to environmental leaching of the plutonium and/or added HLW components, but it also means that it will be more difficult to recover the WGPu from the glass host form.

While a great deal of work has been done to make glasses more chemically resistant, less work has been done on developing techniques to dissolve the glass. The rate of dissolution of borosilicate glasses is surface area controlled.[32] Most acids will attack borosilicate glass; hydrofluoric (HF) acid and phosphoric acid (H_3PO_4) having the strongest effect.[33] (Phosphoric acid at 100°C results in the loss of 0.014 mg/cm^2 in 24 hours)[34] Alkali solutions will also attack borosilicate glasses. A 5 vol. % solution of sodium hydroxide (NaOH) at 95°C resulted in a weight loss from the glass of just over 10 mg/cm^2 after 50 hours.[35]

In examining the use of borosilicate glass as a host form for the disposition of WGPu, the Plutonium Vitrification Task Group at Savannah River suggests the following procedure for extracting the plutonium from the borosilicate glass. After removing the glass log from its container, the plutonium-loaded glass (either with or without added HLW) would be crushed, perhaps pulverized. Nitric acid would then be added and heated to 90°C to 95°C

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[32] Shand, E. B. Glass Engineering Handbook. 1958. pp. 80-100. (S3)
[33] ibid. pp. 80-100. (S3)
[34] ibid. pp. 80-100. (S3)
[35] ibid. p. 95. (S3)

to dissolve the plutonium. The solution would then be processed to remove the soluble silicon and undissolved material (using a "head-end gelatin strike" and centrifugation to remove the "cake" and undissolved material).[36]

Another possible extraction technique for borosilicate glass is alkali fusion. One such process is used to determine the boron oxide concentration of the glass. A 0.25 gram sample of glass is intimately mixed with 2 to 6 grams of sodium bicarbonate (Na_2CO_3) in a platinum crucible and heated over a blast burner until a clear melt is obtained. The crucible is then removed from the heat and rotated so that the melt solidifies in a thin layer. After the melt has cooled, the crucible is inverted over a 250 ml Erlenmeyer flask, allowing the melt to fall into the flask. Adhering material on the lid and on the crucible is removed with hydrochloric acid (HCl) and hot water, and then washed into the flask with more water. HCl is then added to the flask until the melt is dissolved. After the melt has been dissolved, it is neutralized using sodium hydroxide (NaOH) or calcium carbonate ($CaCO_3$) until the solution has a pH of approximately 5. Attach a condenser to the flask, and bring the flask to a boil. Remove the flask and condenser from the heat and cool. Rinse the fluid from the condenser back into the flask with a minimal amount of water. Filter the solution.[37]

2.4.2 Monazite

Monazite is chemically very inert. However, as it is the primary source of thorium (as well as a source of rare earth elements, zirconium, and titanium, which are co-recovered along with the thorium) commercial processes have been developed for "opening up monazite and making its constituents sufficiently reactive to permit extraction and separation of thorium, uranium, and rare earths."[38] The two general methods used are reaction with hot, concentrated caustic soda solution and dissolution in hot, concentrated sulfuric acid.

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[36] McKibben, et. al. *Vitrification of Excess Plutonium.* Westinghouse Savannah River Co. May 1993. p 7. (M1)

[37] This procedure is taken from Tooley, Fay V. The Handbook of Glass Manufacture. Vol. II. 1974. pp. 1043-1044. (T1)

[38] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 299. (B2)

2.4.2.1 Caustic Soda Process[39]

The monazite sand is ground with water in a ball mill until 96.5% passes through a 325 mesh and then passed into a stainless steel reactor. A liquid caustic solution containing 73% sodium hydroxide (NaOH) is fed into the reactor. The resulting slurry initially contains 1.5 kg of NaOH and 1.7 kg water per kilogram (kg) of sand. The mixture is then heated to 140°C for 3 hours. The mixture is then diluted with the wash solution of caustic and trisodium phosphate (from a later step) and digested for 1 hour at 105°C. The resulting hot slurry contains practically all the original phosphorous in solution as trisodium phosphate, and thorium, cerium, and rare earth elements as solid hydrous metal oxides.

The slurry is then filtered at 80°C, and the raffinate solution is processed (removing more than 95% of the trisodium phosphate) and recycled for sand digestion and later neutralization steps. The hydrous cake is brought into solution by dissolving in 37% hydrochloric acid (1.5 kg/kg sand) at 80°C for 1 hour before diluting the acid solution with water. The thorium is separated from the rare earths by selective precipitation of thorium hydroxide at a pH of 5.8, which is effected using the recovered caustic solution.

2.4.2.2 Sulfuric Acid Process[40]

Monazite sands are digested in 93% sulfuric acid (1.56 grams acid per gram sand, based on 100% sulfuric acid) for 4 hours at 210°C, resulting in a rubber-like dough that is soluble in cold water. Cold water is added to solubilize the monazite sulfates (10 grams of water per gram sand), and part of the resulting solution is decanted.

The monazite sulfate solution is diluted with 4.5 parts by volume of water and the pH is raised to about 1.5 by adding concentrated ammonium hydroxide.

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[39] the description of the caustic soda process was taken from Benedict, et. al., Nuclear Chemical Engineering. 1981. pp. 300-301. (B2)

[40] the description of the sulfuric acid process was taken from Barghusen and Smutz, "Processing of Monazite Sands" Ind. Eng. Chem. Dec. 1958. pp. 1754-1755. (B1)

The thorium and rare earths are then precipitated as oxalates by adding a 10% solution of oxalic acid in water. A 10% excess of oxalate ions is added to ensure complete precipitation. The precipitate is then filtered and washed with an oxalic acid solution (1% oxalic acid in 0.3 N nitric acid). This precipitation will separate the thorium and the rare earths from any uranium present in the monazite, as well as separating the thorium and rare earths from sulfate and phosphorous ions, which would interfere with the subsequent solvent extraction separations used to recover the thorium.

The oxalate filter cake is digested directly with 2.5 N sodium hydroxide solution for 1 hour at 95°C. This results in a mixture of thorium and rare earth hydroxides in a solution of sodium oxalate (done to recover the oxalate). The hydroxide cake is then washed of sodium oxalate with several batches of hot water. The resulting cake is then dried at 100°C to 120°C to oxidize the majority (over 95%) of the cerium in the cerous state to the higher valence state to allow greater recovery of the cerium in the solvent extraction process (the cerium is co-recovered with the thorium). For greater recovery of the cerium, the hydroxide cake must be calcined at 500°C for 1 hour. The resulting calcined hydroxides are dissolved in 8 N nitric acid (and brought back to 8 N by the addition of concentrated nitric acid), and then the thorium is extracted using tributyl phosphate in a solvent extraction process.

2.4.3 Zircon

Natural zircon is a primary source of zirconium and hafnium. While it is quite chemically resistant, there are industrial processes for chemically breaking down the zircon and separating the zirconium and hafnium from the silicon.[41] Three of the most important of these processes are chlorination in the presence of carbon; fusion in alkalis, followed by solution in acid; and fusion with K_2SiF_6.

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[41] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 330. (B2)

2.4.3.1 Chlorination of Zircon[42]

The chlorination of zircon has been the primary process used in the U.S., as it produces zirconium chloride. In early plants, the zircon was first converted to zirconium carbide by reaction with graphite in a graphite-lined arc furnace at 1800°C. The silicon monoxide is distilled off at this temperature. The zirconium carbide is then converted to zirconium chloride by chlorination at 500°C. The modern process directly chlorinates a mixture of zircon and carbon at 500°C to form zirconium chloride, silicon chloride, and carbon monoxide.

2.4.3.2 Alkali Fusion[43]

The alkali-fusion process was developed by the Ames Laboratory of the U.S. Atomic Energy Commission. Zircon sand is mixed with from 1 to 1.5 times its weight of sodium hydroxide (NaOH), and the mixture is heated in a furnace at 565°C. The sodium hydroxide melts at 318°C, and as the temperature rises, the NaOH reacts with the zircon to form Na_2ZrO_3, Na_2SiO_3, and water. The water is evolved as steam, and the remaining mixture is eventually converted to a fragile, porous solid frit as the temperature reaches 530°C. The frit is then cooled, ground, and leached with water to extract the Na_2SiO_3. The residue is then leached with acid, dissolving the Na_2ZrO_3, leaving the unreacted zircon to be re-used.

2.4.3.3 Fluosilicate Fusion[44]

Fluosilicate fusion has been used in the Former Soviet Union (FSU) to produce feed for the fractional crystallization separation of zirconium from hafnium. In this process, the zircon is ground to pass 200 mesh and mixed with potassium fluosilicate and potassium chloride. The mixture is sintered in a rotary furnace at 650°C to 700°C to form K_2ZrF_6 and silicon dioxide. The sinter is then cooled and ground to pass 100 mesh before it is leached with 1 %

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[42] Taken from Benedict, et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 331. (B2)

[43] Taken from Benedict, et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. pp. 331-332. (B2)

[44] Taken from Benedict, et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 333. (B2)

hydrochloric acid (HCl) at 85°C. The product is then filtered at 80°C before it is cooled to crystallize the K_2ZrF_6 and K_2HfF_6.

2.5 Decontamination Techniques

Once the host form has been 'cracked' and the plutonium has been brought into solution, it will be necessary to decontaminate (purify the plutonium by removing other components from the feed stream) the plutonium before it is suitable for use in a weapon. There are three general types of decontamination techniques: chemical, solvent extraction, and ion exchange. All three of these techniques could potentially be used to obtain an essentially pure plutonium stream (which could then be fabricated into a metal for use in a weapon).

2.5.1 Chemistry of Plutonium

Plutonium is a man-made, transuranic element with atomic number 94. The most stable oxidation state for plutonium is the Pu(IV) state.[45] In aqueous solution, plutonium can exist in the five oxidation states: Pu(III), Pu (IV), Pu(V), Pu(VI), and Pu(VII). Due to the small differences in oxidation potentials of Pu(III) through Pu(VI), all of the first four oxidation states can exist simultaneously in solution.[46]

2.5.2 Chemical Decontamination Techniques

During the Manhattan project, a number of possible chemical decontamination processes were developed in an attempt to obtain pure plutonium. Most of these processes separate the plutonium through the use of alternating oxidation and reduction stages. Before designing the first plutonium extraction plant, the plutonium chemistry group considered the following processes:[47]

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[45] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 436. (B2)

[46] ibid. p. 436. (B2)

[47] Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

2.5.2.1 Sodium Uranyl Acetate Method[48]

Sodium acetate and sodium nitrate are added to an 11 % uranyl nitrate (UNH) solution (this was a solution of uranium that had been irradiated to produce plutonium) to precipitate all of the uranium as sodium uranyl acetate, leaving the plutonium in solution in its reduced state. The plutonium is then oxidized and precipitated using a 5 % sodium uranyl acetate solution. More than 98% of the plutonium and only about 1 % of the fission activity precipitates with this step.

2.5.2.2 Bismuth Phosphate Method

The original design of the process, created during the Manhattan Project, was as follows. First, the plutonium, in its reduced form, is co-precipitated with bismuth phosphate from a 20 % UNH solution, with a yield of approximately 98 % of the plutonium and 7 % of the gamma activity. The precipitation was done at 70°C from a solution of 1 N sulfuric acid (H_2SO_4). The resulting bismuth phosphate may be dissolved in nitric (HNO_3) or hydrochloric acid (HCl). From a HCl solution, the plutonium can be precipitated with lanthanum fluoride and a wet fluoride red-ox cycle may be carried out (see lanthanum fluoride cycle, [6.2.1.X]).[49]

The bismuth phosphate cycle was improved and used as the first large-scale extraction process. The current process, as described by Katz, Seaborg, and Morss (K2) is described below. $NaNO_2$ is added to the dissolver solution to adjust the plutonium to the Pu(IV) state, while setting the neptunium to the Np(V) state and leaving the uranium in the U(VI) state. Sulfate is also added before the first extraction to complex the uranium and prevent the precipitation of the uranium along with the plutonium. The plutonium is then precipitated along with bismuth phosphate, leaving the uranium, neptunium, and part of the fission products in the supernant solution.[50]

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[48] Taken from Taken from Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

[49] Original bismuth phosphate cycle description taken from Taken from Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

[50] The bismuth phosphate cycle is taken from Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. 1986. pp. 512-515. (K2)

The bismuth phosphate precipitate is dissolved in concentrated nitric acid, and the plutonium is oxidized to Pu (VI) using a strong oxidant (sodium bismuthate, potassium permanganate, or potassium dichromate). A by-product bismuth phosphate precipitation at this stage carries the fission products, leaving the plutonium, as PuO_2^{2+}, in the supernant solution. The plutonium is then reduced to the Pu (IV) state using Fe^{2+}, and another precipitation is made (beginning the cycle again). As some of the fission products follow the plutonium through the bismuth phosphate cycle, a 'cross-over' red-ox cycle is used, such as the lanthanum fluoride process (see lanthanum fluoride cycle, [2.5.2.6])[51]

2.5.2.3 Adsorption Method[52]

Plutonium in a reduced form in a 10% UNH solution (post irradiation) is passed through a column of diatomaceous earth. This removes all of the plutonium, 5 % of the uranium, and 15 % of the fission products from the solution. The column is washed with 5 N nitric acid, during which the leading edge will remove the plutonium together with the uranium and less than 2 % of the original fission product gamma activity.

2.5.2.4 Crystallization Method[53]

The uranyl nitrate solution (UNH), with the plutonium in a reduced state and with an excess of nitric acid, is cooled from 60°C to room temperature with stirring. This results in the crystallization of the UNH, and results in the concentration of approximately 85% of the plutonium in the liquid phase. By a three stage, counter-current process, 99 % of the plutonium can be concentrated with only 8 - 12 % of the uranium. The fission product concentrations in these stages are not known. This process was regarded as unreliable by Seaborg and the plutonium chemistry team.

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[51] Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. 1986. pp. 512-515. (K2)

[52] Taken from Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

[53] Taken from Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

2.5.2.5 Iodate Method[54]

Plutonium in a reduced form is co-precipitated with thorium iodate from a 10 % UNH solution. The precipitate carries more than 95 % of the plutonium with less than 5 % of the uranium and 20 % of the fission products. The thorium iodate precipitate is separated by centrifuge and dissolved readily in dilute HCl. The plutonium is then oxidized by means of the addition of dichromate ions and a second thorium iodate precipitation is made. This leaves the plutonium in an oxidized state with approximately 5 % of the uranium and 5 % of the fission product gamma activity.

2.5.2.6 Lanthanum Fluoride process[55]

Another process developed during the Manhattan project to separate plutonium for use in nuclear weapons is the lanthanum fluoride process. Starting with uranium, plutonium, and fission products in a uranyl nitrate solution, the uranium is removed by extraction with diethyl ether. This leaves the plutonium in the Pu(IV) state in the aqueous phase, along with the bulk of the fission products. Lanthanum and fluoride ions are added to the aqueous phase, precipitating lanthanum fluoride, which carries the plutonium and some of the fission products. The lanthanum fluoride is now solubilized by either fuming with sulfuric acid, dissolution in 1 M nitric acid (saturated with H_3BO_3 or $Al(NO_3)_3$), or conversion to lanthanum hydroxide (which is soluble in nitric acid). The plutonium is then oxidized with a strong oxidizer before a second lanthanum phosphate precipitation is made by adding more fluoride ions. The plutonium will remain in the supernant solution as PuO_2^{2+}. If further decontamination is wanted, the plutonium can be reduced and the cycle repeated.

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[54] Taken from Kathren, R. L., et. al., ed. The Plutonium Story: The Journals of Prof. Glenn T. Seaborg. p. 241 (K1)

[55] The lanthanum fluoride process is taken from Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. 1986. pp. 511-512. (K2)

2.5.3 Solvent Extraction Techniques

"Plutonium can be extracted from aqueous solution into any one of a number of water-immiscible organic liquids."[56] The extraction of plutonium from fission products by solvent extraction depends on the differences in extractability of the various oxidation states into the organic phase.[57] "For the most part, solvent extraction is applied to nitrate systems, since strongly complexing anions, such as sulfate, phosphate, fluoride, or oxalate, tend to maintain plutonium and the actinide elements in the aqueous phase and thus hinder extraction."[58]

The Purex (Plutonium Uranium Reduction EXtraction) process is widely used to extract plutonium and uranium from reprocessed spent fuel. The Purex process uses tributyl phosphate (TBP), in a hydrocarbon diluent, to extract uranyl nitrate and tetravalent plutonium nitrate from an aqueous solution containing nitric acid.[59] The Purex process, on a plant-scale, has a decontamination factor of $2*10^4$ for the decontamination of fission products from plutonium in the first cycle, and $2*10^3$ for the second cycle.[60] (the decontamination factor is the ratio of the concentration of a given contaminant, relative to the concentration of plutonium, before the decontamination step to the relative concentration before the decontamination step. Thus, the decontamination factor is ratio by which the relative concentration of a given element is reduced by a given process).

In the Purex process, as it is used in reprocessing, the spent fuel, containing plutonium and fission products, is de-cladded and dissolved in hot nitric acid. The acidity of the solution is adjusted to a pH of 2.5, and the plutonium is brought to its most extractable valence of 4, by the controlled addition of N_2O_4 (formerly, sodium nitrite was used). The uranium and plutonium are then separated from more than 99 percent of the fission

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[56] Katz, et.al. The Chemistry of the Actinide Elements. p. 516 (K2)

[57] ibid. p. 518 (K2)

[58] ibid. p. 516 (K2)

[59] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 461. (B2)

[60] Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 534 (K2)

products by solvent extraction with a 30 vol. % solution of TBP in a paraffinic hydrocarbon diluent. The plutonium is then separated from the uranium by reducing the plutonium to the less extractable valence of 3. The plutonium can be further purified by repeating the Purex cycle.[61]

2.5.4 Ion Exchange Techniques

Plutonium in any of its oxidation states is readily taken up by cation-exchange resins from dilute aqueous solutions, and Pu(IV) and Pu(VI) for anionic complexes in hydrochloric and nitric acid solutions. Consequently, both anion and cation exchange techniques can be used for the separation and purification of plutonium from other actinides and rare-earth elements.[62]

"Ion-exchange techniques based on nitrate media are of major importance in the recovery and purification of plutonium from impurities. Both anion- and cation-exchange procedures in nitrate media have been reported."[63] At Los Alamos, nitrate ion-exchange is routinely used to separate and purify large quantities of plutonium, up to kilogram amounts. The plutonium is adjusted to Pu(IV) and the feed solution is brought to the desired nitric acid concentration (around 7 M). The solution is then sorbed on Dowex 1 x 4 resin (50-100 mesh). The column is washed with 7 M nitric acid to remove impurities before the plutonium is eluted with 0.3 M $NH_2OH*HNO_3$. Except for Pd, Ir, Pt, Au, and Th, all other elements are separated effectively, with decontamination factors of greater than 1000.[64]

A cation-exchange process based on nitrate has also been developed and used at Oak Ridge and Savannah River. In this process, the plutonium is reduced to Pu(III) and the solution adjusted to 0.25 M nitric acid. The solution is then loaded on a cation-exchange resin. Uranium is eluted from the resin with 0.25 M sulfuric acid / 0.25 M hydroxylamine sulfate, and then the

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[61] Taken from Benedict, et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. pp. 466-468. (B2)

[62] Katz, et. al. The Chemistry of the Actinide Elements. p. 550 (K2)

[63] ibid. p. 553 (K2)

[64] ibid. p. 557. (K2)

plutonium is stripped back using 5.7 M nitric acid / 0.3 M NH_2SO_3H. The column is then regenerated using 0.1 M nitric acid / 0.1 M NH_2SO_3H.[65]

2.6 Fabrication of Plutonium Metal

Numerous techniques for obtaining plutonium metal from a plutonium nitrate solution have been developed. The plutonium nitrate can be converted either to plutonium dioxide or to intermediate compounds suitable for reduction to plutonium metal. Plutonium nitrate can be directly decomposed (thermally) to plutonium dioxide but the plutonium nitrate feed solution must be very pure. Industrial-scale operations usually begin by the precipitation of plutonium peroxide or plutonium oxalate, resulting in further decontamination.[66]

2.6.1 Plutonium peroxide precipitation process[67]

Plutonium nitrate solutions of any oxidation state can be used as the feed for peroxide precipitation, as the plutonium will be converted to the Pu(IV) state by the hydrogen peroxide. A solution of 30 to 50 percent hydrogen peroxide (H_2O_2) is added slowly to the plutonium-nitric acid solution, using about 3 peroxide oxygen atoms per plutonium atom. The precipitation is carried out at low temperatures, about 30°C or less, to minimize the decomposition of the peroxide. The Savannah River plant performs the precipitation at 15°C, followed by digestion at 6°C. The filtered plutonium peroxide cake can be calcined at 150°C to form plutonium dioxide, although a final temperature of 900°C is required to form stoichiometric plutonium dioxide. Typical decontamination factors obtained through the peroxide precipitation process are greater that 6.7 for sodium, 25 for boron, greater than 5 for lanthanum, almost 60 for cerium (58.8) and about 1.06 for thorium.[68]

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[65] Katz, et. al. The Chemistry of the Actinide Elements. p. 562. (K2)

[66] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 440. (B2)

[67] Plutonium peroxide precipitation process taken from Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. pp. 441-442. (B2) with the exception of the decontamination factors.

[68] Decontamination factors calculated from data presented in Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 571 (K2)

2.6.2 Plutonium (IV) oxalate precipitation process[69]

Tetravalent plutonium oxalate can be precipitated from a nitric acid solution of Pu(IV) nitrate by the following process. First, the plutonium is adjusted to the Pu(IV) state by the addition of hydrogen peroxide, whether before or during the addition of oxalic acid. Best precipitations occur at temperatures between 50°C and 60°C and for time periods of oxalic acid addition between 10 and 60 minutes. The nitric acid concentration of the solution must be adjusted such that the final slurry concentration is between 1.5 and 4 M HNO_3 in order to minimize the co-precipitation of impurities and to maximize the effectiveness of the plutonium precipitation. The slurry is then filtered to recover the oxalate cake (containing the plutonium). The oxalate cake is then calcined at 300°C, followed by a restructuring at 900°C to form stoichiometric plutonium dioxide (PuO_2).

As compared with peroxide precipitation, the oxalate process achieves less decontamination from impurities, but the solutions and solids are more stable and safer to handle. The plutonium (IV) oxalate precipitation process achieves a decontamination factor of 3-6 for zirconium and niobium; 12 for ruthenium; 100 for aluminum, chromium, and nickel; 60 for uranium; and a decontamination factor of 1 for americium and thorium.[70]

2.6.3 Calcination of $Pu(NO_3)_4$[71]

The need for an intermediate precipitation process can be avoided by the direct calcination of the plutonium nitrate solution to plutonium dioxide (PuO_2). The calcination has been carried out at 350°C in a liquid-phase screw calciner, with half a mole of ammonium sulfate added to the feed solution per mole of plutonium in order to increase the production of reactive PuO_2. As the

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[69] Plutonium(IV) oxalate precipitation process taken from Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 442. (B2) with the exception of the decontamination factors.

[70] Decontamination factors taken from in Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 569 (K2)

[71] the direct calcination of plutonium nitrate process was taken from Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 443. (B2)

direct calcination of plutonium nitrate does not involve any chemical separations, the process will not provide any decontamination of the plutonium from any impurities in the nitrate solution. As such, a very pure plutonium nitrate solution is desired for this process.

2.6.4 Production of Plutonium Metal

One of the many techniques that have been developed for the production of plutonium metal is the thermochemical reduction of plutonium dioxide to plutonium metal. Elements that have been considered for reducing plutonium dioxide are hydrogen, sodium, and calcium. When choosing a reducing agent, it is important to consider that the reaction must be sufficiently exothermic that the reacting mixture will self-heat to the temperature range of 1500 K.[72] "The thermodynamically favorable reduction of PuO_2 with calcium has the disadvantage that the CaO co-product is not molten, so that the resulting plutonium metal and unreacted calcium metal remain finely dispersed throughout the slag. However, the dispersed plutonium can be recovered as a massive metal by preferentially extracting the calcium oxide and unreacted calcium with molten calcium chloride at temperatures above the melting points of plutonium and calcium, leaving consolidated plutonium metal with yield efficiencies in excess of 99.9 percent."[73]

2.7 Weapon Design

A nuclear weapon functions by taking a fissile material (U-235 or Pu-239 in most designs) in a sub-critical state and quickly forcing it into a super-critical state. This can be accomplished by increasing the density of the fuel, usually by implosion using conventional explosives. Once a super-critical state is reached, the weapon will release energy at an exponentially increasing rate until the expansive forces generated cause disassembly of the super-critical state into a sub-critical state again and the release of the energy liberated by the nuclear chain reaction stops.

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[72] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 447. (B2)

[73] Benedict, M., et. al. Nuclear Chemical Engineering. McGraw-Hill, Inc. 1981. p. 447. (B2)

In order for a weapon to achieve a super-critical state, however, it must contain at least enough fissile material to sustain a chain reaction. This amount of fissile material is referred to as a critical mass. The amount of fissile material required to build a nuclear device will be at least one critical mass or more. For example, the weapon design for the Trinity test (the first plutonium implosion weapon test) used three critical masses[74] to fuel the nuclear reaction.

The minimum, water reflected critical mass for a pure Pu-239 metal sphere is 5.425 kg.[75] Due to neutron capture in Pu-239 as it is produced in nuclear reactor fuel, there will be some level of higher plutonium isotopes present, which will tend to increase this minimum critical mass since the higher plutonium isotopes act as poisons to the chain reaction.

The relative enrichment of these higher isotopes determines the quality of the plutonium. Plutonium is considered to be weapons-grade if it is composed of greater than 94% Pu-239, while reactor-grade plutonium is typically composed of less than 80% Pu-239.[76] Typical isotopics of reactor-grade (RGPu) and weapons-grade (WGPu) are presented below in table 2.3.

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[74] Sylvester, K. *A Strategy for Weapons-Grade Plutonium Disposition.* p. 43 (S5)

[75] Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 502 (K2)

[76] DeVolpi A. *Fissile Materials and Nuclear Weapons Proliferation*, Ann. Rev. Nucl. Part. Sci., V36, 1986. pp. 83-114. (D1)

Table 2.3: Typical Plutonium Isotope Composition

Table 2.3: This table contains typical isotopic concentrations for weapons-grade plutonium (WGPu) and reactor-grade plutonium (RGPu).

	WGPu[77]	RGPu[78]
% ^{238}Pu	0.012	1.31
% ^{239}Pu	93.9	60.8
% ^{240}Pu	5.81	24.5
% ^{241}Pu	0.23	8.37
% ^{242}Pu	0.22	5.04

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[77] Normalized isotopics for WGPu taken from Berkhout, F., et al. *Disposition of Separated Plutonium.* Science and Global Security. Vol. 3. 1992. p. 13 (B3)

[78] Normalized isotopics for RGPu taken from Plutonium Fuel: An Assessment. OECD. Paris. 1989. p. 50. (O1)

3. Technical Investigation

3.1 Scope

One of the major questions about vitrifying WGPu is how difficult would it be for a would-be proliferator to recover the material from the borosilicate glass host form. In this work, this issue was examined through laboratory experiments on a borosilicate glass host form under investigation here at MIT. This host form used the ARM-1 frit (with simulated fission products), with the addition of thorium (Th) as an analog for the WGPu. Rare earth elements (europium (Eu), gadolinium (Gd), and samarium (Sm)) were also added to the glass for criticality control as well as to potentially increase the proliferation resistance of the host form.

The task of recovering the WGPu from the host form was broken down into three stages: extraction, decontamination, and fabrication. The extraction stage involves extracting the WGPu analog from the host form into solution. The WGPu is then purified for use in a nuclear weapon in the decontamination stage. Finally, the WGPu is fabricated into metal for use in a weapon. The extraction and decontamination stages were examined experimentally in this work. Initial scoping experiments were performed to determine which techniques were the most successful for each stage, and then these techniques were examined in more detail. The fabrication of plutonium metal from aqueous solutions is fairly well established, and has been detailed in section 2.6 of this work.

3.2 General Laboratory Procedures

Unless otherwise noted, the following procedures were used in the experiments performed for this work.

3.2.1 Concentration Measurements

The elemental concentrations of liquid samples were determined using Inductively Coupled Plasma (ICP) flame spectroscopy. The samples were first filtered with a 0.45 μm filter, and then acidified to at least 5 volume % (vol. %) nitric acid. The samples were then analyzed on the Spectroflame ICP, using the measurement parameters and equipment settings describe in appendix C2.

The average of the 3 concentration measurements was used as the solution concentration. A brief description of how the ICP works is included in the appendix (appendix C1). The laboratory ICP operations document has also been included here, in appendix C4.

For the single element determinations (thorium only, done for the scoping experiments for the extraction process), the Thorium concentrations were measured by observing the 283.73 nm line. For the multi-elemental analyses, the lines used for each element are provided in table 3.1. The elements examined in this work were chosen for the following reasons. Thorium, and to some extent cerium, were chosen because they can serve as an analog for plutonium (thorium is used in this work as the plutonium analog). The rare earths (europium, gadolinium, samarium, and neodymium) were included due to their large cross sections as well as to determine the effect these elements have on the proliferation resistance of the glass host form. Sodium and silicon were included in order to gain some understanding of what is happening to the glass itself, as both elements are primary components in the glass. Boron was included not only because it was a major component of the glass, but also due to its large cross section. Finally cesium was included so that it would be possible to observe the intensity of the radiation barrier throughout the processes.

Table 3.1: Characteristic Photon Lines Used for ICP Analysis

Table 3.1: This table contains the characteristic photon lines used to determine the concentrations of the listed elements by ICP analysis

element	line used
cerium (Ce)	418.66 nm
thorium (Th)	283.73 nm
europium (Eu)	381.97 nm
gadolinium (Gd)	342.25 nm
samarium (Sm)	359.26 nm
neodymium (Nd)	401.23 nm
cesium (Cs)	455.53 nm
silicon (Si)	250.69 nm
sodium (Na)	589.59 nm
boron (B)	249.68 nm

3.2.2 Acid Concentrations

As a convention for this work, the concentrations of the acid solutions used are given in terms of the volume percent concentrated acid solution used to make the solution. Thus, a 5 vol. % solution of nitric acid is a solution of 5 vol. % concentrated nitric acid solution in de-ionized water (DI water).

The concentrated stock solution of nitric acid which was used for these experiments was 70.5 wt. % HNO_3, or 15.5 M HNO_3 (based on laboratory density measurements of stock concentrated nitric acid solution). Thus, the 5 vol. % solutions used in most experiments are actually 0.78 M HNO_3.

3.2.3 Equipment Cleaning

All glassware (and plasticware) was cleaned using the following protocol. If no organic solutions were used with the equipment, it was allowed to soak overnight in a 0.5 M HNO_3 solution (the contaminated bath). It was then rinsed with DI water and placed into another bath containing 0.5 M HNO_3. The glassware was then dried for use.

If organic solutions were used with the glassware, the glassware would first be rinsed with acetone, then with ethyl alcohol, and finally with DI water before being placed into the first acid bath.

Vials used for sample storage were never re-used, and thus were not subject to the above cleaning process.

3.2.4 Glass Sample Composition and Designations

The glass samples used in these experiments were made by K. Sylvester as part of his thesis work (Sylvester, Ref. [S5]). The nominal composition of the glass is given in appendix A1. The actual composition of the glass (not accounting for any volatilization of components while the glass was being made) can be found in the experimental work done by Sylvester as part of his thesis work (S5). The actual compositions were usually within 1-3% of the nominal composition detailed in appendix A1. The batch in which the glass was made is designated by T1Px, where T1 indicates that the glass was made by using the ARM-1 glass as the frit and the Px (x being any number) indicates the batch number. The batches were all made the same way and have approximately equal composition (within 1-2% of the nominal values for the added elements). However, there may be some inhomogeneity between batches due to heterogeneity in the ARM-1 glass used as frit.

3.2.5 Definition of Parameters Used

Defined below are the parameters used in this work. The thorium subscript (Th) was typically dropped for simplicity. Therefore, in the body of this work, the lack of a subscript on a term (i.e. CF) would mean that the given factor is determined relative to thorium.

3.2.5.1 Extraction Efficiency (e_{th}, e_i)

The extraction efficiency of a process (e_i) is defined to be the ratio of the mass of a given element in solution to the mass of that element in the glass. This parameter is a measure of the effectiveness of a given extraction process. Of particular importance is the extraction efficiency of thorium (e_{th}), which is used as an analog to the WGPu in the glass. Unless specified elsewhere, the concentration of a given element in the borosilicate glass matrix was assumed to be the nominal value (see Appendix A1) for determining the extraction efficiency.

$$e_{th} = \frac{\text{mass of Th recovered in solution}}{\text{mass of Th in the glass}} \leq 1 \qquad (3.1)$$

3.2.5.2 Recovery Efficiency (r_{th}, r_i)

The recovery efficiency of a process (r_i) is defined to be the ratio of the mass of a given element in the product stream (final solution) to the mass of the same element in the feed stream (initial solution). This parameter is used to measure the efficiency of a decontamination process. The most used recovery efficiency in this work was the recovery efficiency of thorium (r_{th}):

$$r_{th} = \frac{\text{mass of Th recovered in product stream}}{\text{mass of Th in the feed stream}} \leq 1 \qquad (3.2)$$

3.2.5.3 Process Efficiency (p_{th})

The process efficiency for thorium is defined to be the ratio of the total mass of thorium in the final product to the total mass of thorium in the host form (in this case, in the borosilicate glass. Again, nominal glass compositions were used). The process efficiency is a measure of the efficiency of the entire process, from the initial extraction to the production of the final product. If the final product is a partially decontaminated nitrate solution of WGPu, then the process efficiency is simply the product of the extraction efficiency of the extraction phase and the recovery efficiency of the decontamination phase.

$$p_{th} = \frac{\text{mass of Th recovered in product}}{\text{mass of Th in the host form}} \leq 1 \qquad (3.3)$$

$$p_{th} = e_{th} \times r_{th} \leq 1 \qquad (3.3a)$$

3.2.5.4 Contamination Factor (CF_i)

The contamination factor of a given solution or form is defined as the ratio of the mass of element i to the mass of thorium (typically). If the contamination factor is to be calculated relative to a different element, it will be explicitly stated. The contamination factor provides a measure of the relative concentrations of a given contaminant relative to the plutonium analog (Th).

$$CF_i = \frac{\text{mass of element i in solution}}{\text{mass of thorium in solution}} \tag{3.4}$$

3.2.5.5 Decontamination Factor (DF_i)

The decontamination factor of a given process is defined as the ratio of the contamination factor (CF_i) in the feed stream to the contamination factor in the product stream for a given element. This provides a metric for the effectiveness of a given process in reducing the relative amount of a given contaminant. A decontamination factor greater than 1.0 indicates that the relative concentration of a given contaminant (as compared with thorium) has been reduced.

$$DF_i = \frac{CF_i \text{ of Feed stream}}{CF_i \text{ of Product stream}} \tag{3.5}$$

3.3 Overview of Experimental Work

The experimental work described here was performed between March and December of 1995 at MIT. A detailed account of the experiments is provided in appendix B.

The task of recovering weapons-usable plutonium metal from a host form, such as borosilicate glass, can be broken into three sub-tasks: extraction, decontamination or purification, and reduction to metal. The experimental work of this thesis, which was the recovery of a plutonium analog (thorium), can also be divided into these three tasks. The reduction of to metal was not undertaken as part of this work.

3.3.1 Extraction

Two methods were examined for extracting thorium (as an analog for plutonium) from borosilicate glass: acid dissolution and alkali fusion. While both methods were to some extent successful in extracting the thorium, acid dissolution proved to be more efficient and simpler than alkali fusions. The alkali fusion techniques examined were able to extract between 40 % to 50 % of the thorium from the glass, while the acid dissolution technique was able to extract more than 80 % [B.1]. Both techniques required that the glass be crushed into a powder in order to extract a significant amount of thorium from the glass.

3.3.2 Decontamination

Once the decision to use acid dissolution for the extraction of thorium from borosilicate glass was made, the thorium-containing solutions generated by the acid dissolution experiments were used to examine a number of decontamination processes. Two types of process were examined: precipitation processes and solvent extraction processes.

Three different precipitation processes were examined: hydroxide precipitation, fluoride precipitation, and phosphate precipitation. The hydroxide precipitation process was based on the final decontamination step of the caustic soda method for extracting thorium from monazite [2.5.2.1]. The fluoride and phosphate precipitation processes mimic the initial stages of the lanthanum fluoride [2.6.1.6] and bismuth phosphate [2.6.1.2] decontamination processes. However, as thorium does not have the same oxidation states as plutonium, it was not possible to do the REDOX reactions required for complete decontamination of the rare earths and fission products. The recovery efficiencies (r_{th}) and decontamination factors (DF) for these three processes, as well as for a 2 cycle hydroxide precipitation process, are shown in table 3.2

In addition to precipitation decontamination processes, a solvent extraction was examined as a technique for purifying the thorium stream. The experiments done here were based on the PUREX process [2.6.2.1], which is currently used at most reprocessing plants worldwide. The process basically consists of contacting the acidified thorium-containing solution with a 30 vol. % solution of TBP (Tri-Butyl Phosphate) in kerosene, which preferentially absorbs the thorium (and plutonium), leaving most other components behind. The thorium is then stripped from the organic using DI water. The one-cycle process did just that. Then, an acid wash stage was added to the process, in which the thorium-loaded organic was contacted with 3M nitric acid to increase the decontamination of the rare earths from the thorium. This was referred to as the acid wash stage, and this variation of the solvent extraction process was called the 1+1 extraction.

In addition to the one cycle and 1+1 solvent extraction process experiments were also done with a 2 cycle solvent extraction process, in which the final product solution was acidified to 3M HNO_3 and then used as the feed solution to another cycle of solvent extraction. Two variants of the 2-cycle solvent extraction process were examined: one using fresh organic solvent each cycle, the other recycling the organic solution from the first cycle for use in the second cycle. It is important to note that the organic solution was not pre-equilibrated with nitric acid before these experiments.

Table 3.2: Precipitation Process Decontamination Factors

Table 3.2: This table contains the decontamination factors (DF) and recovery efficiencies (r_{th}) for the hydroxide precipitation process (OH), fluoride precipitation process (F), phosphate precipitation process (PO_4), and 2 cycle hydroxide precipitation process (2*OH).

element	OH	F	PO_4	2*OH
Ce	3.14	0.24	0.78	2.51
Eu	1.27	0.48	0.73	1.42
Gd	1.31	0.62	0.75	1.47
Sm	1.36	0.33	0.72	1.49
Nd	1.93	0.49	0.75	1.88
Si	0.87	0.21	14.23	0.23
Na	53.24	0.99	27.94	612.13
B	4.41	8.20	19.48	136.23
r_{th}	**49.3%**	**10.9%**	**25.3%**	**42.5%**

Table 3.3: Solvent Extraction Decontamination Processes

Table 3.3: This table contains the decontamination factors (DF) and recovery efficiencies (r_{th}) for the solvent extraction experiments performed: the one cycle extraction (1-cycle), the one cycle with acid wash (1+1) the 2 cycle extraction without recycle (2-cycle), and the 2 cycle extraction process with recycled solvent (recycle).

element	1 Cycle	1+1	2-Cycle	Recycle
Ce	17.69	88.00	17.53	17.47
Eu	9.06	28.92	8.63	11.35
Gd	9.69	29.54	9.39	11.91
Sm	9.29	22.82	9.47	12.01
Nd	12.97	32.42	14.00	14.25
Si	<50.0	10.17	82.35	31.73
Na	26.39	37.77	20.04	18.31
B	31.58	67.82	23.09	19.44
r_{th}	**47.2%**	**29.2%**	**10.2%**	**19.7%**

3.3.3 Crushed Glass - Acid Dissolution Process (V2)

The final procedure chosen for the extraction and decontamination of thorium from borosilicate glass consists of an acid dissolution extraction process coupled with a 1+1 solvent extraction (1 cycle with and acid wash of the solvent). The final version of the Crushed glass - Acid dissolution, or CA (V2), process is

1) The glass sample was crushed using a ceramic mortar and pestle so that it passes through a 60 mesh filter (particle size less than 250 microns)

2) The crushed glass was put in a beaker and a 25 vol. % solution of nitric acid (approximately 17.87 wt. % HNO_3) was added in a 30:1 mass ratio (acid:glass).

3) The sample was stirred and covered with a watch glass before being placed in the oven.

4) The samples were then heated in an oven for 2 hours at 90°C. Every 30 minutes, the samples were removed from the oven for stirring.

5) After 2 hours, the samples were weighed and then the liquid solution was decanted off using a disposable pipette leaving the undissolved glass in the beaker. A small portion of this sample was taken, filtered and diluted for ICP analysis.

6) The remaining sample was then added to a glass bottle (shaker) and mixed with an equal volume of pre-equilibrated 30 vol. % TBP in kerosene. The pre-equilibrated organic solution was prepared by mixing the TBP+kerosene mixture with an equal volume of 3M nitric acid.

7) The sample was then shaken for 1 minute and allowed to settle. The organic phase was recovered with a disposable pipette and transferred to a clean shaker.

8) An equal volume of 3M nitric acid was then added to the organic solution. The mixture was then shaken for 1 minute and allowed to settle before the organic solution was again recovered and transferred to a clean shaker with a disposable pipette.

9) The organic solution was then mixed with an equal volume of DI water and shaken for 1 minute. After settling, the organic phase was removed, leaving only the aqueous solution. The aqueous phase was then acidified to approximately 3M HNO_3 by the addition of concentrated nitric acid. This sample was then filtered and diluted for ICP analysis.

3.3.4 Thorium Extraction and Decontamination Data

Using the CA (V2) procedure, thorium was extracted and purified from borosilicate glass to determine the thorium extraction efficiency, the thorium recovery efficiency, the contamination factors, and the decontamination factors for the CA (V2) process. Glass from 2 batches (T1P1 and T1P2) was used, and 5 samples were prepared using each glass. The extraction and decontamination of the thorium from the borosilicate glass host form was performed in two stages: the extraction stage (I) and the decontamination stage (II). The average contamination factors for the product solution of the extraction process (stage I) along with the 97.7% confidence interval (2 standard deviation) are shown in table 3.4 for both the T1P1 and T1P2 glass.

While the average contamination factors of most elements are not within 2 standard deviations between the two glasses the extraction efficiencies are. This can most likely be attributed to some inhomogeneity in the ARM-1 frit or some slight variations in the glass composition (due to laboratory error, etc...). Comparing the contamination factors in the extraction solution with the nominal contamination factors in the glass (Table 3.5), shows that, for the most part, most elements are easier to extract from the glass matrix than the thorium (shown by decontamination factors less than 1.0). The one exception to this is silicon itself, which is extracted into solution almost 100 times less than thorium.

The average contamination factors for the product solution of the decontamination process (stage II) along with the 97.7% confidence interval (2 standard deviation) spread are shown in table 3.6 for both the T1P1 and T1P2 glass.

Unlike the extraction part of the CA (V2) process, the spread associated with the observed contamination factors for the decontamination stage was quite large. The difference between the two glasses was not as evident as the disparity between individual runs from a given batch which suggests that the large spread in the data is due to the decontamination process itself. Given the crudeness of the process, this is not unexpected. Using the average values of the contamination factors from the decontamination process (table 3.6) and the extraction process (table 3.4), the decontamination factors for the solvent extraction decontamination process can be determined. From the extraction efficiency and the recovery efficiency, the process efficiency can be determined.

The analysis of the decontamination stage of the CA process (stage II) assumes a Gaussian distribution for the data. However, the data (Appendix B, section [B.5.2]) may be better described by some other distribution.

Nevertheless, it may be more informative to look at the mean values for the decontamination process along with the highest and lowest decontamination factors. This will provide not only an average performance level for the second stage of the CA process, but will also provide both an optimistic and pessimistic limit for the decontamination factors for the process. As the composition of the extraction solution obtained from the glass samples used was quite similar (especially when compared to the relative error associated with the stage II contamination and decontamination factors), the data from the 2 samples was combined for this analysis.

From these values, an average value for the Stage II decontamination factor (DF) can be determined. From the average extraction and recovery efficiencies, the process efficiency can be determined with equation 3.3a.

Process Efficiency (P_{th}) = 26.72 %

Table 3.4: CA Process - Stage I Contamination Factors

Table 3.4: This table contains the average contamination factors for the product solution of the extraction process (stage I). The absolute error values listed are the 97.7% confidence interval spread of the experimental data. Also included are the extraction efficiencies (e_{th}) for the 2 batches.

element	T1P1 Batch		T1P2 Batch	
	CF	error	CF	error
Ce	0.627	0.023	0.681	0.008
Eu	1.060	0.040	1.050	0.031
Gd	0.997	0.024	1.048	0.015
Sm	1.140	0.033	1.147	0.013
Nd	2.330	0.181	2.736	0.060
Si	0.130	0.044	0.154	0.029
Na	4.063	0.380	4.208	0.333
B	2.012	0.089	2.254	0.013
e_{th}	**90.71%**	**6.00%**	**86.16%**	**3.14%**

Table 3.5: CA Process - Stage I Decontamination Factors

Table 3.5: This table shows a comparison of the average contamination factors in the product solution from the extraction process (stage I) and the contamination factors in the borosilicate glass host form (from Appendix A1). The decontamination factors obtained by the extraction process were determined from the ratio of the contamination factor of a given element in the host glass to the contamination factor of that element in the extracted solution.

element	Glass	T1P1 Batch		T1P2 Batch	
	CF	CF	DF	CF	DF
Ce	0.642	0.627	1.024	0.681	0.943
Eu	0.983	1.060	0.927	1.050	0.936
Gd	0.989	0.997	0.992	1.048	0.944
Sm	0.977	1.140	0.857	1.147	0.852
Nd	2.67	2.330	1.146	2.736	0.976
Si	11.35	0.130	87.31	0.154	73.70
Na	3.75	4.063	0.923	4.208	0.891
B	1.835	2.012	0.912	2.254	0.814

Table 3.6: CA Process - Stage II Contamination Factors

Table 3.6: This table contains the average contamination factors for the product solution of the decontamination process (stage II). The absolute error values listed are the 97.7% confidence interval spread of the experimental data. Also included are the recovery efficiencies (r_{th}) for the 2 batches.

element	**T1P1 Batch**		**T1P2 Batch**	
	CF	**error**	**CF**	**error**
Ce	0.021	0.012	0.026	0.030
Eu	0.066	0.057	0.079	0.072
Gd	0.057	0.046	0.071	0.063
Sm	0.067	0.052	0.081	0.076
Nd	0.085	0.084	0.123	0.138
Si	0.020	0.031	0.005	0.010
Na	0.047	0.036	0.055	0.112
B	0.027	0.037	0.049	0.084
r_{th}	**30.35%**	**7.53%**	**30.06%**	**7.89%**

Table 3.7: CA Process - Stage II Decontamination Factors

Table 3.7: This table contains the decontamination factors (DF) calculated for the solvent extraction decontamination process (stage II) of the CA process. The DF's were calculated from the average contamination factors of the final product stream (table 3.6) and the initial feed stream (table 3.4) to the decontamination process. The error shown below is the absolute error at the 97.7% confidence interval.

element	T1P1 Batch		T1P2 Batch	
	DF	error	DF	error
Ce	29.9	17.1	26.2	30.2
Eu	16.1	13.9	13.3	12.1
Gd	17.5	14.1	14.8	13.1
Sm	17.0	13.2	14.2	13.3
Nd	27.4	27.2	22.2	25.0
Si	6.5	10.3	30.8	61.9
Na	86.4	66.7	76.5	155.9
B	74.5	102.2	46.0	78.9

Table 3.8: Average Contamination Factors for the CA Process

Table 3.8: This table contains the average contamination factors for the product solutions from the first and second stages of the CA process. Stage I is the product of the extraction process. Stage II represents the product solution from the decontamination process. Also included are the average extraction and recovery efficiencies, respectively.

element	Stage I CF's	Stage II CF's
Ce	0.654	0.024
Eu	1.055	0.073
Gd	1.023	0.064
Sm	1.144	0.074
Nd	2.533	0.104
Si	0.142	0.013
Na	4.136	0.051
B	2.133	0.038
	e_{th} = 88.44 %	**r_{th} = 30.21 %**

Table 3.9: Average Decontamination Factors for the CA Process

Table 3.9: This table contains the average decontamination factors (DF) for the product solution from the second stage of the CA process. These DF's were determined from the average contamination factors for the feed and product solutions to the decontamination process (stage II). Also provided are the highest and lowest decontamination factors observed during the experimental work.

element	Average DF	High	Low
Ce	27.25	55.19	13.83
Eu	14.45	35.24	8.90
Gd	15.98	35.10	9.59
Sm	15.46	34.20	9.30
Nd	24.36	68.09	12.60
Si	10.92	1498.2	11.54
Na	81.10	1608.5	24.53
B	56.13	568.0	19.04

3.4 Observations and Discussion of Experimental Work

Over the course of the experimental work performed as part of this project a number of problems were encountered. This section will discuss the problems encountered, as well as detailing the observations and decisions (such as which processes to pursue to extract the thorium, for example) made during this project.

3.4.1 Development of Crushed Glass- Acid Dissolution Process (CA process)

The Crushed Glass-Acid dissolution (CA) process that was used in this work to extract and purify the thorium from the borosilicate glass was developed in two separate stages: the extraction stage and the decontamination stage. The decision-making processes involved in developing this process are detailed below.

3.4.1.1 Choice of Extraction Technique

The initial extraction experiments examined the effectiveness of the two techniques suggested by the background research: acid dissolution and alkali fusion. The first extraction scoping experiments were performed on 'large' (on the order of 1 cm^3 in volume) pieces of borosilicate glass (see appendix B, section [B.1]), without much success in extracting the thorium into solution. The subsequent experiments using crushed glass however, were much more successful.

In order to compare the two extraction techniques, the extraction experiments using crushed glass were repeated and analyzed for not only the extraction of thorium but also the relative concentrations of various spoiler elements [B.2]. The two acid extraction experiments showed extraction efficiencies greater than 80% for thorium. The alkali fusion (combining all of the extraction streams) had an extraction efficiency of around 40%. The alkali fusion technique did, however, reduce the relative levels of contaminants in the product (thorium-bearing) solution (tables B.2 and B.4 show contamination factors that are less than 1.0 for all three added rare earths, indicating a relative reduction in their concentrations).

In the end, however, the acid dissolution technique was chosen over the alkali fusion technique for two reasons: simplicity and extraction efficiency. The alkali fusion technique, at least at the bench top scale, had a great number of unresolved parameters associated with using a lab top burner to heat the fusion (eventually, the laboratory furnace would be necessary to do any larger (more than 0.5 grams of glass) extraction experiments). Also, after the fusion was created, it was necessary to dissolve the salts out of the crucible (without losing any material, etc...). In comparison, the acid dissolution technique required only that the samples be stirred every 30 minutes and that the laboratory ovens be monitored to control the oven temperature. While not a factor at the time, the choice of the acid dissolution method simplified the use of a solvent extraction process for the decontamination stage (as the product of the acid dissolution process is a nitric acid solution).

3.4.1.2 Choice of Decontamination Technique

After the acid dissolution technique was chosen to be the extraction technique, it was used to create a large volume of extracted solution to facilitate some scoping experiments on decontamination experiments. The first techniques examined were precipitation techniques based on the original decontamination experiments done to purify plutonium for the Manhattan Project [2.5]. As thorium was used as the plutonium surrogate, it was not possible to examine the effectiveness of the reduction-oxidation techniques normally used to purify plutonium. Of the precipitation techniques examined [B.3.1], none provided any significant decontamination factors for the rare earth elements. However, the hydroxide and phosphate precipitation techniques did seem to be able to remove some of the glass formers (silicon boron, and sodium). Hydroxide precipitation (table B.7) reduced the relative concentration of sodium by a factor of 50 and reduced the relative concentration of boron by a factor of 4. The phosphate precipitation process (table B.9) and a decontamination factor of greater than 10 for silicon, sodium, and boron. While these processes were not chosen for the decontamination stage of the CA process, they could possibly be used as head--end strike processes to remove the glass-former elements if desired.

As the precipitation processes were unable to sufficiently remove the added rare earths (europium, samarium, and gadolinium), it was necessary to examine other techniques. The most obvious choice was to examine solvent extraction as a possible decontamination technique. After examining the effects of an acid wash stage, solvent recycle, and multiple stage cycles, the 1+1 decontamination process (1 solvent extraction cycle with 1 acid wash cycle [B.4.2]) was chosen as the best trade off between high decontamination factors and high recovery efficiency for thorium.

3.4.2 Acid Concentration and Extraction Efficiency

Initially, the acid extraction stage of the CA process was done with a 5 vol. % nitric acid solution (see CA version 1, appendix B.2.6.1), which was the acid concentration used in the scoping experiments. The initial extraction experiments, using the 5 vol. % acid solution, had an extraction efficiency of around 80 % (which is why this method was chosen to extract the thorium from the glass). However, when experiments were performed to confirm the effectiveness of the CA procedure (CA V1, acid extraction with 5 vol. % nitric acid), the extraction efficiency was observed to be only 30 - 40 % [B.2.6.2]. The original experiments were re-analyzed to determine if some error had been made, but none was found. Thus, for some reason, the extraction efficiency of the acid dissolution process appears to alternate between 40 % and 80 %,, without spanning the intermediate values.

In order to determine why the extraction efficiency would sometimes be over 80% and sometimes be only 40%, a number of other factors were examined. The factors examined were oven temperature, acid concentration, and particle size. For all of these experiments, the same procedure was used (except for the variable of interest) for extracting the thorium from the glass. Also, all of these experiments were performed using glass from the T1P1 batch to avoid any differences in glass composition between experiments.

The acid concentration examined were 5 vol. %, 10 vol. %, and 25 vol. % [B.2.7.1]. For all three acid concentrations, the observed thorium extraction efficiency was over 80% (between 83 % and 84%).

Oven temperatures examined were 80°C, 90°C, and 100°C. Two experiments, one at 80°C and the other at 100°C, were done the same day. The 90°C run from the acid concentration experiment was used for the baseline condition. Both the 80°C and 100°C experiments were observed to have extraction efficiencies greater than 90% (which may mean that the temperature selected for the CA process is not the optimal temperature), which suggested that the slight variations (+/- 5°C) that were normally observed during the extraction experiments were not likely responsible for the change in the extraction efficiency.

Finally particle size was examined [B.2.7.3]. The crushed glass was sorted by particle size (using a set of mesh screens). For the particles that did not pass through a 25 mesh screen, the extraction efficiency in 5 vol. % nitric acid was observed to be only 28%, while for particles that did pass through a 25 mesh screen the extraction efficiency was over 40%. For particles smaller than the 60 mesh screen openings, but that did not pass through a 120 mesh screen the extraction efficiency was observed to be almost 60%. As a result of this experiment, it was decided to standardize the CA procedure somewhat by requiring that the crushed glass all pass through a 60 mesh screen. However, the effects of particle size alone still did not explain the observation that the extraction efficiency would sometimes be around 40% and sometimes be around 80%.

No reason for the apparently bi-modal extraction efficiency of the acid dissolution procedure has been determined. However, it is possible that this event may be due to variations in the acid concentration of the 5 vol. % nitric acid solution (perhaps the 5 vol. % is near the shoulder of a very steep extraction curve or is near to some threshold value). In any event, it was decided to increase the acid concentration to 25 vol. % (3.9 M HNO_3) to avoid this phenomenon. Further experiments using the more concentrated acid solution have not shown a similar phenomenon.

3.4.3 Determination of Cesium by ICP analysis

In analyzing the experimental data it was discovered that there was a problem with the cesium measurements. According to the cesium concentrations measured by the ICP, over 200% of the cesium present in the glass was extracted into solution. After observing this discrepancy, it was discovered that there was a spectral interference at the wavelength used to determine the cesium concentration (455.5 nm) due to cerium. As there were no other lines available for the determination of cesium concentration, another technique had to be investigated.

While there are no interference-free lines available to determine the concentration of cesium, there are interference-free lines available for cerium. Thus, it was proposed to measure the apparent cesium concentration due to cerium and determine a correlation between cerium concentration and apparent cesium concentration (a technique originally used to resolve spectral interferences in Neutron Activation Analysis). By subtracting the apparent cesium concentration (due to the cerium interference) from the observed cesium concentration, it theoretically would be possible to determine the actually cesium concentration in a given sample.

In attempting to calibrate the ICP to determine the cesium concentration it was discovered that without the added activity associated with the presence of cerium, there was not sufficient activity at the 455 nm wavelength to detect the peak above the background. This suggests that the actual detection limit for cesium is above 10 ppm (the highest concentration limit used in the calibration attempt). In order to determine the cesium concentrations in the sample, it would be necessary to use a more concentrated sample. However, the more concentrated samples from the CA process were not archived as they contained some amounts of the organic solution used in the decontamination process which was observed to react with the sample storage containers. Also, samples with significant organic concentrations can not be run through the ICP as they might damage some of the components of the system.

3.5 Summary of Experimental Work

Thorium can be recovered from a borosilicate glass matrix by using the CA process, which involves crushing the glass, dissolving the glass in nitric acid, and removing the contaminants via a solvent extraction process. The extraction step of the bench top process was able to extract 88.4 ± 6.8 % of the thorium from the glass in the initial extraction (the glass could possibly be recycled to extract the remaining thorium). The bench top solvent extraction process was able to reduce the levels of contaminants in the thorium to the levels seen in table 3.9, and was 30.2 ± 10.9 % efficient in recovering the thorium in the product stream (the recovery efficiency could be increased by recovering the thorium from the waste streams of the decontamination process). Overall, the CA process efficiency was 26.7 ± 9.9 %.

4. Analysis of Data

The primary focus of this work was to determine if (and how) a would-be proliferator could recover weapons-usable material from a borosilicate glass WGPu host form. The experimental work (described in the previous chapter) shows that it is possible to extract and purify plutonium (actually, thorium was used as a plutonium surrogate) from a borosilicate glass host form that contains not only fission products (simulated), but also criticality control elements (europium, samarium, and gadolinium; as proposed and examined by Sylvester (S5)). In this chapter, the question of weapons-usability will be addressed by determining the compressed critical mass of the recovered plutonium compounds. From the compressed critical mass results and the extraction and recovery efficiencies (determined in chapter 3 for the CA process), it will also be possible to determine the quantity of WGPu-loaded (2 wt. %) borosilicate glass that would be required to recover enough plutonium to construct one Trinity type device (3 critical masses).

4.1 Computational Techniques

The compressed critical mass of the reduced plutonium metal recovered from the borosilicate glass host forms was determined for a number of cases using the Monte Carlo Neutron Photon transport code to analyze a bare sphere of metal. The compressed critical mass was examined (as opposed to the uncompressed critical mass, for example) as it provides a "slightly more realistic configuration"[1] for determining the amount of plutonium needed for a weapon. Also, compressed critical mass was used for consistency in comparing the results of this work with the initial analysis of this particular borosilicate glass host form (S5)[2].

4.1.1 Monte Carlo Neutron Photon Transport Code

As the name of the code suggests, the Monte Carlo Neutron Photon transport code (MCNP) uses Monte Carlo techniques to follow the transport of a number of individual neutrons or photons through space. For each particle

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[1] Sylvester. A Strategy for Weapons-Grade Plutonium Disposal. p 37 (S5)

[2] Sylvester. A Strategy for Weapons-Grade Plutonium Disposal. (S5)

examined, statistical distributions are used to determine when, where, and how the particle interacts with the specified material. After examining the interactions of thousands of particles with the specified system, the results of the particle 'runs' are averaged to determine the characteristics of the system. A sample MCNP input deck is provided in appendix A3.

4.1.2 Computational Model[3]

Three principle assumptions were made for the purpose of determining the compressed critical mass of the recovered plutonium: homogeneity, a bare sphere geometry, and the use of fission products instead of neodymium and cerium in the materials.

Barring any separation of phases during the reduction of the plutonium solution to plutonium metal (4.2.1), the final metal should be fairly homogenous. Thus the assumption of homogeneity should be fairly accurate.

The assumption of a bare sphere geometry, with the metal surrounded by a vacuum, was made primarily to simplify the calculations (In an actual device, the plutonium pit would most likely be surrounded by neutron reflectors and explosives). However inaccurate this assumption may be, it should provide results that are adequate enough for comparative purposes.

One further assumption was required for the compressed critical mass calculations. The MCNP code does not have cross sections for either cerium or neodymium. These elements were present in the ARM-1 frit to simulate the behavior of fission products in the glass. For this calculation, it was assumed that the combined levels of cerium and neodymium in the final product were representative of the levels of fission products remaining in product. As such, the cross sections provided by MCNP for the average fission products were used.

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[3] paraphrased from Sylvester. A Strategy for Weapons-Grade Plutonium Disposal. pp. 36- 37 (S5)

To determine the critical mass of the recovered plutonium, an initial estimate for the critical radius of the sphere and the density of the material were provided to the MCNP code, which used the estimated values to determine the k_{eff} (the effective neutron multiplication value) of the system. The estimate of the critical radius was then adjusted until a k_{eff} value between 0.999 and 1.001 was reached (a neutron multiplication value of 1.0 implies that the system is exactly critical, with one neutron produced for every neutron absorbed). For the initial runs, a total of 40,000 particles were used to determine the critical radius that results in a k value within 0.05 (or less) of 1.0. For the next set of runs, a total of 80,000 particles were used and the target k value was within 0.01 to 0.005 of 1.0. Then the critical radius was found by using 200,000 particles over 50 cycles.

The density of the compressed plutonium metal was estimated to be twice that of uncompressed alpha-phase plutonium metal. Alpha-phase plutonium metal has a density of 19.5 g/cc[4]. The implicit assumption that the density of the recovered plutonium metal is relatively unchanged by the presence of the contaminant elements should not present a problem, especially when compared with the assumption that the fissile material in the device is compressed by exactly a factor of 2. If the final plutonium alloy has a density significantly less than alpha phase plutonium metal, it was assumed that the compression was sufficient so that the compressed plutonium alloy has a density of 39.0 g/cm^3. This value was used for the compressed density for all critical mass calculations for internal consistency.

4.2 Production of Plutonium Metal

The extraction and decontamination processes examined and detailed as part of the CA process yield a final product that contains plutonium ions in a nitric acid solution. In order to build a device, a would-be proliferator would most likely reduce the plutonium ions to metallic plutonium. Plutonium metal is the most likely form as it will provide the smallest critical mass for a given amount of plutonium (for example, the use of plutonium oxide, PuO_2, would

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[4] DeVolpi, A. *Fissile Materials and Nuclear Weapons Proliferation.* p. 93. (D1)

increase the compressed critical mass from 2.7 to 7.1 kg)[5]. A number of processes that could potentially be used to reduce the plutonium ions to plutonium metal are detailed in section 2.6 of this work.

The reduction of the thorium (the plutonium analog) and fabrication of thorium metal were not attempted experimentally in this work. While the processes do not appear to be incredibly complex or difficult, the safe reduction of thorium (and plutonium) does require special equipment, which was not available.

As the reduction was not carried out experimentally, the following assumptions were made in order to determine the composition of the plutonium metal that would be recovered using the CA process:

1) The reduction process does not result in the loss of plutonium. Thus, it does not reduce the process efficiency;

2) The reduction process does not provide any additional removal of contaminants from the plutonium. No additional decontamination is provided by the reduction processes.

The first assumption that no material is lost is not a bad assumption, as it should be possible for a would-be proliferator to recover almost all material 'lost' from the reduction process (it may not be economical, but it is possible). The second assumption is fairly conservative, as the various processes involved in the reduction of plutonium metal have been demonstrated to provide some additional decontamination. However, as decontamination factors were not available for all of the elements involved for all of the processes that could potentially be used in the reduction process, it was simpler to just assume that no additional decontamination was provided by the reduction process. As a result of this assumption, the plutonium compounds analyzed will be more contaminated and will most likely have a larger critical mass than plutonium

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[5] Sylvester. A Strategy for Weapons-Grade Plutonium Disposal. p. 39 (S5)

compounds actually recovered by the CA process and reduced to plutonium metal.

4.3 Cases Examined

Five separate plutonium compositions were examined to determine the compressed critical mass of the plutonium recovered from a borosilicate glass host form (with added spoiler elements). The first three examined compositions were determined from the experimental performance of the CA process in this work (after a theoretical reduction of the nitric acid solution to metal). In order to bound the performance of the CA process, the compressed critical mass was determined not only for the average CA process product composition, but also for the 'best' and 'worst' product compositions obtained (where best and worst refer to the plutonium weight fraction in the reduced metal; the 'best' composition had the highest plutonium weight fraction and the 'worst' composition had the lowest). The other two cases examined assumed that a theoretical one-cycle PUREX process [2.5.3] was used to decontaminate the product of an average acid dissolution extraction process (the first stage of the CA process).

4.3.1 Baseline Case

The baseline case for this work used the composition of the average product solution generated by the crushed glass in acid dissolution process (the CA process). The composition of the recovered plutonium metal (if we substitute plutonium for thorium) is given in table 4.1.

Using the isotopics listed for weapons-grade plutonium in table 2.3, the radius of a critical bare sphere was determined using MCNP to be 3.18 cm, which corresponds to a compressed critical mass of 4.72 kg of alloy. If we assume that the borosilicate glass is loaded at 2 wt. % plutonium oxide and if we use the average process efficiency (p_{th} = 26.72 %), then a would-be proliferator would need to obtain 2087.4 kg of glass (14.16 kg of plutonium alloy) in order to recover enough fissile material for a Trinity type device.

Table 4.1: Baseline Plutonium Alloy Composition

Table 4.1: This table contains the average composition of the plutonium recovered using the CA process. The mass fraction of the individual contaminants are given below as a percentage of the total mass.

Element	Mass Fraction (%)
Plutonium (Pu)	**69.4 %**
Europium (Eu)	5.1 %
Gadolinium (Gd)	4.4 %
Samarium (Sm)	5.1 %
Fission Products (avg. FP)	8.9 %
Silicon (Si)	0.9 %
Sodium (Na)	3.5 %
Boron (B)	2.6 %

4.3.2 Best CA Product case

In this case, the composition of the plutonium metal was taken to be that of the product solution of the CA run that had the highest weight percentage of plutonium (experiment LB [B.5.2]). This case was chosen as it provides an upper bound on the effectiveness of the CA process (as it was done in this experiment), and thus could be considered the best a would-be proliferator could achieve without using more advance technology and equipment. The plutonium metal composition used for this case is given in table 4.2.

The compressed critical mass of this alloy, determined by MCNP, is 3.295 kg, which corresponds to a bare sphere of radius 2.82 cm. The process efficiency for the LB experiment (the 'best' CA product) can be determined from the extraction efficiency (e_{th} = 88.9 %) and the recovery efficiency (r_{th} = 28.5 %) using equation 3.3a to be 25.3 %. Given this process efficiency, a would-be proliferator would require 1870.8 kg of borosilicate glass (at 2 wt. % PuO_2) for a Trinity type device, without having to recover plutonium from the waste streams of the CA process. If the average CA process efficiency (p_{th} = 26.7 %) were used in this calculation, the amount of glass needed drops to 1797.0 kg of glass.

Table 4.2: CA Process- 'Best' Plutonium Alloy Composition

Table 4.2: This table contains the best composition of the plutonium recovered using the CA process (the least contaminated). The mass fraction of the individual contaminants are given below as a percentage of the total mass.

Element	Mass Fraction (%)
Plutonium (Pu)	**85.47 %**
Europium (Eu)	2.65 %
Gadolinium (Gd)	2.48 %
Samarium (Sm)	2.91 %
Fission Products (avg. FP)	3.90%
Silicon (Si)	0.77 %
Sodium (Na)	1.45 %
Boron (B)	0.34 %

4.3.3 Worst CA Product case

In this case, the composition of the plutonium metal was taken to be that of the product solution of the CA run that had the lowest weight percentage of plutonium (experiment 02 [B.5.2]). This case was chosen as it provides a lower bound on the effectiveness of the CA process (as it was done in this experiment), and thus could be considered the best that the waste form could perform in regards to deterring or complicating the recovery of the WGPu from the glass.

The compressed critical mass of this alloy was determined to be 8.237 kg using MCNP, based on a critical radius for the bare sphere of 3.83 cm. The process efficiency for the 02 experiment (the 'worst' CA product) can be determined from the extraction efficiency (e_{th} = 86.9 %) and the recovery efficiency (r_{th} = 23.8 %) using equation 3.3a to be 20.7 %. Given this process efficiency, a would-be proliferator would require 3618.0 kg of borosilicate glass (at 2 wt. % PuO_2) to recover the three compressed critical masses needed for a Trinity type device, without recovering plutonium from the waste streams of the CA process. If the average CA process efficiency (p_{th} = 26.7 %) were used in this calculation, the amount of glass needed would be 2802.6 kg.

Table 4.3: CA Process- 'Worst' Plutonium Alloy Composition

Table 4.3: This table contains the worst composition of the plutonium recovered using the CA process (the most contaminated). The mass fraction of the individual contaminants are given below as a percentage of the total mass.

Element	Mass Fraction (%)
Plutonium (Pu)	**53.28 %**
Europium (Eu)	6.18 %
Gadolinium (Gd)	5.81 %
Samarium (Sm)	6.39 %
Fission Products (avg. FP)	14.12%
Silicon (Si)	0.69 %
Sodium (Na)	7.19 %
Boron (B)	6.34 %

4.3.4 Ideal PUREX Decontamination

The CA process used to recover the plutonium from the borosilicate glass uses a very crude solvent decontamination process. While this may be representative of the technology available to a sub-national or terrorist group, nation state and weapons states interested in recovering the plutonium would most likely have access to more modern decontamination techniques and equipment, such as a PUREX plant. This case examined the use of a PUREX facility to decontaminate the plutonium solutions extracted from the glass. In this case, a decontamination factor of 10^4 was used for all contaminants[6]. It was assumed that the concentration of contaminants in the feed solution for the PUREX process was the average contaminant concentrations from the first stage of the CA process (table 3.8). For this case it was also assumed that head-end and/or tail-end strike processes were used to provide sufficient decontamination from silicon, sodium, and boron, which are not typically

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[6] A value of $2*10^4$ is given as the decontamination factor for the first stage of a commercial PUREX facility in Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 534 (K2)

present in spent fuel elements and which may be problematic to the PUREX process.

The compressed critical mass calculated for this alloy composition is 2.425 kg with a critical radius of 2.55 cm for the bare sphere (again using MCNP). If we assume that the extraction process was as efficient as the average CA process was in the lab (avg. e_{th} = 86.2 %) and that the PUREX type solvent extraction process is 95 % efficient (which is probably on the low side) in recovering plutonium, then it would be possible to recover enough material from 504.0 kg of borosilicate glass (loaded to 2 wt. % plutonium oxide) to create a device similar in design to the Trinity device.

Table 4.4: Plutonium Alloy Composition for Ideal PUREX case

Table 4.4: This table contains the composition of the plutonium metal resulting from an ideal PUREX decontamination process. The mass fraction of the individual contaminants are given below as a percentage of the total mass.

Element	Mass Fraction (%)
Plutonium (Pu)	**99.87 %**
Europium (Eu)	0.0105 %
Gadolinium (Gd)	0.0102 %
Samarium (Sm)	0.0114 %
Fission Products (avg. FP)	0.032 %
Silicon (Si)	0.0014 %
Sodium (Na)	0.0413%
Boron (B)	0.0213 %

4.3.5 Non-Ideal PUREX Decontamination

As mentioned in the previous case, the PUREX process was not designed to remove the glass-forming elements (silicon, sodium, and boron), which are not normally present in appreciable quantities in spent fuel. The PUREX process, which is basically a multi-stage solvent extraction process, should be able to achieve at least the same decontamination factor for these elements as the simple solvent extraction process used as part of the CA process. For this case, a decontamination factor of 10^4 was used for the rare earth elements (typical of the first stage of a commercial PUREX plant[7]) and the average decontamination factors from the CA process (table 3.9) were used for silicon (DF = 10.92), sodium (DF = 81.10), and boron (DF = 56.13). The composition of the plutonium metal after a non-ideal PUREX process and a theoretical reduction process is given in table 4.5.

The compressed critical mass calculated the non-ideal PUREX decontamination case is 2.460 kg (the critical radius was determined by MCNP to be 2.56 cm). If we assume that the extraction process was as efficient as the average CA process was in the lab (avg. e_{th} = 86.2 %) and that the PUREX type solvent extraction process is 95 % efficient (which is probably on the low side) in recovering plutonium, then it would be possible to recover three compressed critical mass (enough for a Trinity type device) from 464.4 kg of borosilicate glass (loaded to 2 wt. % plutonium oxide). Note that this value is lower than for the ideal PUREX decontamination case, even though the concentration of non-fissile elements is higher. This can most likely be attributed to the process by which the critical radii were determined, as the radii were selected when k_{eff} was within 0.001 of 1.0 (which is not an incredibly small difference for neutron multiplication values), as well as the statistical spread associated with the k_{eff} values determined using MCNP (which was typically on the order of 0.002 or less for the final k_{eff} determinations).

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[7] A value of $2*10^4$ is given as the decontamination factor for the first stage of a commercial PUREX facility in Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 534 (K2)

Table 4.5: Plutonium Alloy Composition for Non-Ideal PUREX case

Table 4.5: This table contains the composition of the plutonium metal resulting from a non-ideal PUREX decontamination process. The mass fraction of the individual contaminants are given below as a percentage of the total mass.

Element	Mass Fraction (%)
Plutonium (Pu)	**90.695 %**
Europium (Eu)	0.0095 %
Gadolinium (Gd)	0.0092 %
Samarium (Sm)	0.0103 %
Fission Products (avg. FP)	0.0235 %
Silicon (Si)	1.179 %
Sodium (Na)	4.625 %
Boron (B)	3.446 %

4.4 Summary of Analytical Work

Using the bare sphere computational model describe above, the compressed critical masses were determined for a number of scenarios. The first three scenarios show the effectiveness of the CA process in recovering a usable plutonium alloy from the borosilicate glass host form. For the CA process, the average, best, and worst product compositions were examined to determine the potential range of performance for the process. Additionally, two cases were examined in which the bench top solvent extraction process was replaced with a plant-scale PUREX decontamination process. In the first PUREX case, it was assumed that all contaminants were reduced by a factor of 10^4 (typical for a 1 stage PUREX process). In the second, non-ideal case, it was assumed that all elements except for the primary glass constituents (sodium, silicon, and boron) were removed with a decontamination factor of 10^4, while the glass constituents were removed with the same decontamination factor that was observed in the bench top experiments.

From these critical masses and the average process efficiencies for the CA process (with a recovery efficiency of 95% assumed for the 2 PUREX cases), the amount of 2 wt. % WGPu glass needed to extract enough fissile material to build a device similar to the Trinity device (3 critical masses).

If the WGPu is disposed of in 2000 kg glass logs (at 2 wt % plutonium oxide), a would-be proliferator using the CA process would most likely have to either steal two logs or use some kind of recovery process to recover the plutonium from the waste streams of the CA process in order to recovery enough material for a Trinity type nuclear device. However, a would-be proliferator using the acid extraction and a PUREX-type decontamination process (or a decontamination process with a similar recovery efficiency), could recover more than enough material from 1 log for 3 Trinity type devices.

Table 4.6: Compressed Critical Mass Calculation Results

Table 4.6: This table contains the compressed critical mass (CCM) results determined for the 5 listed cases using MCNP. The amount of WGPu-bearing borosilicate glass (2 wt. % loading) required to recover 3 CCM (1 Trinity mass) is also provided.

Case Examined	CCM	Glass Required
Average	4.72 kg	2087.4 kg
Best Case	3.295 kg	1797.0 kg
Worst Case	8.237 kg	3618.0 kg
Ideal PUREX	2.425 kg	504.0 kg
Non-Ideal PUREX	2.460 kg	464.4 kg

5. Summary and Conclusions

5.1 Summary of Experimental Work

The primary focus of this work was to examine the question of retrieving weapons-grade plutonium (WGPu) from a borosilicate glass host form in order to determine what, if any, resistance to proliferation could be gained by vitrifying the WGPu. The host form studied in this work was a borosilicate glass matrix with added simulated fission products (the ARM-1 or Advanced Reference Material)[1]. The glass frit was further modified by the inclusion of thorium, europium, gadolinium, and samarium. The thorium was added as a surrogate for plutonium, and constituted 2 wt. % of the final glass composition. The rare earths (Eu, Gd, and Sm) were added for long-term criticality control and to possibly increase the proliferation resistance of the host form[2].

After examining a number of potential extraction and decontamination processes, the Crushed glass - Acid dissolution process (CA process) was developed to recover the plutonium from the glass. In brief, the CA process uses a 25 vol. % nitric acid solution (3.8M) to leach the plutonium and other elements from the pulverized glass matrix (particle size > 250 microns). The fission products, criticality control elements, and remaining glass formers are separated from the plutonium using a simple solvent extraction process.

Once the CA process had been developed, it was tested experimentally to determine its effectiveness. On average, the extraction stage of the process was able to remove 88.44 ± 6.77 % of the plutonium surrogate from the glass. The average concentration of the contaminants, relative to the plutonium surrogate concentration in solution, and the associate 97.7 % confidence limits (2 standard deviation error) are shown below in table 5.1.

The extracted solution was then decontaminated with a solvent extraction process. In the laboratory, the recovery efficiency of this stage of

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[1] Sylvester, K. A Strategy for Weapons-Grade Plutonium Disposition. p. 47 (S5)
[2] ibid. pp. 62-71 (S5)

the process was 30.21 ± 10.91 %, meaning that around 30 % of the plutonium surrogate in the feed solution (from the extraction stage) was recovered in the product solution. From the recovery efficiency and the extraction efficiency, the overall process efficiency for the CA process was determined to be 26.7 ± 9.9 % (by equation 3.3a). The average decontamination factors observed for the solvent extraction process are listed in table 5.2, along with the best and worst observed decontamination factors.

Finally, MCNP was used to determine the compressed critical mass of the plutonium recovered from the borosilicate glass to see how the vitrification would affect the suitability of the plutonium for building a weapon. Once the compressed critical mass was determined, it was possible to determine how much glass a would-be proliferator would need to be able to recover one compressed critical mass (CCM) of plutonium. To determine this value, it was assumed that the WGPu-loading in the borosilicate glass was 2 wt. % plutonium oxide. Using the average process efficiency, the amount of glass required to recover enough plutonium to build a device similar to the Trinity device was determined for the average product composition of the CA process, as well as for the 'best' and 'worst' case compositions, with the assumption that the proliferator does not recover any plutonium from the waste streams. These results are shown below in table 5.3

To account for the crude nature of the solvent extraction cycle, it was assumed that a one stage plant-scale PUREX was used for the decontamination process in two additional cases. In the first case, it was assumed that a decontamination factor (DF) of 10^4 was obtained for all contaminants[3]. In the second case, it was assumed that the 10^4 decontamination factor was for all of the fission products and rare earths. The average decontamination factors for the solvent extraction done in the lab were used for the decontamination factors for this non-ideal PUREX process for silicon, sodium, and boron. This second case was examined because the PUREX process was not designed to

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[3] Katz, et. al., list a decontamination factor of $2*10^4$ for the first stage of a commercial PUREX plant. Katz, Seaborg, and Morss. The Chemistry of the Actinide Elements. p. 534. (K2)

handle these elements and there has been some concern that these elements may pose problematic for the PUREX process. The observed DF's were used for sodium, silicon, and boron because it was assumed that any large scale process should be able to at least meet the same decontamination that was obtained in the lab. A recovery efficiency of 95% for plutonium was assumed for the plant-scale PUREX process to account for the use of solvent recycle and other recovery techniques. The critical mass and glass requirements for recovering the material to build one Trinity type device are given in table 5.4 for these cases.

The glass required to recover enough material for a Trinity type device from borosilicate glass using a non-ideal PUREX process was determined to be less than the amount required with an ideal process, even though the ideal process would result in significantly less contamination of the plutonium alloy. One possible explanation of this could be that the critical radii determine through MCNP for the two cases were very close to each other. The method for determining the critical radius of the cases did have some associated standard deviation (due to the statistical nature of the process), which would be magnified by this calculation (the critical mass is determined from the volume of the sphere, which is proportional to the cube of the radius).

Table 5.1: Average Contaminant CF's for Extraction Process

Table 5.1: This table contains the average contamination factors (CF's) for the extraction stage of the CA process. Along with the average CF is the absolute error associated with the 97.7 % confidence interval (2 standard deviation).

element	CF	error
Ce	0.654	0.024
Eu	1.055	0.051
Gd	1.023	0.028
Sm	1.144	0.035
Nd	2.533	0.191
Si	0.142	0.053
Na	4.136	0.505
B	2.133	0.090

Table 5.2: Average Decontamination Factors for the CA Process

Table 5.2: This table contains the average decontamination factors (DF) for the product solution from the second stage of the CA process, along with the highest and lowest observed DF's. (note: this table is also given as table 3.9)

element	Average DF	High	Low
Ce	27.25	55.19	13.83
Eu	14.45	35.24	8.90
Gd	15.98	35.10	9.59
Sm	15.46	34.20	9.30
Nd	24.36	68.09	12.60
Si	10.92	1498.2	11.54
Na	81.10	1608.5	24.53
B	56.13	568.0	19.04

Table 5.3: Compressed Critical Mass Results for the CA Process

Table 5.3: This table contains the compressed critical masses (CCM) for the average product of the CA process, as well as for the best and worst case scenarios. Also included is the amount of glass that a would be proliferator would require to recover enough material for one Trinity type device (three compressed critical masses) without waste recycle.

Case Examined	CCM	Glass Required
Average	4.72 kg	2087.4 kg
Best Case	3.295 kg	1797.0 kg
Worst Case	8.237 kg	3618.0 kg

Table 5.4: Compressed Critical Mass Results for the PUREX Cases

Table 5.4: This table contains the compressed critical masses (CCM) for the two PUREX decontamination cases, described above. The glass required entry indicates the amount of borosilicate glass that would be required to recover enough material for 1 Trinity type device (3 CCM's).

Case Examined	CCM	Glass Required
Ideal PUREX Decontamination	2.425 kg	504.0 kg
Non-Ideal PUREX Decontamination	2.460 kg	464.4 kg

5.2 Conclusion

After a search of the open literature, it was possible to extract a plutonium surrogate (thorium) from borosilicate glass using common laboratory equipment and techniques. At the bench top scale, the extraction required a mortar and pestle to crush the glass, a laboratory oven, and some common chemicals and glassware (the chemicals were nitric acid, tributyl phosphate, and kerosene). A pilot plant version of the process could be done with a ball mill and some mixer-settlers. On average, this process recovered enough of a plutonium surrogate (thorium) to build a Trinity-type device from 2087 kg of glass (loaded at 2 wt. % plutonium). With some work, the process efficiency could be increased, which would reduce the amount of material required to recover enough WGPu for a Trinity-type device (for example, with the best results for the CA process, only 1797 kg of glass would be needed). For a more sophisticated proliferator, the amount of glass required to recover the enough WGPu for a Trinity-type device would be much less (between 450 kg and 500 kg of 2 wt. % WGPu glass)

Without a radiation barrier, the chemical processing required to extract WGPu from borosilicate glass is not sufficient to prevent a would-be proliferator from easily recovering the plutonium for use in a nuclear device. The presence of a radiation barrier would significantly complicate the process, as remote handling and operations would be required for most of the process. The radiation barrier would be a factor in handling the glass logs, as well as in the crushing, extraction, and decontamination stages. After the decontamination stage, the radiation barrier (primarily cesium) should be reduce enough to permit hands-on work for the reduction stages. Using the CA process, the radiation barrier would be reduced by a factor of 80 or more (using sodium as an analog for cesium, as cesium data could not be determined). This would reduce the radiation barrier from a reference level of 2000 rad/hr to 25 rad/hr. A more sophisticated proliferator could expect to reduce the cesium levels by a factor of 10^4 (the PUREX process is designed to remove fission products such as cesium), which would reduce the reference radiation barrier to only 0.2 rad/hr.

6. Observations and Future Work

In order to determine if a host form is an acceptable final form for the final disposition of WGPu, it is necessary to consider whether or not the host form meets the spent fuel standard proposed by the National Academy of Sciences [2.2.1] . For the various vitrification/ceramification proposals, it is also beneficial to examine how a given host form would compare to other vitrification/ceramification options. These issues will be addressed in this section, along with some possible means of increasing the proliferation resistance provided by vitrifying WGPu in a borosilicate glass host form.

6.1 Spent Fuel Standard

The National Academy of Sciences (NAS) recommends that the United States and Former Soviet Union states (FSU) dispose of the excess weapons-grade plutonium (recovered from dismantling the nuclear weapons programs) "in a form from which the plutonium would be as difficult to recover for weapons use as the larger and growing quantity of plutonium in commercial spent fuel"[1]. This statement is the basis of the spent fuel standard for the disposition of WGPu. It is important to note that this is the only definition of the spent fuel standard (SFS). Neither the NAS nor the U.S. Office of Fissile Materials (OFMD) defined any quantitative measures for determining if a given option meets or exceeds the SFS.

6.2 Barriers to Proliferation

One way to examine the proliferation resistance provided by a given WGPu disposition option is to examine the barriers to the recovery and re-use of the WGPu the final host form presents to a would-be proliferator. Some barriers to consider in determining if a host form meets the spent fuel standard could include the following:

Physical: How much material would-be proliferator need to recover enough WGPu to make a device?

Chemical: How difficult would it be for a would-be proliferator to extract weapons-usable plutonium from the host form?

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[1] NAS report. *Management and Disposition of Excess Weapons Plutonium.* 1994. p 2. (N1)

Isotopic: How much of the plutonium is ^{239}Pu?

Radiation: Does the host form provide itself with a self-protecting radiation field? Is remote handling required to work with the material?

Institutional: How well guarded is the material? How easy would it be for a would-be proliferator to steal the material?

Informational: How well know are the technology and processes that will be needed to recover and re-use the WGPu in a device?

If a host form provides the same barriers to the recovery of plutonium as spent fuel, it would should meet the spent fuel standard. However, it may not be necessary for a host form to provide all of the barriers to proliferation listed above to meet the spent fuel standard. For example, vitrifying WGPu in borosilicate glass with High Level Waste (HLW) is considered to meet the SFS by the NAS, even though it does not alter the isotopics of the plutonium (and thus provide an isotopic barrier to proliferation).

6.3 Recovery of Plutonium from Spent Fuel

In order to compare a host form with spent fuel, it is first necessary to examine how a proliferator would recover plutonium from spent nuclear fuel. The first step in the recovery of plutonium from spent fuel is to physically cut the fuel. The fuel is then dissolved in nitric acid, leaving the cladding relatively intact. The chemistry of the resulting solution is then adjusted in preparation for the primary decontamination stage, which is accomplished by contacting the feed solution (the nitric acid solution containing the plutonium and the fission products) with a 30 vol. % solution of TBP in a paraffinic hydrocarbon diluent (the PUREX process). The plutonium and uranium from the dissolved fuel are preferentially taken up in the organic phase, which is then physically separated from the aqueous phase. The plutonium in the organic phase is then reduced to the trivalent state and separated from the uranium. The solvent extraction decontamination processes is then repeated to further purify the plutonium stream.[2] The recovered plutonium can then

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[2] PUREX process paraphrased from Benedict, et. al. Nuclear Chemical Engineering. pp. 466-468. (B2)

be reduced to metallic plutonium via a number of well-known processes [2.6]. The plutonium recovered from spent nuclear fuel is not normally weapons-grade plutonium (unless the reactor was run in such a way as to produce WGPu), and typically has the isotopic composition given for RGPu in section 2.7 (table 2.3).

6.4 Recovery of Plutonium from Borosilicate Glass

The CA process developed as part of this work could easily be scaled up for use in recovering plutonium from borosilicate glass at the plant scale (unlike the laboratory scale experiments done here). The monolithic glass logs would be mechanically cut into pieces suitable as the feed into a ball mill (or other similar piece of equipment), which will crush the glass until it passes a 60 mesh screen. The crushed glass would then be poured into a reaction vessel, where it would be leached with a 25 vol. % nitric acid solution (3.8M HNO_3) at 90°C for 2 hours. The solution could then be filtered to remove the undissolved glass, which could conceivably be recycled to remove any remaining plutonium. The leachate solution could then be used as the feed for a PUREX-type solvent extraction process to purify the plutonium (as done in the CA process). Any head-end strike processes that are determined to be necessary to prepare the feed for the decontamination process can easily be added to the process line before the decontamination stage.

6.5 Borosilicate Glass and the Spent Fuel Standard

The recovery of WGPu from borosilicate glass uses almost exactly the same procedure as the PUREX process for recovering plutonium from spent fuel. The primary exception is that instead of decladding the fuel and dissolving the mixed oxide fuel pellets, a would-be proliferator would have to crushed the glass and dissolve out the plutonium oxide with nitric acid. Once the plutonium is in solution, the same equipment could be used to decontaminate and recover the WGPu as to recover the RGPu from spent fuel.

While the general procedure is for recovering plutonium from a borosilicate glass host form is almost identical to reprocessing spent fuel to recover the plutonium, recovering the WGPu from the borosilicate glass does provide a few additional challenges. Unlike dissolved spent fuel, the dissolved WGPu-loaded glass solution contains some of the glass-forming elements, such as boron, sodium, and silicon. These elements may prove to be a bit of a problem for the PUREX process as they may build up to appreciable levels in the organic solvent. In this work, for example, the decontamination factors for silicon were reduced when the solvent was recycled and used for a second decontamination cycle compared to a two-cycle decontamination process that used fresh solvent for both stages (tables B.14 and B.15). This may require the addition of some head-end processes to remove the silicon (and possibly the other glass forming elements as well) to the standard PUREX process.

In terms of a chemical barrier to proliferation, borosilicate glass provides a barrier to the recovery of plutonium that meets or possibly even exceeds (depending on the complexity of any needed head-end processes). Borosilicate glass also provides a physical barrier to proliferation by increasing the amount of material that a would-be proliferator would need to steal from just a few kilograms of metal (a 'pit') to almost 155 kilograms of glass (almost 700 kg of glass would be required if a PUREX plant was not available for the decontamination and not waste recycling were used). With the addition of cesium or radioactive waste to the glass, borosilicate glass can provide the same radiation barrier as spent fuel. Borosilicate glass does not, however, alter the isotopic composition of the plutonium. However, isotopic dilution of ^{239}Pu is not an explicit requirement of the spent fuel standard, and unless it becomes a part of the standard, then borosilicate glass appears to meet the Academy's spent fuel standard.

6.6 Comparison with Other Immobilization Host Forms

In addition to vitrifying the WGPu in borosilicate glass and burning it in a reactor, the Office of Fissile Materials Disposition (OFMD) is examining embedding the WGPu in various ceramics. Two of the front-runners for ceramic host forms are Zircon and monazite. While both of these minerals are chemically quite durable (which is part of the reason they are being considered as host forms for WGPu), both minerals are also the primary sources of a number of rare earths and other elements. As such, commercial processes have been developed to extract rare earths (and thus actinides, presumably) from these matrices.

6.6.1 Recovery of Plutonium from Monazite

Monazite is one of the primary sources of thorium, as well as some rare earths which can be co-recovered along with the thorium. It has been suggested that the WGPu can be embedded in monazite, replacing the thorium in the matrix. As the plutonium is assumed to replace the thorium in the matrix, it can also be assumed that the plutonium can be recovered by the same techniques. Two commercial processes for the recovery of thorium from monazite are listed in section 2.4.2 of this work. Of these two, the sulfuric acid process[3] will be discussed, as the extracted thorium solution is typically purified by a solvent extraction process. Thus, it can be expected that the plutonium-bearing nitric acid solution would be suitable for use as a feed in a PUREX plant (if desired)

In this process, monazite sands are digested in concentrated sulfuric acid (93% sulfuric acid) for 4 hours at 210°C to create a water soluble 'dough'. The monazite sulfates are then dissolved in water, diluted, and the pH is raised to 1.5 before the thorium (and presumable plutonium) is precipitated by the addition of oxalic acid. The oxalates are then digested with sodium hydroxide to form hydroxides (and to allow the recovery of the oxalic acid), which is then dissolved in nitric acid. The resulting nitric acid solution can then be adjusted as desired for use as a feed solution in any desired decontamination process (for thorium, typically a solvent extraction procedure is used).

The processing required to recover plutonium from monazite is significantly more complicated than for recovering plutonium from borosilicate glass. Both processes require that the monolith (it is assumed that the monazite or glass will be formed as large monoliths to increase physical barrier) be crushed into a powder. However, the sulfuric acid process requires two additional digestion stages (the sulfuric acid digestion and the hydroxide digestion of the oxalate cake), as well as an additional precipitation step before the plutonium would be in a nitric acid solution that could be used in a PUREX-type decontamination procedure. Thus, monazite would provide a stronger chemical barrier to proliferation than either borosilicate glass or

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[3] Barghusen and Smutz. "Processing of Monazite Sands", Ind. Chem. Eng. Dec. 1958. pp. 1754-1755. (B1)

spent fuel. If cesium can be incorporated into the monazite matrix, then monazite would be able to provide a radiation barrier. Embedding the WGPu in monazite does not, however, alter the isotopics of the plutonium (no isotopic barrier).

6.6.2 Recovery of Plutonium from Zircon

Natural zircon is a primary source of both hafnium and zirconium. As such, a number of processes have been developed to 'crack' zircon. One of the more straight-forward methods is the alkali fusion method [2.4.3.2], which was developed by the Ames laboratory. In this process, the zircon would be mixed with sodium hydroxide and heated in a furnace at 565°C. As the temperature rises, the melted sodium hydroxide will react with the zircon to form water and a number of sodium oxides (such as Na_2ZrO_3 and Na_2SiO_3). The resulting porous frit is then ground and leached with water to extract the silicon (Na_2SiO_3). The residue is then leached with acid to dissolve the zirconium (Na_2ZrO_3) into solution leaving the un-reacted zircon to be re-used.

This process has not yet been used to extract plutonium from a synthetic zircon. A would-be proliferator would have to do some experiments to determine where the plutonium is extracted and what other contaminants are extracted with the plutonium. As with monazite, chemically recovering WGPu from zircon is more complicated than recovering WGPu from either spent fuel or borosilicate glass. Also, the recovery of plutonium from zircon is currently an area of research, and until a process is developed, there will be an information barrier that a would-be proliferator would have to overcome to recover the WGPu. Embedding the WGPu in zircon will not provide any isotopic dilution, and will provide a radiation barrier only if cesium is incorporated in the zircon matrix.

6.7 Strategies to Increase the Proliferation Resistance of Borosilicate Glass

The primary goal of vitrifying the WGPu in borosilicate glass is to increase the difficulty a would-be proliferator would encounter in trying to recover the WGPu for use in a nuclear weapon. One of the primary reasons for studying how a proliferator would go about extracting the WGPu from a host form is to determine what could be done to complicate the recovery process.

In order to recover usable WGPu from borosilicate glass (with fission products and added rare earth elements), the proliferator would need to build and operate a facility to accomplish the following stages of the CA process: removing the glass from its container/cask, crushing the glass into a powder, dissolving the glass in a nitric acid solution, and then decontaminating the plutonium solution (presumably using a solvent extraction process). Anything that is done to interfere with or complicate any of these steps will serve to complicate the recovery of WGPu from borosilicate glass.

6.7.1 Opening the Container

The task of opening the cask or container containing the glass (whatever the final container for the WGPu glass will be, along with any overpack, etc... required for storage, transport, or disposal) could be complicated in a number of ways.

As a first line of defense, either some or all of the casks could be booby-trapped in such a way that they explode if the cask is cut open. If all the casks were rigged to explode, it would require a would-be proliferator to take the time (and effort) to disarm the containers before the recovery process could begin, or else risk damaging equipment and personnel. This could be quite expensive if remote handling equipment (which would be needed to overcome the radiation barrier) were damaged and needed to be replaced or repaired (especially after the equipment and work area had been contaminated) Also, it would be harder to conceal the proliferation efforts if there were a lot of explosions on the site. If only some of the casks were booby-trapped, a would-be proliferator would wither have to treat all of the casks as rigged or would have to find some method to determine if a cask had been rigged to explode. This method would, however, increase the risks associated with the recovery of the plutonium if it ever becomes necessary. Also, the explosives may be degraded by exposure to a strong radiation field, which could either render them more dangerous (which might further complicate the handling and disposal of the casks) or degrade their effectiveness.

A milder version of this technique would be to rig the containers to emit a radio signal when opened, or to perhaps fill the containers with some easy-to-trace gas compound that would be released when the container is opened.

Both of these mechanisms could be used by a monitoring agency to determine that a container has been opened as well as to possibly trace the organization responsible. This type of protection would only work if the proliferator didn't know of it's existence (locator type systems such as these would be fairly easy to defeat) and if the proliferator had some reason to fear detection.

6.7.2 Crushing the Glass

Once the glass is removed from its container/cask, it will be necessary to crush the glass into a fairly fine powder. Two possible ways to complicate this process are to modify the glass so that it is more difficult to make it into a fine powder and to modify the glass so that might damage the equipment crushing it.

In order to make the glass more difficult to crush into a fine powder, it might be possible to add to the glass matrix (or to the backfill of the canister) some kind of cementing agent (or glue) that would be activate by pressure or perhaps by water (if water or an acid solution are used to allow the glass powder to be pumped around more easily). The purpose of the cementing agent would be to increase the particle size of the resulting glass powder, which will decrease the surface area available for the extraction process and reduce the amount of plutonium extracted from the glass in the first pass.

Perhaps a more feasible technique to complicate the grinding process would be to include some kind of ultra-hard material (silicon carbide, for example) in the glass to try to damage the equipment used. If a would-be proliferator is force to replace or repair the grinding equipment (which would be contaminated by fission products in the glass), it could slow down the recovery process as well as increase the cost of recovering the plutonium. Damaging the equipment would also serve to add additional contaminants to the plutonium stream (whatever material is ground off of the equipment), which may or may not effect the decontamination process. Before this is considered, it would be necessary to determine the effects of adding the ultra-hard material inclusions on the long-term durability of the glass.

6.7.3 Acid Dissolution

After the glass is crushed, the plutonium must be extracted from the glass powder. This can be accomplished by dissolving the glass in a nitric acid solution. One way to complicate this stage of the recovery process would be to include some unreacted metals (in a fine powder, perhaps) in the glass matrix itself. When the glass powder (containing the unreacted metal) comes into contact with the acid, the metal would react to generate hydrogen, which would have to be controlled to prevent an explosion.

6.7.4 Solvent Extraction

The final stage of the recovery process is the decontamination stage, which presumably would be a solvent extraction process, such as the PUREX process.

One way to complicate the decontamination process would be to add something to the glass that would form phosphate or sulfate ions in solution, as these ions tend to interfere with the solvent extraction of plutonium. This would require a would-be proliferator to either add a head-end strike process to remove the phosphate or sulfate ions, or to use another process to decontaminate the plutonium.

Another way to complicate the solvent extraction process would be to attack the organic solvent. One way this could be done by increasing the radiation barrier in the glass to accelerate the radiation-induced breakdown of TBP. Another way would be to coat the glass with an organic that will interact with the TBP and reduce its affinity for plutonium. To combat these processes, a would-be proliferator would have to either replace the organic solvent more often (increasing the cost of the recovery) or add in a process before the solvent extraction to remove the agent responsible (either the radionuclides or the organic). How either of these techniques would affect the durability of the glass would need to be determined.

One last way to complicate the solvent extraction process would be to increase the relative loading of contaminants to such a degree that an additional decontamination cycle would be needed. This would probably require not only increasing the concentration of the contaminant in the glass, but also reducing the loading of plutonium in the glass, and would most likely increase the cost of vitrifying the plutonium.

6.7.5 Variable Plutonium Loading and the Recovery Process

In order to avoid criticality problems during the recovery process, the amount of plutonium that can be present in any given piece of equipment must be kept below the level at which that given plutonium concentration would be critical (with some margin for safety). By determining this limit for all of the stages in the recovery process, the maximum recovery rate for the system as a whole will determined. If the plutonium loading of the glass is a known, constant value, then the system can be run at near optimum capacity by feeding the glass into the system so that the plutonium concentration in the system is at or near the maximum levels.

If the plutonium concentration in the glass is varied, the proliferator will have to make a decision on how to run the recovery process. One choice would be to analyze the glass more frequently to determine the plutonium concentration of the glass and adjust the feed rate of glass into the process to keep the total plutonium feed rate near the optimum value. If the plutonium loading was varied for each log, then the proliferator would have to determine the plutonium level in each log (not an easy task, especially if there is a radiation barrier in the glass). If the plutonium level in the glass was varied within a given log, then the proliferator would have to make multiple measurements of each log in order. Unless a simple technique for determining the plutonium loading of borosilicate glass is developed, this additional testing will delay the recovery of the plutonium.

The second operating option available to the proliferator would be to operate the recovery process using the maximum plutonium level in the glass to determine the feed rate. This method would have the mean that the proliferator would not need to continually measure the plutonium concentration of the glass. However, it would mean operating the recovery system at a sub-optimal rate, increasing the time required to recover a given amount of plutonium.

In addition to varying the plutonium concentration in the glass, it would also be possible to alter the concentration of the neutron absorbers in the glass. As the levels of these absorbers in solution will also affect the criticality of a given system, varying the levels of the absorbers in the glass along with the levels of plutonium would further enhance the difficulties described above. Some of the disadvantages of varying the composition of the glass are that it would complicate the vitrification process and it would cause problems with trying to verify the plutonium concentration in the glass. Vitrifying the plutonium would present similar criticality issues as recovering it would, which would slow down the vitrification process and probably increase the cost involved. If the logs are not homogeneous, it would be necessary to take samples from each log in order to determine the plutonium concentrations in the log for verification purposes, which would increase the costs and time requirements associated with verification.

6.8 Future Work

The proliferation resistance and reversibility of the various options for the final disposition of weapons-grade plutonium is one of the criteria that will be used in deciding on a final disposition option for WGPu. While some progress has been made in this area, a great deal of work remains to be done.

The next step that needs to be taken with this work on borosilicate glass is to optimize the CA process for recovering plutonium from the glass, particularly the decontamination phase of the process. Along these lines, experiments should be done to determine the effect better chemistry control (such as the addition of reducing agents, etc...) on the solvent extraction process. Other decontamination processes could be examined as well, such as ion exchange. Also, work should be done to see if and how the process could be scaled up to handle larger amounts of material (to determine what would be required to recover significant quantities of plutonium from borosilicate glass).

The borosilicate glass formulation used in this work is not the only glass formulation being considered. These other formulations should also be examined to determine how to recover the plutonium from them. Similar work should also be done on the other immobilization host forms being considered as host forms for WGPu, such as zircon, monazite, and possibly synroc.

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APPENDIX

Appendix A1

Nominal Glass Composition

The glass used for these experiments is basically the ARM-1 frit (with simulated fission products) to which thorium and rare earth elements have been added. The thorium oxide fraction of the glass was designed to be 2 wt. %, as was the fraction of the europium, samarium, and gadolinium.

Table A1: Nominal Glass Composition

Table A1: This table contains the nominal composition of the borosilicate glass used as the host form is these experiments. The component mass fraction (fraction) is given in terms of grams X per gram glass. The contamination factors of the glass are also provided with regards to Th.

element	fraction	CF_{Th}
Eu	0.0173	0.983
Gd	0.0174	0.989
Th	0.0176	1.000
Sm	0.0172	0.977
Si	0.1998	11.35
Na	0.0660	3.75
B	0.0323	1.835
Nd	0.0470	2.67
Ce	0.0113	0.642
Cs	0.0101	0.574

Appendix A2

ICP Limits of Detection

The detection limits for the elements used in these experiments are tabulated below (along with the corresponding wavelengths) in table A1.

Table A2: Spectroflame ICP limits of detection[1]

Table A2: This table contains the limits of detection for the Spectroflame ICP. These limits of detection were determined using a 2 second counting interval at the given wavelength.

element	wavelength (nm)	detection limit (ppb)
B	249.773	2
Ce	380.152	20
Eu	381.967	0.6
Gd	342.247	3
Na	589.92	15
Nd	430.358	16
Si	251.611	6
Th	283.730	5

Note: There was no listed detection limits for either cesium (Cs) or samarium (Sm)

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[1] Spectro Analytical Instruments. *Spectroflame ICP Limits of Detection in Aqueous Solutions (2 s) in ppb.* Spectro Analytical Instruments, Fitchburg, MA. (S4)

Appendix A3

Sample MCNP Input Deck

Below is a sample input deck (source file) for the MCNP runs to determine the compressed critical mass. This input deck is for the non-ideal purex decontamination case. Note: the statements in brackets are comments that have been added to the deck listed below for clarity. They are not present in the input deck.

```
{---input deck---}
Non-Ideal Purex - Avg. Feed
   1   1  -39.00  -1          {Defines region 1 - the alloy sphere with density=39}
   2   0           +1         {defines region outside surface 1.  0 is for vaccuum}

   1   so   2.50              {Defines geometry of surface 1 w/ radius}

 mode     n                   {neutron transport mode}
imp: n    1  0                {neutron importance inside and outside sphere}
kcode     500 1.0 40 80       {use kcode;  500 particles  80 cycles (ignore first 40)}
c    ksrc    0 0 0            {create neutron source -edited out after 1st run}
 m1    62149  -0.00010        {wt. % Samarium-149 in alloy}
        5000   -0.03446       {wt. % natural Boron in alloy}
        11023   -0.0425       {wt. % Sodium-23 in alloy}
       14000   -0.01179       {wt. % natural Silicon in alloy}
        50120   -0.00024      {wt. % average Fission Products in alloy}
        63000   -0.00010      {wt. % natural Europium in alloy}
        64000   -0.00009      {wt. % natural Gadolinium in alloy}
        94238   -0.00011      {wt. % Plutonium-238 in alloy}
        94239   -0.85072      {wt. % Plutonium-239 in alloy}
        94240   -0.05260      {wt. % Plutonium-240 in alloy}
        94241   -0.00209      {wt. % Plutonium-241 in alloy}
        94242   -0.00020      {wt. % Plutonium-242 in alloy}
print
```

{comments were included after the print statement, which marks the end of the input deck (as far as MCNP is concerend}

Appendix B

Experimental Results

Table of Contents (Appendix B)

List of Tables (Appendix B)

B.1 Extraction Scoping Experiments

The first stage a would-be proliferator would have to complete to recover WGPu from borosilicate glass is to extract the WGPu from the glass into solution. Two potential techniques that could be used to do this are to dissolve the glass in acid (acid dissolution) and alkali fusions. Both of these techniques were examined. In these initial experiments, only the thorium concentrations of the product solutions were determined using ICP analysis.

B.1.1 Acid dissolution techniques (scoping experiments)

The initial, scoping, experiments with acid dissolution techniques can be roughly broken down into two distinct sections: whole glass experiments and crushed glass experiments. The whole glass experiments were performed using pieces of glass that were on the order of 1 cc in volume. For the crushed glass experiments, the glass was crushed into a powder using a ceramic mortar and pestle. For these initial experiments, only the thorium concentration of the final solution was determined (using ICP).

B.1.1.1 Whole glass - concentrated acid (3/16/95)

Concentrated sulfuric and nitric acid were used in an attempt to recover the thorium from the borosilicate glass. Pieces of the glass (approximately 1 cc) were placed in beakers along with 150 ml of concentrated acid (One sample with concentrated nitric acid and one with concentrated sulfuric acid). The beakers were covered with watch glasses and left in a small oven overnight at 90°C . No visible changes in the glass were noticed when the samples were removed from the oven. The acid was then poured off and saved for analysis. DI water was added to the beakers, which contained the undissolved glass and some traces of the concentrated acids, and allowed to stand for just over 2 weeks at room temperature. The water was then poured off and analyzed, and the remaining glass was dried and weighed. No significant weight changes were observed in the glass.

The liquid samples were neutralized with sodium bicarbonate, and then acidified and filtered for ICP analysis. The extraction efficiencies for thorium were determined to be

Concentrated nitric acid	$e_{th} = 8.7$ %
Concentrated sulfuric acid	$e_{th} = 7.8$ %
Water Wash (Nitric acid sample)	$e_{th} = 0.03$ %

B.1.1.2 Acid Dissolution with crushed glass (5/22/95)

In order to increase the surface are of the glass exposed to the acid, the borosilicate glass was crushed by hand using a ceramic mortar and pestle into a coarse powder. This glass (batch T1P6) was then poured into Pyrex beakers. To one of these beakers, a 5 vol. % solution of nitric acid was added (26.3:1 acid solution to glass ratio). Concentrated nitric acid was added to the other sample, in a 50:1 ratio. The samples were then covered with watch glasses and heated in an oven for 2 hours at 90°C. The samples were stirred every 30 minutes. The samples were then filtered (with filter paper) to separate the solution from the undissolved solids, and the raffinate solutions were then diluted and filtered for ICP analysis.

Concentrated Nitric Acid	(50.5:1 acid/glass)	$e_{th} = 4.53$%
5 vol. % Nitric Acid	(26.3:1 acid/glass)	$e_{th} = 53.8$%

B.1.2 Alkali fusion techniques (scoping experiments)

The initial, scoping, experiments with alkali fusion techniques can be roughly broken down into two sections: whole glass experiments and crushed glass experiments. The individual experimental attempts to extract the thorium from the borosilicate glass using various alkali fusion techniques are detailed below.

B.1.2.1 Sodium Hydroxide (NaOH) Fusion -Large Scale (3/16/95)

A large piece of borosilicate glass (from batch T1P3, mass = 5.77 g) was placed into a ceramic crucible and covered with sodium hydroxide (NaOH) crystals (approximately 10 g NaOH per gram glass). This mixture was then heated in the furnace at 490°C for 2 hours. The resulting product appeared to be a fused solid mass, which rapidly became moist as the sample was allowed to cool.

NaOH Fusion (large batch)	$e_{th} = 5.9$ %

B.1.2.2 Sodium Bicarbonate ($NaHCO_3$) Fusion (large batch) (4/13/95)

A small piece of borosilicate glass (0.874 g, batch T1P6) was mixed with sodium bicarbonate in a 3:1 ratio, alkali to glass. The resultant mixture was then heated to 400°C for 1 hour, which had no apparent effect. The same sample was then heated to 500°C and kept at temperature for 2 hours, again with no apparent results. The sample was then heated to 900°C and kept at temperature for about half an hour, which was apparently sufficient to melt the sodium bicarbonate. After cooling for 1 hour, 20 ml of DI water was added to the mixture. This water was then removed, filtered, acidified, and later analyzed.

The crucible was allowed to sit for a few days, and then a 5 vol. % nitric acid solution was added to the mixture to attempt to dissolve the remaining fusion mixture. The acid-fusion mixture was stirred and any particles that adhered to the sides and bottom of the crucible were scraped off into solution. The resulting acid wash was then filtered and acidified in preparation for ICP analysis.

Sodium Bicarbonate Fusion-water wash	$e_{th} = 2.4$ %
Sodium Bicarbonate Fusion-acid wash	$e_{th} = 2.5$ %

B.1.2.3 Potassium Hydroxide (KOH) Fusion (5/10/95 and 5/15/95)

Approximately 0.6 g of borosilicate glass (T1P5 batch) was placed into a nickel crucible and covered with potassium hydroxide (KOH). A ratio of 2.5 grams KOH per gram of glass was used. Next, the crucible was heated using a lab-top furnace until the KOH was melted and then removed from the heat. DI water was then added to attempt to dissolve the mixture, and the resulting water solution was filtered and analyzed using ICP.

Potassium Hydroxide Fusion	$e_{th} = 0.27$ %

This experiment was repeated (5/15/95), using 0.2 g glass (T1P5 batch) and a 10.1:1 ratio of KOH to glass. The crucible containing the mixture was then heated with the lab-top furnace until the KOH melted. After approximately 1 minute (after the melting of the KOH), the crucible was removed from the furnace and DI water was added to dissolve the fusion. Once the crucible had cooled, the water solution was poured off and filtered to recover any undissolved fusion material. The water solution (which will be referred to as the water wash) was then acidified and prepared for ICP analysis. The undissolved solids were then recovered from the filter paper and dissolved in a 5 vol. % solution of nitric acid (this is the acid wash stage).

KOH Fusion (water wash) $e_{th} = 0.58$ %

KOH Fusion (acid wash) $e_{th} = 11.4$ %

B.1.2.4 Mixed Alkali (KOH + $KHCO_3$) Fusion (5/17/95)

Borosilicate glass (T1P5 batch) was combined in a 10:1 alkali to glass ratio with a mixture of potassium hydroxide (KOH) and potassium carbonate ($KHCO_3$) in a nickel crucible. The ratio of KOH to $KHCO_3$ was 3:1. This mixture was heated, using the lab-top furnace, until the alkali had appeared to melt. At this time, the mixture appeared cloudy (a milky white, opaque color). The crucible was left on the furnace until the cloudy color disappeared. The fusion was allowed to cool slightly before DI water was added to attempt to dissolve the fusion. The water solution was then filtered and prepared for ICP analysis. After the water solution had been poured off, a significant amount of the fusion material remained on the crucible. This material was not removed by subsequent washes with both DI water and a 5 vol. % solution of nitric acid. It was removed by a wash with concentrated nitric, but this acid also reacted with the nickel crucible.

Mixed Alkali Fusion (water wash) $e_{th} = 0.29\%$

B.1.2.5 KOH Fusion with crushed glass (5/22)

Borosilicate glass (batch T1P6) was crushed into a powder using a mortar and pestle. Approximately 0.5 g of this crushed glass was then mixed with about 5 g of KOH (alkali : glass ratio = 10:1) in a nickel crucible, which was subsequently heated using the lab-top furnace in order to form a fusion. The mixture was allowed to remain on the furnace for 1 minute after the KOH had melted. At this time, the mixture had become visibly cloudy. The fusion was allowed to cool slightly before DI water was added. The water solution was poured off and stored for analysis (denoted as the water wash). A 5 vol. % nitric acid solution was added to the crucible to dissolve any remaining material. This acid solution was also stored for analysis (denoted as the acid wash). Both these samples were acidified with nitric acid and filtered for ICP analysis. No thorium was detected in either solution

KOH Fusion (water wash) $e_{th} = 0$ %
KOH Fusion (acid wash) $e_{th} = 0$ %

The solids recovered by filtration from the acid wash and water wash were then dissolved in concentrated nitric acid and heat at 90°C for 1 hour. These concentrated acid solutions were then filtered and diluted with DI water for ICP analysis. The solution from the water wash precipitate stream was analyzed twice (I and II below).

Precipitate stream (water wash) I $e_{th} = 48.4$ %
Precipitate stream (water wash) II $e_{th} = 36.4$ %
Precipitate stream (acid wash) $e_{th} = 7.77$ %

The undissolved solids from the nitric acid dissolution of the water wash of the fusion were dissolved in concentrated hydrochloric acid (HCl). The HCl solution, containing the undissolved solids from the water wash stream, was then heated at 80°C for 1 hour and then filtered to recover undissolved solids. The HCl solution was then diluted and prepared for ICP analysis.

HCl dissolution $e_{th} = 0.78$ %

B.1.3 Caustic dissolution with crushed glass (5/24/95)

In this experiment, potassium hydroxide solutions were used to attempt to dissolve the borosilicate glass. The glass (T1P6 batch) was crushed into a powder using a ceramic mortar and pestle. Approximately 0.5 g of this crushed glass was added to 2 Pyrex beakers. Concentrated KOH solution was added to one of these beakers and a 1M solution of KOH to the other (the concentrated solution was actually a saturated solution, at room temperature, of KOH). The beakers were then covered and heated in an oven at 90°C for 2 hours. After being removed from the oven, the solutions in the beakers were poured off, filtered, and prepared for ICP analysis. No thorium concentration was detected in either sample.

Caustic dissolution, 1M KOH solution	$e_{th} = 0\ \%$
Caustic dissolution, sat. KOH solution	$e_{th} = 0\ \%$

B.2 Extraction Technique Analysis Experiments

After the initial scoping experiments had been performed, 2 processes were chosen for more detailed analysis: acid dissolution of crushed glass with a 5 vol. % nitric acid solution, and alkali fusion (KOH) with crushed glass. These experiments were repeated and the product streams were analyzed to determine the concentrations of zinc (Zn), thorium (Th), cesium (Cs), boron (B), sodium (Na), europium (Eu), cerium (Ce), barium (Ba), titanium (Ti), and molybdenum (Mo). This set of elements was chosen from the elements know to be present in the glass due to their neutron absorption cross sections. This set of elements, however, was only used for this set of experiments (for subsequent analyses, the set of elements described in table 3.1 was used)

B.2.1 Acid Dissolution Experiment (6/1/95)

Glass from the T1P6 batch was crushed into a coarse powder with a ceramic mortar and pestle. This glass was then divided into 2 batches of approximately 1 gram and placed in Pyrex beakers. A 5 vol. % solution of nitric acid was then added to the beakers. The acid solution to glass ratio for the first sample was 36.9:1, and 23.4 for the second. The beakers were then covered with a watch glass and placed into an oven. The beakers were heated at 90°C for 2 hours, and were stirred every 30 minutes. The acid + glass slurry was then filtered with filter paper to separate the liquid from the undissolved solids. The liquid samples were then diluted and filtered for ICP analysis. When determining the thorium extraction ratio, the initial weight of the solution was used (instead of the weight of the solution remaining after the sample is heated), as the weight of the solution before filtering was not recorded.

5 vol. % nitric acid (acid:glass = 36.9) e_{th} = 86.9 %

5 vol. % nitric acid (acid:glass = 23.4) e_{th} = 81.4 %

The contamination factors of the nitric acid solution were also determined.

Table B.1 Acid Dissolution Contamination Factors

Table B.1: This table contains the contamination factors determined for the initial acid dissolution experiments on borosilicate glass.

element	(acid:glass = 36.9)	(acid:glass = 23.4)
Cs	0.41	0.47
B	2.48	2.77
Na	5.52	6.71
Eu	1.24	1.40
Ce	0.69	0.74
Zn	0.99	1.09
Ba	0.41	0.46
Ti	0.88	0.80
Mo	0.64	0.59

B.2.2 Alkali Fusion Experiment (6/1/95)

Crushed borosilicate glass (T1P6) was combined with KOH in a nickel crucible and heated with the lab-top furnace until the KOH had melted. The crucible was left on the furnace for 1 minute after the KOH had melted and then was allowed to cool. After cooling slightly, 5 vol. % nitric acid was added to dissolve the fusion (hot acid wash). The acid solution was then recovered and filtered for ICP analysis. Another wash of 5 vol. % nitric acid was added to the crucible to dissolve the remaining material (cold acid wash). This solution was also filtered and analyzed using the ICP. The material recovered from the filters and from the crucible was then dissolved in concentrated nitric acid, which was diluted and filtered for ICP analysis (designated as crucible stream and filter stream).

(f1) KOH Fusion (hot acid wash) $e_{th} = 0.1$ %
(f2) KOH Fusion (cold acid wash) $e_{th} = 27.4$ %
(f3) Precipitate (crucible stream) $e_{th} = 4.7$ %
(f4) Precipitate (filter stream) $e_{th} = 8.9$ %

The contamination factors for these samples were also determined. In table B.2, an asterisk by the number indicates that the concentration of the element fell outside the calibration range of the ICP (and was estimated by the ICP). An asterisk instead of a number indicates that the concentration of a given element was below the detection limit of the ICP.

Table B.2 Potassium Hydroxide Fusion Contamination Factors

Table B.2: This table contains the contamination factors calculated from ICP concentration measurements on the KOH fusion solutions. The stream designations are provided above. An asterisk next to a number indicates that the ICP measurement was outside the calibrated region and was estimated by extending the calibration. An asterisk instead of a number indicates that the ICP measured a concentration that was zero or less (possible due to straight line calibration curves)

element	f1	f2	f3	f4
Cs	*	0.38	*	0.28
B	1247.*	1.53*	0.89	0.30
Na	10142.*	10.36*	0.57	0.50
Eu	*	1.12*	0.57	1.03
Ce	*	0.81	0.27	0.64
Zn	205.7	0.60	*	0.69
Ba	*	0.38	*	0.46
Ti	*	0.86*	0.56	1.99
Mo	436*	0.46	*	*

B.2.3 Large Scale Acid Dissolution Process (CA process) (6/7/95)

In order to generate material for the decontamination scoping experiments (and to determine the effects of an increase in scale on the CA process), the CA process (Crushed glass in Acid) was repeated with approximately 3 grams of crushed borosilicate glass (T1P4 batch). A 5 vol. % nitric acid solution was added to a Pyrex beaker containing the crushed glass in a 30:1 acid solution to glass mass ratio. The sample was then heated in an oven for 2 hours at 90°C, and was removed for stirring (with a stirring rod) every 30 minutes. The resulting solution was then filtered to recover the undissolved material and stored for analysis and use in the decontamination experiments. As this solution was used as the 'stock' solution for the decontamination scoping experiments, it was analyzed a number of times. The results of each analysis of this solution are given below along with the date the ICP analysis of the solution. The average and standard deviation of the results were also determined.

(x1)	**CA process-large batch (6/21/95)**	e_{th} = 75.4 %
(x2)	**CA process-large batch (6/28/95)**	e_{th} = 72.7 %
(x3)	**CA process-large batch (7/11/95)**	e_{th} = 83.7%
(x4)	**CA process-large batch (7/11/95)**	e_{th} = 84.0 %
(x5)	**CA process-large batch (7/26/95)**	e_{th} = 83.1%
(x6)	**CA process-large batch (7/31/95)**	e_{th} = 81.4 %
	CA process-large batch (Average)	**e_{th} = 80.1 %**
	- standard deviation	= 4.8%

The contamination factors were also determined in most of these analyses of the large batch CA process sample.

Table B.3 Contamination Factors for Large-Batch CA Process

Table B.3: This table contains the contamination factors (CF's) observed in the final product solution of the large-scale CA process experiment. The CF's were calculated from the observed concentrations for each of the ICP runs. The average of the measurements is also provided (AVG).

element	6/28	7/11	7/26	7/31	AVG.
Ce	0.65	0.58	0.58	0.59	**0.60**
Eu	1.02	0.90	0.92	0.92	**0.94**
Gd	1.10	0.97	0.99	0.99	**1.01**
Sm	1.14	1.01	1.03	1.03	**1.05**
Nd	3.16	2.72	2.80	2.81	**2.87**
Cs	2.47	2.23	2.19	1.98	**2.22**
Si	0.41	0.33	0.34	0.36	**0.36**
Na	5.91	4.38	4.40	4.33	**4.76**
B	2.53	2.29	2.24	2.24	**2.33**

B.2.4 Potassium Hydroxide (KOH) Fusion (6/8/95)

The KOH fusion experiment was repeated. A KOH/borosilicate glass fusion (10:1 by mass) was formed by mixing KOH pellets with crushed borosilicate glass. This mixture was heated using the lab-top furnace until the KOH had melted and until any visible reaction had stopped. The mixture was then removed from the furnace and allowed to cool slightly before DI water was added to dissolve the fusion. This solution was then filtered and prepared for ICP analysis (water wash). Then, a 5 vol. % solution of nitric acid was added to the crucible to dissolve any remaining material. This solution was also recovered, filtered, and prepared for ICP analysis (acid wash). The material recovered on the filters from both the acid and water wash were then dissolved in concentrated nitric acid (acid wash precipitate stream and water wash precipitate stream, respectively). No thorium (above the limit of detection) was detected in either the acid or water wash stream. The observed contamination factors for the precipitate streams are given in table B.4.

KOH Fusion (water wash) $e_{th} = 0\%$
KOH Fusion (acid wash) $e_{th} = 0\%$
Precipitate (water wash) $e_{th} = 15.3\ \%$
Precipitate (acid wash) $e_{th} = 6.4\%$

Table B.4 Potassium Hydroxide Fusion Contamination Factors

Table B.4: This table contains the contamination factors determined for the precipitate streams from the KOH fusion with crushed borosilicate glass.

element	Precip. (water wash)	Precip. (acid wash)
Ce	0.65	0.50
Eu	0.75	0.53
Gd	0.84	0.67
Sm	0.88	0.74
Nd	2.79	2.76
Cs	2.15	2.06
Si	0.03	0.28
Na	0.24	0.38
B	0.23	0.30

B.2.5 Acid Dissolution Parameter Experiments

In order to optimize the crushed glass is nitric acid dissolution process (CA process), a number of experiments were performed to determine the effect of varying certain parameters such as acid concentration, particle size, re-using crushed glass, temperature, etc...

B.2.5.1 Acid Concentration I (6/19/95)

This set of experiments was the first done to examine the effect of acid concentration on thorium extraction efficiency. Two solutions were examined: 1 vol. % concentrated nitric acid and 10 vol. % concentrated nitric acid. These acid solutions were added to crushed glass in a 30:1 mass ratio (acid:glass), and the resulting solutions were heated for 2 hours at 90°C. The solutions were stirred every 30 minutes during the heating. After 2 hours, the samples were filtered with filter paper to remove the undissolved solids and the solutions were prepared for ICP analysis.

1 vol. % Nitric acid $e_{th} = 7.02\%$

10 vol. % Nitric acid $e_{th} = 39.5\%$

B.2.5.2 Other CA Parameter Experiments (6/21/95)

Two additional parameters in the CA process were examined: the effect of stirring the solution during heating and the re-use of the crushed glass. To determine the effects of stirring the mixture, the CA process was repeated using 5 vol. % nitric acid solution in a 30:1 mass ratio with the crushed glass. The solution was heated to 90°C for 2 hours, but it was not stirred every 30 minutes. The solution was then filtered and prepared for ICP analysis.

CA Process: No Stirring $e_{th} = 10.8\%$

To determine the extraction efficiency of a second extraction phase, the undissolved glass from the 6/1/95 experiment (the sample with the acid:glass ratio of 36.9) was used instead of 'fresh' glass in the CA process. Again, 5 vol. % nitric acid was used in a 30:1 mass ratio to the glass. The samples were heated for 2 hours at 90°C, and were stirred every 30 minutes. The sample was then filtered and prepared for ICP. Two extraction ratios were determined for this sample. The first is the additional extraction efficiency gained by adding a second extraction phase, and is the ratio of the recovered thorium from the second extraction to the total thorium present in the virgin glass.

Additional Extraction Efficiency $e_{th} = 2.2\%$

The second extraction efficiency calculated was the ratio of the total thorium recovered to the thorium remaining in the used glass after the first extraction. This was done assuming that all of the thorium not recovered in the first extraction remained in the glass.

Second Stage Extraction Efficiency $e_{th} = 11.3\%$

B.2.6 Crushed Glass in Acid Process (V1) Verification

After the initial experiments with crushed glass in nitric acid, experiments were performed to determine the effectiveness of the extraction procedure.

B.2.6.1 Crushed Glass in Acid Dissolution Process (CA V1) Protocol

The initial protocol for the Crushed Glass in Acid process (CA process) was as follows.

1) The glass sample was crushed in a coarse powder using a ceramic mortar and pestle.

2) The crushed glass was put in a beaker and a 5 vol. % solution of nitric acid (approximately 3.5 wt. % nitric acid) was added in a 30:1 mass ratio (acid:glass).

3) The sample was stirred and covered with a watch glass before being placed in the oven.

4) The samples were then heated in an oven for 2 hours at 90°C. Every 30 minutes, the samples were removed from the oven for stirring.

5) After 2 hours, the samples were weighed and then were filtered to remove the undissolved glass using filter paper. The liquid sample was then filtered again and diluted for ICP analysis.

B.2.6.2 CA Process Verification (7/24/95)

The CA process (V1) was used to extract thorium from three samples of T1P1 glass (samples A, B, and C). However, instead of separating the solution from the undissolved glass by filtering with filter paper, the supernate solution was recovered by decanting off the liquid phase (using a pipette).

5 vol. % Nitric acid (A)	$e_{th} = 30.8\%$
5 vol. % Nitric acid (B)	$e_{th} = 32.4\%$
5 vol. % Nitric acid (C)	$e_{th} = 32.5\%$

The contamination factors were determined below.

Table B.5 CA (V1) Process - Contamination Factors (batch 1)

Table B.5: This table contains the contamination factors for the first batch of experiments to confirm the results from the CA (V1) process.

element	A	B	C
Ce	0.82	0.84	0.82
Eu	1.75	1.79	1.80
Gd	1.78	1.84	1.79
Sm	1.99	2.06	2.05
Nd	4.41	4.48	4.44
Cs	3.50	3.58	3.67
Si	0.97	0.93	0.93
Na	6.82	6.92	6.89
B	3.72	3.74	3.69

This experiment was repeated (7/26/95 and 7/30/95). On 7/26/95, glass from the T1P1 batch was used, following the CA (V1) protocol. On 7/30, glass from both the T1P1 and T1P5 batch were used in the CA (V1) protocol. For these experiments, however, the glass was ground into a much finer powder than before. The analysis of these experiments is given below.

CA (V1) T1P1 glass 7/26 (D) eth = 38.8%
CA (V1) T1P1 glass 7/30 (s1) eth = 44.0%
CA (V1) T1P1 glass 7/30 (s5) eth = 32.2%

Table B.6 CA (V1) Process - Contamination Factors (batch 2)

Table B.6: This table contains the contamination factors for the second batch of experiments to confirm the results from the CA (V1) process.

element	D	s1	s5
Ce	0.69	0.77	0.98
Eu	1.57	1.49	1.99
Gd	1.53	1.50	2.08
Sm	1.78	1.71	1.91
Nd	3.45	3.74	4.55
Cs	3.21	2.90	3.25
Si	0.82	0.65	0.97
Na	5.31	5.72	6.69
B	2.75	2.94	3.54

B.2.7 Crushed Glass - Acid Dissolution Parameter Experiments (take 2)

In order to try to find out what had caused the dramatic change in the extraction efficiency of the CA (V1) process experiments were performed to examine the effects of acid concentration, oven temperature, and particle size on extraction efficiency.

B.2.7.1 CA Process (V1) Parameter Experiment: Acid Concentration (8/11/95)

Thorium was extracted from crushed T1P1 glass following the protocol given for the CA (V1) process [B.2.6.1]. However, instead of using a 5 vol. % nitric acid solution, the acid concentration was varied. The three samples were heated in the same oven in order to minimize the possible effects of any temperature fluctuations (the samples should all see the same temperature). Acid concentrations of 5 vol. %, 10 vol. %, and 25 vol. % nitric acid were used.

5 vol. % Nitric Acid solution e_{th} = 84.8%
10 vol. % Nitric Acid solution e_{th} = 83.4%
25 vol. % Nitric Acid solution e_{th} = 84.4%

B.2.7.2 CA Process (V1) Parameter Experiment: Temperature (9/1/95)

Thorium was extracted from crushed T1P1 glass following the protocol given for the CA (V1) process [B.2.6.1]. However, instead of trying to maintain the oven temperature at 90°C, the oven temperature was varied. Two different temperatures were used, 80°C and 100°C, with one sample at each temperature. The results of these two experiments, along with the 5 vol. % nitric acid run from the acid concentration experiments (8/11/95) [B.2.7.1], are shown below

CA (V1) Process: 80°C	eth = 98.9%
CA (V1) Process: 90°C (8/11/95)	eth = 84.8%
CA (V1) Process: 100°C	eth = 100.6%

B.2.7.3 CA Process (V1) Parameter Experiment: Particle Size (10/27/95)

Thorium was extracted from crushed T1P1 glass following the protocol given for the CA (V1) process [B.2.6.1]. The crushed glass was then separated by particle size into 5 groups, listed below. The glass from each group was then used in the CA (V1) protocol to determine the effects of particle size on extraction efficiency. The size categories are listed in terms of the mesh of the screens that the particles passed through and stopped on. For example, the group 25 mesh > X > 60 mesh refers to glass particles that passed through the 25 mesh screen but did not pass through the 60 mesh screen.

X > 25 mesh	eth = 28.2%
25 mesh > X > 60 Mesh	eth = 47.3%
60 mesh > X > 80 Mesh	eth = 57.0%
80 mesh > X > 120 Mesh	eth = 59.5%
X < 120 Mesh	eth = 44.5%

B.3 Decontamination Scoping Experiments

Using the product solutions from the acid dissolution (CA or Crushed glass in Acid) process, a number of decontamination techniques were tried in order to purify the thorium stream. As thorium was used as an analog for plutonium, it was not possible to test the decontamination of REDOX (reduction-oxidation) processes, such as the lanthanum fluoride process [2.6.1.6] and the bismuth phosphate process [2.6.1.2]. The initial experiments involved precipitation processes (modeled after the REDOX processes, but without the reduction or oxidation stages). Subsequent decontamination attempts involved a solvent extraction process (PUREX - see section [2.6.2.1])

B.3.1 Precipitation Decontamination Experiments

For these experiments, the product solution from the large batch CA process [B.2.3] was used as the feed stream. In addition to the contamination factors (CF's) of the product streams and the decontamination factors (DF's) of the process, the recovery efficiency (r_{th}) [3.2.5.2] was also determined for each process examined.

B.3.1.1 Hydroxide Precipitation (6/12/95)

Using a 1M solution of KOH, the feed solution was titrated to pH = 5.8 in order to precipitate thorium hydroxide (similar to the separation stage of the caustic soda process for cracking monazite [2.5.2.1]). The solution was filtered and the precipitate was recovered. After drying, the precipitate was dissolved in 5 vol. % nitric acid. This solution was then filtered and analyzed.

Hydroxide Precipitation $r_{th} = 49.3\%$

The contamination factors (CF) and decontamination factors for the process are shown in table B.7.

Table B.7 Hydroxide Precipitation Decontamination Factors

Table B.7: This table contains the contamination factors (CF) and decontamination factors (DF) for the hydroxide precipitation decontamination experiment.

element	CF	DF
Ce	0.21	3.14
Eu	0.80	1.27
Gd	0.84	1.31
Sm	0.84	1.36
Nd	1.64	1.93
Cs	0.63	3.93
Si	0.47	0.87
Na	0.11	53.24
B	0.57	4.41

B.3.1.2 Fluoride Precipitation Process (6/13/95)

A saturated solution of sodium fluoride (NaF) was added in a 1:1 ratio to the feed solution in order to precipitate out thorium fluoride (essentially the first stage of an LaF decontamination process [2.6.1.6] without the lanthanum ion for a carrier). The solution was then heated at 80°C for 1 hour, stirring every 30 minutes, before it was filtered to recover the precipitate.

The paper filter and filtrate were allowed to dry overnight. Then the precipitate was recovered and dissolved in concentrated nitric acid. The acid solution was then heated for 1 hour at 80°C. After it was heated, it was diluted with DI water and filtered for ICP analysis.

Fluoride Precipitation $r_{th} = 10.9\%$

Table B.8 Fluoride Precipitation Decontamination Factors

Table B.8: This table contains the contamination factors (CF) and decontamination factors (DF) for the fluoride precipitation decontamination experiment.

element	CF	DF
Ce	2.73	0.24
Eu	2.10	0.48
Gd	1.78	0.62
Sm	3.39	0.33
Nd	6.49	0.49
Cs	1.81	1.36
Si	1.95	0.21
Na	5.98	0.99
B	0.31	8.20

B.3.1.3 Phosphate Precipitation Process (6/14/95)

A saturated phosphate ion (PO_4^-) solution was added to the feed solution in a 1:1 mass ratio to precipitate the thorium out of solution. The mixture was heated for 1 hour at 80°C before it was filtered to recover the precipitate. After drying overnight, the precipitate was recovered from the filter paper and dissolved in concentrated nitric acid. After heating the concentrated acid solution for 1 hour at 80°C, DI water was added and the solution was filtered and prepared for ICP analysis.

Phosphate Precipitation $r_{th} = 25.3\%$

Table B.9 Phosphate Precipitation Decontamination Factors

Table B.9: This table contains the contamination factors (CF) and decontamination factors (DF) for the phosphate precipitation decontamination experiment.

element	CF	DF
Ce	0.83	0.78
Eu	1.39	0.73
Gd	1.47	0.75
Sm	1.57	0.72
Nd	4.25	0.75
Cs	1.48	1.66
Si	0.03	14.23
Na	0.21	27.94
B	0.13	19.48

B.3.1.4 2 Cycle Hydroxide Precipitation Process (7/5/95)

Using a 1M solution of sodium hydroxide (NaOH), approximately 15 g of the feed solution was titrated to a pH of around 5.8 in order to precipitate out thorium hydroxide. The resulting solution was then filtered to recover the precipitate, and the precipitate was recovered from the filter paper. The recovered precipitate was dissolved in 5 vol. % nitric acid. Samples of this solution and the raffinate solution were taken for ICP analysis. The process was then repeated with the dissolved precipitate as the feed solution. The recovery efficiencies of each stage were

1st Stage Raffinate solution $r_{th} = 1.4\%$
1st Stage Precipitate solution $r_{th} = 56.9\%$
2nd Stage Raffinate solution $r_{th} = 0.71\%$
2nd Stage Precipitate solution $r_{th} = 74.7\%$

Note that the second stage efficiencies were determined relative to first stage precipitate stream (which was used as the feed for the second stage), not to the initial feed stock solution.

The contamination factors (CF's) and decontamination factors (DF's) were determined for each stage. For the first stage, the CF's and DF's are given in table B.10.

Table B.10 Analysis of First Stage of Hydroxide Precipitation

Table B.10: This table contains the contamination factors (CF) and Decontamination factors (DF) for the raffinate and precipitate streams of the first stage of the hydroxide precipitation process.

element	Raffinate		Precipitate	
	CF	DF	CF	DF
Ce	21.18	0.03	0.22	2.59
Eu	16.41	0.05	0.63	1.41
Gd	19.20	0.05	0.66	1.47
Sm	21.51	0.05	0.65	1.54
Nd	80.70	0.03	1.37	1.98
Cs	97.03	0.02	0.64	3.46
Si	0.74	0.45	0.35	0.95
Na	315.23	0.01	0.09	50.34
B	109.38	0.02	0.45	5.11

For the second stage, the CF's and DF's are given in table B.11. For some of the values, the measured concentrations were zero (below detection limits for the given concentration range). They are recorded here with asterisks (*). The decontamination factors shown below are relative to the feed stream for the second stage (the 'product' stream from the first stage).

Table B.11 Analysis of Second Stage of Hydroxide Precipitation

Table B.11: This table contains the contamination factors (CF) and Decontamination factors (DF) for the raffinate and precipitate streams of the second stage of the hydroxide precipitation process.

element	Raffinate		Precipitate	
	CF	DF	CF	DF
Ce	0.08	2.75	0.23	0.97
Eu	*.**	*.**	0.63	1.01
Gd	*.**	*.**	0.66	1.00
Sm	1.01	0.65	0.68	0.97
Nd	0.53	2.58	1.44	0.95
Cs	2.30	0.28	0.65	0.99
Si	11.42	0.03	1.48	0.24
Na	52.91	0.01	0.01	12.16
B	66.78	0.01	0.02	26.66

B.4 Solvent Extraction Scoping Experiments

Using the solution from the CA (V1) process as a feed solution, a number of experiments were performed to evaluate the effectiveness of a solvent extraction process in purifying the plutonium analog stream. These experiments involved a crude version of the PUREX process [2.6.2.1]. The product solution from the 7/24/95 CA (V1) process experiments [B.2.6.2] was acidified to approximately 3M HNO_3 through the addition of concentrated nitric acid and then used as the feed solution for these solvent extraction scoping experiments.

B.4.1 One Cycle PUREX Separation (8/2/95)

Approximately 30 g of feed solution (sample A, [B.2.6.2]) was placed in a 250 ml glass bottle with a screw-on cap (henceforth referred to as a shaker). An approximately equal volume of 30 vol. % TBP in kerosene solution was added, and the mixture was shaken vigorously by hand for 1 minute. The solution was then allowed to settle until the organic and aqueous phases had separated. Then, the organic phase was transferred to another shaker using a disposable pipette.

An equal volume of DI water was then added to the organic, and the mixture was shaken for 1 minute. After it had settled, the organic was again separated off using a disposable pipette. The water solution was then acidified to approximately 10 % nitric acid through the addition of concentrated nitric acid and filtered for ICP analysis. The calculated contamination and decontamination factors are displayed below in table B.12, and the recovery efficiency was

1 Cycle PUREX extraction $r_{th} = 47.2\%$

Table B.12 Analysis of One Cycle PUREX extraction

Table B.12: This table contains the contamination factors (CF) and decontamination factors (DF) from the one cycle PUREX extraction experiment, as well as the feed stream CF's.

element	Feed CF	CF	DF
Ce	0.88	0.05	17.69
Eu	1.79	0.20	9.06
Gd	1.83	0.19	9.69
Sm	2.03	0.22	9.29
Nd	4.46	0.34	12.97
Cs	3.55	0.21	16.59
Si	0.53	>0.01	<50.0
Na	6.83	0.26	26.39
B	3.63	0.11	31.58

B.4.2 One Cycle PUREX Separation with Acid Wash Stage (8/9/95)

Approximately 20 g of feed solution (sample A, [B.2.6.2]) was placed in a shaker with an equal volume of 30 vol. % TBP in kerosene solution. After being shaken by hand for 1 minute, the organic and aqueous phases were allowed to separate. The organic phase was then transferred to another shaker using a disposable pipette. An equal volume of 3M HNO_3 was then added to the organic, and the mixture was shaken for 1 minute. After settling, the organic was transferred to a third shaker, where it was mixed with DI water to recover the plutonium analog. The mixture was shaken for 1 minute and allowed to settle before the organic phase was removed. The resulting aqueous solution was then acidified to approximately 3M HNO_3 and filtered for ICP analysis. The recovery efficiency and decontamination factors are given below.

1 Cycle + 1 Acid Wash PUREX $r_{th} = 29.2\%$

Table B.13 Analysis of 1 Cycle + 1 Acid Wash PUREX extraction

Table B.13: This table contains the contamination factors (CF) and decontamination factors (DF) from the one cycle PUREX extraction with one acid wash stage experiment, as well as the feed stream CF's.

element	Feed CF	CF	DF
Ce	0.88	0.01	88.0
Eu	1.79	0.06	28.92
Gd	1.83	0.06	29.54
Sm	2.03	0.09	22.82
Nd	4.46	0.14	32.42
Cs	3.55	>0.01	<300.0
Si	0.53	0.05	10.17
Na	6.83	0.18	37.77
B	3.63	0.05	67.82

B.4.3 Two Cycle PUREX Separation, No Acid Wash, No Recycle (8/18/95)

Approximately 25 g of feed solution (sample A, [B.2.6.2]) was placed in a shaker with an equal volume of 30 vol. % TBP in kerosene solution. After being shaken by hand for 1 minute, the organic and aqueous phases were allowed to separate. The organic phase was then transferred to another shaker using a disposable pipette, where it was mixed with DI water to recover the plutonium analog. The mixture was shaken for 1 minute and allowed to settle before the organic phase was removed. The resulting aqueous solution was then acidified to approximately 3M HNO_3. This process was then repeated.

2 Cycle PUREX, no wash, no recycle $r_{th} = 10.2\%$

Table B.14 Analysis of 2 Cycle PUREX (No Wash, No Recycle)

Table B.14: This table contains the contamination factors (CF) and decontamination factors (DF) from the two cycle PUREX extraction (with no acid wash stage and no solvent recycle) experiment, as well as the feed stream CF's.

element	Feed CF	CF	DF
Ce	0.88	0.05	17.53
Eu	1.79	0.21	8.63
Gd	1.83	0.19	9.39
Sm	2.03	0.21	9.47
Nd	4.46	0.32	14.00
Cs	3.55	0.24	15.03
Si	0.53	0.01	82.35
Na	6.83	0.34	20.04
B	3.63	0.16	23.09

B.4.4 Two Cycle PUREX Separation with Solvent Recycle (8/23/95)

Approximately 20 g of feed solution (sample A, [B.2.6.2]) was placed in a shaker with an equal volume of 30 vol. % TBP in kerosene solution. After being shaken by hand for 1 minute, the organic and aqueous phases were allowed to separate. The organic phase was then transferred to another shaker using a disposable pipette, where it was mixed with DI water to recover the plutonium analog. The mixture was shaken for 1 minute and allowed to settle before the organic phase was removed. The recovered organic was saved for use in the second cycle.

The aqueous solution from the first cycle was acidified to 3M HNO_3, and then the recovered organic was returned to the shaker. After 1 minute of vigorous shaking, the mixture was allowed to settle. Then the organic phase was separated from the aqueous phase and transferred to another shaker. The thorium was then stripped from the organic phase by adding DI water, shaking the resulting mixture for 1 minute, and then recovering the aqueous phase. The recovered aqueous solution was then acidified to 3M HNO_3, and filtered for ICP analysis.

2 Cycle PUREX with solvent recycle $r_{th} = 19.7\%$

Table B.15 Analysis of 2 Cycle PUREX with Solvent Recycle

Table B.15: This table contains the contamination factors (CF) and decontamination factors (DF) from the two cycle PUREX extraction with solvent recycle experiment, as well as the feed stream CF's.

element	Feed CF	CF	DF
Ce	0.88	0.05	17.47
Eu	1.79	0.16	11.35
Gd	1.83	0.15	11.91
Sm	2.03	0.17	12.01
Nd	4.46	0.31	14.25
Cs	3.55	0.23	15.46
Si	0.53	0.02	31.73
Na	6.83	0.37	18.31
B	3.63	0.19	19.44

B.5 Crushed Glass in Acid (V2) Process Confirmation

As a result of the experiments with the parameters of the CA process, the procedure was revised. This revised procedure was then run on glass from two different batches five times on each batch, in order to determine the effectiveness of the process. The revised procedure and the results of the confirmation experiments are provided in this section.

B.5.1 Crushed Glass in Acid (V2) Procedure

The revised procedure for the extraction and subsequent decontamination of thorium (plutonium) from borosilicate glass is detailed below.

1) The glass sample was crushed using a ceramic mortar and pestle so that it passes through a 60 mesh filter (particle size less than 250 microns)

2) The crushed glass was put in a beaker and a 25 vol. % solution of nitric acid (approximately 17.87 wt. % HNO_3) was added in a 30:1 mass ratio (acid:glass).

3) The sample was stirred and covered with a watch glass before being placed in the oven.

4) The samples were then heated in an oven for 2 hours at 90°C. Every 30 minutes, the samples were removed from the oven for stirring.

5) After 2 hours, the samples were weighed and then the liquid solution was decanted off using a disposable pipette leaving the undissolved glass in the beaker. A small portion of this sample was taken, filtered and diluted for ICP analysis.

6) The remaining sample was then added to a glass bottle (shaker) and mixed with an equal volume of pre-equilibrated 30 vol. % TBP in kerosene. The pre-equilibrated organic solution was prepared by mixing the TBP+kerosene mixture with an equal volume of 3M nitric acid.

7) The sample was then shaken for 1 minute and allowed to settle. The organic phase was recovered with a disposable pipette and transferred to a clean shaker.

8) An equal volume of 3M nitric acid was then added to the organic solution. The mixture was then shaken for 1 minute and allowed to settle before the organic solution was again recovered and transferred to a clean shaker with a disposable pipette.

9) The organic solution was then mixed with an equal volume of DI water and shaken for 1 minute. After settling, the organic phase was removed, leaving only the aqueous solution. The aqueous phase was then acidified to approximately 3M HNO_3 by the addition of concentrated nitric acid. This sample was then filtered and diluted for ICP analysis.

B.5.2 CA (V2) Process Confirmation

Using the CA (V2) procedure, thorium was extracted and purified from borosilicate glass. The glasses examined were ARM-1 glass, with thorium and rare earths added, from batch T1P1 and T1P2 (made by K. Sylvester, ref. S5). For each glass used, five experiments were done. In order to prevent confusion, the contamination factors determined in these experiments are shown below, first for the extraction process and then for the decontamination process. The experiment designation is given for each experiment.

Table B.16 Contamination Factors from Extraction Process

Table B.16: This table contains the contamination factors (CF) from the extraction process of the CA (V2) procedure for the T1P1 glass. The column titles are the experimental designations of each of the experiments

element	LA	LB	MA	MC	N1
Ce	0.627	0.645	0.623	0.614	0.626
Eu	1.071	1.084	1.061	1.032	1.050
Gd	1.005	1.014	0.990	0.987	0.988
Sm	1.138	1.167	1.138	1.137	1.121
Nd	2.301	2.327	2.318	2.228	2.476
Cs	2.156	2.176	2.088	2.086	1.957
Si	0.162	0.139	0.125	0.118	0.104
Na	4.181	4.276	4.067	4.019	3.774
B	2.007	2.047	2.016	1.940	2.050

Table B.17 Contamination Factors from Extraction Process

Table B.17: This table contains the contamination factors (CF) from the extraction process of the CA (V2) procedure for the T1P2 glass. The column titles are the experimental designations of each of the experiments

element	N2	O1	O2	PB	PC
Ce	0.681	0.674	0.682	0.684	0.684
Eu	1.034	1.041	1.041	1.070	1.062
Gd	1.036	1.052	1.049	1.056	1.047
Sm	1.140	1.144	1.144	1.157	1.150
Nd	2.701	2.743	2.721	2.782	2.735
Cs	2.079	2.031	2.069	2.099	2.060
Si	0.172	0.165	0.149	0.135	0.151
Na	4.164	4.061	4.052	4.421	4.341
B	2.246	2.263	2.258	2.253	2.251

Table B.18 Contamination Factors from Decontamination Process

Table B.18: This table contains the contamination factors (CF) from the decontamination process of the CA (V2) procedure for the T1P1 glass. The column titles are the experimental designations of each of the experiments

element	LA	LB	MA	MC	N1
Ce	0.020	0.012	0.024	0.019	0.028
Eu	0.053	0.031	0.082	0.059	0.106
Gd	0.048	0.029	0.069	0.050	0.090
Sm	0.057	0.034	0.081	0.059	0.103
Nd	0.073	0.034	0.098	0.070	0.148
Cs	0.106	0.073	0.082	0.069	0.130
Si	0.010	0.009	0.027	0.008	0.044
Na	0.058	0.017	0.058	0.046	0.058
B	0.026	0.004	0.029	0.021	0.055

Table B.19 Contamination Factors from Decontamination Process

Table B.19: This table contains the contamination factors (CF) from the decontamination process of the CA (V2) procedure for the T1P2 glass. The column titles are the experimental designations of each of the experiments

element	N2	O1	O2	PB	PC
Ce	0.019	0.014	0.049	0.034	0.014
Eu	0.061	0.049	0.116	0.120	0.049
Gd	0.055	0.045	0.109	0.100	0.044
Sm	0.062	0.049	0.120	0.124	0.048
Nd	0.092	0.074	0.216	0.176	0.058
Cs	0.065	0.057	0.158	0.141	0.058
Si	0.008	0.004	0.013	0.001	0.001
Na	0.040	0.008	0.135	0.087	0.003
B	0.032	0.029	0.119	0.054	0.011

The extraction efficiencies and recovery efficiencies were also determined for these experiments. For the experiments with the glass from the T1P1 batch, the extraction and recovery efficiencies, along with the mean and 97.7 % confidence interval (2 standard deviations), are given below

Table B.20 Experimental Efficiencies for CA (V2) Process

Table B.20: This table contains the extraction and recovery efficiencies calculated for the CA (V2) experiments with glass from the T1P1 batch. Also included is the arithmetic mean and the 2 standard deviation confidence limit (spread) of the data.

exp. ID	E_{th}	R_{th}
MA	89.21%	24.60%
MC	95.76%	33.17%
LA	88.51%	33.37%
LB	88.91%	28.50%
N1	91.15%	32.12%
AVG.	90.71%	30.35%
Spread	6.00%	7.53%

The extraction efficiencies and recovery efficiencies were also determined for these experiments. For the experiments with the glass from the T1P2 batch, the extraction and recovery efficiencies, along with the mean and 97.7 % confidence interval (2 standard deviations), are given below

Table B.21 Experimental Efficiencies for CA (V2) Process

Table B.21: This table contains the extraction and recovery efficiencies calculated for the CA (V2) experiments with glass from the T1P2 batch. Also included is the arithmetic mean and the 2 standard deviation confidence limit (spread) of the data.

exp. ID	E_{th}	R_{th}
N2	85.98%	32.12%
O1	86.44%	35.46%
O2	86.90%	23.75%
PB	87.83%	31.65%
PC	83.63%	27.31%
AVG.	86.16%	30.06%
Spread	3.14%	7.89%

The Decontamination factors botained with the solvent extraction (1+1) process were determined from the ratio of the contamination factor of a given element in the feed stream (the 'product' of the extraction process) and the contamination factor of hte element in the product solution of the decontamination process. These decontamination factors are shown below in tables B.22 and B.23.

Table B.22 Decontamination Factors from T1P1 glass runs

Table B.22: This table contains the decontamination factors (DF) from the decontamination process of the CA (V2) procedure for the T1P1 glass. The column titles are the experimental designations of each of the experiments

element	LA	LB	MA	MC	N1
Ce	30.69	55.19	26.36	32.98	22.53
Eu	20.19	35.24	12.98	17.48	9.89
Gd	20.77	35.10	14.25	19.56	10.97
Sm	20.06	34.20	13.98	19.28	10.86
Nd	31.50	68.09	23.62	32.04	16.73
Cs	20.34	29.65	25.53	30.44	15.11
Si	16.72	15.26	4.64	14.74	2.38
Na	72.24	244.36	70.32	86.82	24.53
B	76.07	568.02	69.84	92.76	37.43

Table B.23 Decontamination Factors from T1P2 glass runs

Table B.23: This table contains the decontamination factors (DF) from the decontamination process of the CA (V2) procedure for the T1P2 glass. The column titles are the experimental designations of each of the experiments

element	N2	O1	O2	PB	PC
Ce	35.46	48.45	13.83	20.28	50.30
Eu	16.98	21.31	9.00	8.90	21.86
Gd	18.73	23.37	9.59	10.54	23.61
Sm	18.32	23.37	9.50	9.30	23.91
Nd	29.48	37.16	12.60	15.78	47.48
Cs	32.12	35.71	13.13	14.86	43.06
Si	22.77	39.58	11.54	116.52	1498.21
Na	105.10	537.45	30.01	51.09	1608.49
B	71.00	79.34	19.04	41.88	210.92

B.6 ICP Experiments

This section details two sets of experiments to determine the accuracy and precision of the ICP for elements in question in this work in the sample matrix. The first experiment was to determine the error associated with the ICP measurements. The second experiment examined a technique for eliminating the effects of the cerium interference in the determination of cesium.

B.6.1 ICP Precision Measurement (10/18/95)

To determine the error associated with the ICP concentration measurements in this work, the following experiment was performed. Three standards were created, containing all 10 elements examined in this work. The concentrations of these standards were 10 ppm, 5 ppm, and 1 ppm. These standards were then used to create an ICP method (which was also used for the final confirmation experiments[B.5]). Each standard was measured 5 times. A Gaussian distribution of the measurements was assumed, and the standard deviation of the data was determined using the techniques presented in Tsoulfanidis (T2)[1]. The 97.7% confidence intervals (2 standard deviations) at 10 ppm, 5 ppm, and 1 ppm for each element are provided below.

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[1] Tsoulfanidis presents a summary of the statistics and error propagation techniques in chapter 2 of his text (ref. T2).

Table B.22 Error Measurement for ICP Measurements

Table B.22: This table contains the 97.7 (2 standard deviation) confidence limits on the relative errors associated with concentrations measured by ICP. The relative error, shown as a percentage of the mean concentration, associated with the concentration measurements was determined at 10 ppm, 5 ppm, and 1 ppm for the elements examined.

element	10 ppm	5 ppm	1 ppm
Ce	3.75 %	4.55 %	3.92 %
Th	3.58 %	3.93 %	3.31 %
Eu	2.61 %	3.19 %	3.17 %
Gd	2.92 %	3.80 %	3.43 %
Sm	4.18 %	5.72 %	4.23 %
Nd	2.45 %	2.28 %	5.34 %
Cs	3.85 %	8.36 %	44.21 %
Si	4.45 %	2.13 %	9.51 %
Na	3.81 %	3.79 %	9.49 %
B	2.60 %	2.07 %	7.63 %

B.6.2 Cesium Determination using ICP

In analyzing the experimental data it was discovered that there was a problem with the cesium measurements (over 200% of the cesium present in the glass was extracted into solution). This discrepancy was eventually attributed to a spectral interference from cerium. While there is an interference-free line to use in determining cerium concentrations there is no such line for cesium. To compensate for this it was proposed to measure the apparent cesium concentration due to cerium and determine a correlation between cerium concentration and apparent cesium concentration. Then by subtracting the apparent cesium concentration (due to the cerium interference) form the observed cesium concentration it would be possible to determine the actually cesium concentration.

In the process of calibrating the ICP to measure cesium (without the additional cerium interference), it was discovered that without the cerium it was not possible to identify the cesium peak above the background for the calibration range of interest (1 to 10 ppm). While it may be possible to use more concentrated samples to determine the cesium concentration these samples were not archived, due to problems associated with storing samples containing organics (previous archived samples from the PUREX scoping experiments had seriously degraded the sample containers).

B.7 Glass Composition Verification

The Pacific National Laboratory (PNL) procedure number APSL-03 (see Appendix C3) was used to attempt top verify the composition of the borosilicate glass from the T1P1 batch. The procedure was done twice, on 8/1/95 and 8/8/95. The measured composition of the glass from each experiment, the average experimental composition, and the nominal composition of the glass (Appendix A1) are compared below.

Table B.23 Measured Glass Composition

Table B.23: Using the APSL-03 procedure [C3], the composition of the T1P1 glass was determined. The measured compositions are shown below along with the average of the two measurements and the assumed (nominal) composition.

element	8/1	8/8	AVG.	nominal
Ce	1.012%	0.717%	0.865%	1.13%
Th	1.310%	0.847%	1.079%	1.76%
Eu	1.417%	1.373%	1.395%	1.73%
Gd	1.451%	1.369%	1.410%	1.74%
Sm	1.647%	1.625%	1.636%	1.72%
Nd	3.994%	3.801%	3.898%	4.70%
Cs	2.906%	2.445%	2.676%	1.01%
Si	19.03%	19.683%	19.357%	19.98%
Na	6.768%	7.255%	7.012%	6.60%
B	3.265%	3.267%	3.266%	3.23%

Discrepancies between the observed composition and the nominal, or predicted, composition can most likely be attributed to laboratory error, as there were difficulties dissolving and accounting for all of the alkali fusion (i.e. small bits of the fusion would stick to the crucible, or were splashed on the outside of the crucible). The observed cesium fraction, which is higher than expected (the only element that was observed to be above the predicted fraction), can be attributed to problems encountered in using the ICP to measure cesium concentrations in the presence of cerium. Cerium provides a spectral interference at the only wavelength available for determining cesium concentrations.

Appendix C1

Principles of Inductively Coupled Plasma (ICP)[1]

Below is a lab document posted in the ICP room at MIT, which describes the principles of inductively coupled plasma (ICP) analysis. ICP was used in the work presented here to determine the concentration of selected elements in solution.

Principles of ICP (Inductively Coupled Plasma)

by Kevin Hsueh, MIT. 1991. (H1)

1) A peristaltic pump ensures a steady flow rate of the sample.

2) The sample is introduced with a nebulizer which injects aerosols into the argon stream entering the plasma.

3) Argon gas flows through an open tube, the end of which is concentrated with RF coil which sets up an oscillating electromagnetic (EM) field.

4) A few argon ions are generated using an igniting device. These charged ions are caught by the oscillating EM field and try to follow the direction of the field.

5) This causes the ions to oscillate rapidly, which in turn results in the ions colliding with more argon atoms. These atoms then become ionized, generating secondary ion pairs of argon ions and electrons.

6) The number of ions rapidly increases until a steady state is reached. This constitutes a plasma.

7) When sample atoms are introduced into the plasma, they collide with the rapidly moving argon ions and become themselves excited.

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[1] Hsueh, Kevin. *Principles of ICP.* Lab procedures No. 41. 1/11/93. (H1)

8) The excited sample atoms and ions pass through the plasma, relax to lower energy states, and emit characteristic photons.

9) A spectrometer measures the intensity of certain selected photon wavelengths.

10) After calibration, chemical elements can be determined by their characteristic wavelengths.

Appendix C2

ICP Equipment Settings and Measurement Parameters

The following equipment settings and measurement parameters were used for all ICP measurements (unless otherwise noted) performed as part of these experiments

Coolant Temperature:	15°C
Argon Pressure:	100 psi
Coolant Flow	40
Nebulizer Pressure:	3.3 bar (cross-flow nebulizer)
Pre-flush Time:	45 s
High Flush Time:	20 s
Pump Speed:	3 (high flush)
Measurement Time:	100
Pump Speed:	2 (for measurements)
# of Measurements:	3

Appendix C3

Glass Composition Verification[2]

The procedure used to determine the final glass compositions, originally used at MIT by Anthony Brinkley (B4), was originally taken from PNL (Pacific National Labs) procedure number APSL-03. This procedure uses a potassium hydroxide (KOH) fusion to dissolve the glass; this fusion is subsequently dissolved in a hydrochloric acid (HCl) solution. This concentrations of all constituent elements in the glass, except for potassium, can then be determined by measuring the concentrations of the constituents in the resulting solution.

The glass was crushed using a ceramic mortar and pestle until it would pass through a 140 mesh (the original procedure calls for an alloy tool steel mortar and pestle). The crushed glass was weighed out to 0.25 +/- 0.075 grams and placed in a nickel crucible. Approximately 1.8 (+/- 0.4) grams of KOH were added to the nickel crucible. 0.2 +/- 0.1 grams of potassium nitrate (KNO_3) were added to the crucible to further facilitate the dissolution of the glass into the fusion. The contents were then swirled until the ground glass sample mixed with the flux.

Approximately three minutes were needed to melt the KOH pellets, and the total melt time was ten minutes. The crucible was then removed from the burner and allowed to cool to room temperature. De-ionized water (DI water), approximately 10 ml, was added slowly to the crucible to dissolve the cake-like melt. Once dissolved, the liquid was transferred to a 250 ml volumetric flask. This was repeated until all of the melt in the crucible was dissolved. After the transfer (transferred) was completed, the solution in the flask was diluted to approximately 100 ml total volume using DI water. The solution was then acidified using 25 +/- 5 ml of concentrated HCl acid. The solution was swirled, and if any precipitate remained undissolved in solution, 0.3 +/- 0.1 grams of oxalic acid crystals were added. The flask was then filled to the 250 ml mark with DI water.

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[2] the glass composition verification procedure was taken from Brinkley, Anthony L. Master's Thesis. MIT. June 1994. (B4)

Appendix C4

Operation of the ICP[3]

SETTINGS

Coolant Temperature: 15°C
Argon Pressure: 100 psi
Coolant Flow: 40
Nebulizer Pressure: Cross-flow: 3.3 bar Ultrasonic: 3.6 bar

Torch Position: the coil of the three tubes should be 1-2 mm below the coil

Nebulizer Pressure Adjustment
Cross-flow: use 1000 ppm Na solution; adjust small orange flame to be just above the top coil
Ultrasonic: use 100 ppm Na; adjust to be even with coil

Nebulizers:

Cross-flow

less accurate and sensitive
can handle samples with larger amounts of dissolved solids
sturdier and more reliable

Ultrasonic

more sensitive (x10)
easily clogged
prone to breakdowns

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[3] Sautman, Mark. *Operation of the ICP.* Laboratory Document. 1993. Revised by Cerefice, 9/95. (S1)

SAMPLES AND STANDARDS

NEVER RUN UNFILTERED SAMPLES IN ICP!!!!!!!!!!!!!

Filter solutions with syringe filters <1.0 micron

Standards and cleaning solutions do not have to be filtered if made with DI water

Acidify standards and samples to 5 vol. % HNO_3

Make standards by diluting ICP standards, available from PlasmaChem. Do not use AA standards.

Watch out for matrix interferences (e.g. NaCl) which can affect the readings use consistent matrixes in standards and samples

If the standards/samples are stored for more than a few weeks, visually examine the solutions for algae or other biological growths

Do not leave solutions uncovered for long periods of time - dust and other particles can fall in

Make sure containers are clean. **Never place a sample in a container which previously contained sand or other solids.**

Use wipes (Kimwipes, etc...) **to clean off sample tube when switching between samples, standards, blanks, etc...**

OPERATIONS

Startup and shutdown procedures are posted on the ICP and are included at the end of this document. If the ICP is off, you will have to put the system into stand-by mode before following the ICP START procedure. This is done by pressing the <STAND-BY> key.

WATCH THE FLAME DURING IGNITION. If the flame is not tall and narrow, but instead is short fat, and contained within the tube, **PRESS STOP OR STANDBY IMMEDIATELY!** You have had a reverse discharge, and have only about 3 seconds before the torch is melted. Melted torches can be re-blown by Precision Glassblowing in CO.

Reprofile before each use. If not prompted by the ICP, select the option under the F3 functions (press <F3> to get into the menu). Do this before preparing a new method or before recalibrating an existing method. Also you may need to do this again occasionally during operation. If you do reprofile, you will have to recalibrate the ICP afterwards. During reprofiling, the flame will dim and the power will drop to 1000.

Always have solution running through the nebulizer. Use DI water or 5 vol. % nitric acid if no samples are being run. Do no operate with just air!

Power should be 1200 except when reprofiling the ICP.

Run your standards every 4-5 samples to check the calibration of the ICP. If your concentrations are drifting, recalibrate the ICP, using the RECALIBRATE option in the <F3> menus.

Standard deviations should be below 1% except at low concentrations. See troubleshooting section if above 2 %.

Ultrasonic Nebulizer

Start in STANDBY mode. Wait until the condenser and desolvator lights come on before turning on operate.

Operate with the lid closed. If the lid is opened, the desolvator light will typically go off in a few minutes. Do NOT stay in OPERATE mode when the desolvator light is off or the transducer can overheat.

Do not stay in OPERATE mode if no solution is misting because the transducer is no longer being cooled down by the water.

Make sure that the cross-flow pump is not running. Press <PUMP> to turn it off.

PROGRAM CREATION

Menus at the top of the screen are accessed by pressing <ALT> and the first letter of the command. Use <RETURN> to indicate choices or to move to the next parameter. Use <F9> to enter the data and go to the next screen.

For the most part, the ICP itself will prompt you to the next step. You may have to wait, as the ICP computer is fairly slow. If nothing appears to be happening, press <Return> so that the ICP will know that you are ready for the next step.

Creation of a Program to Determine Concentrations

1) Press <F2> to see the menu.
2) Select CREATE
3) Select CREATE NEW
4) Select QUANTITATIVE

I. INITIALIZATION

1) Enter Method Name

II. LINE SELECTION

1) Choose ANALYZE LINE
2) Choose element
3) Choose proposed lines. Press <F5>. Look for disturbances from other elements that may be present in the samples.
4) Choose the wavelength. Avoid wavelengths where the numbers are in red or dark red.
5) Enter the scan name (usually, the element name is used)
6) Scan solution. Allow 45 seconds of pumping for the solution to reach the flame before starting the scan with <F12>.
7) Enter the element.
8) Center the cursor on the line in the spectrum (if prompted). Press <F9>
9) Accept line and measurement time with <F9>
10) For multi-elemental procedures, repeat steps 1-9 until all elements have been selected.
11) End select line

III. STANDARD SAMPLES

1) Create new sample file.
2) Enter File Name.
3) Enter standard sample names. Store with <F9>
4) Enter Concentrations with units. Store with <F9>

IV. MEASURE PARAMETERS

1) Select Measurement parameters:
   Preflush time: 45 s High Flush Time: 15 s Pump Speed: 3
   Meas. Time: 100 Pump Speed: 2
   # of Measurements: 5
   NOTE: Set Pump speeds to 0 if using the ultrasonic nebulizer

2) Select Input Data. Sample Name: y
3) Select Output Data.
   The following are all yes: print, avg., single meas., sample ID, conc. unit, negative conc. allowed
4) Exit parameter.

V. MEASURE STANDARDS

Follow prompts. Start measurements with <F12>
After each standard has been measured, press <F6> to get the average. Then press <F9> to store the result. Then press <F4>, as prompted, to go to the next standard.

VI. REGRESSION

1) Press <RETURN> to accept element.
2) Examine deviations
3) Press <F2> to look at the graph of the regression. Press <ESC> to return.
4) If regression is not acceptable, press <F2> for other regression options.
5) If regressions are acceptable, press <F9>

VII. END CREATING

To use an existing method

1) Reprofile the ICP (in <F3> menu) before recalibrating.
2) Use the <F2> key to get into the menus. Go to ANALYZE main menu.
3) Select quantitative method. Enter method name by using the <PAGE UP> and <PAGE DOWN> keys to move through list of methods
4) Once method has be loaded, you must recalibrate it (if not prompted by ICP). Recalibrate the method using RECALIBRATE option in <F3> menu.
5) Run some of your standards to check the calibration. It may be necessary to recalibrate the ICP again.

Qualitative Scans

These are used to determine if a given element is present, but not what the concentration is. The height of the peak does NOT necessarily represent the magnitude of the concentration.

Choose element and wavelength

Allow 45 seconds of pumping for the solution to reach the flame before starting the scan with <F12>

ICP START Procedure[4]

(1) Switch on exhaust system. (Note: this is usually left on)
(2) Check cooling water level.
(3) Open closing valve of argon tank. Record argon pressure.
(4) Switch on water cooling system.
(5) Tighten tension on sampling tubes.
(6) Check coolant flow rate (press <+>). Then press <STOP> key.
(7) Check nebulizer pressure (press <->). Then press <STOP> key.
(8) Check torch position and clearance.
(9) Press the <START> key.
(10) **Watch ignition of the plasma. If there is a problem, you will have only 3 seconds to stop the ignition before melting the torch.**
(11) Switch on pump (press <PUMP> key) and flush the system with DI water or a 5 vol. % solution of nitric acid for 15 to 30 minutes.
(12) Write down the start time, sample description, and argon pressure in the ICP room log book.

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[4] Hsueh, Kevin. *ICP start up and shutdown procedures.* Lab document #42. 5/24/94. (H2)

ICP STOP Procedure[5]

(1) Flush the system with DI water or a 5 vol. % solution of nitric acid for 10 minutes.

(2) Press the <STOP> key.

(3) Close the closing valve on the argon tank. Record the argon pressure.

(4) Switch off exhaust system. (Note: this system is usually to be left on)

(5) **Release tension in the sampling tubes.**

(6) Wait 5 minutes. Then shut off the water cooling system.

(7) Write down stop time, argon pressure, and initial the ICP room log book.

Note:
If the ICP has not been used recently, it will most likely have to be brought into stand-by mode before beginning the start-up procedures. This is done by pressing the <STAND-BY> key. If the ICP will not be used for some time, it should be shutdown. To do this press the <STAND-BY> key after completing the ICP STOP procedures.

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[5] ibid. (H2)