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# COMPOSITIONS AND DURABILITIES OF GLASSES FOR IMMOBILIZATION OF PLUTONIUM AND URANIUM

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## ABSTRACT

Investigations have been performed to determine the suitability of glass as a host for surplus fissile material removed from nuclear weapons. The U.S. Department of Energy - Office of Technology Development has sponsored research at the Savannah River Site to develop durable glass compositions that are compatible with high concentrations of plutonium and uranium. These investigations also being performed to provide baseline actinide glass durability and processing data.

Two glass forming systems are being evaluated. One of the systems is a commercial borosilicate glass and the other an iron phosphate glass. Both glass systems have a very high degree of compatibility with actinide oxides and are considerably more durable than conventional high-level waste glasses. The iron phosphate glass has a melting temperature in the 1100°C range and has the higher uranium and plutonium solubility. The borosilicate has a melting temperature in the 1425°C range and is the more durable (on the order of fused silica) glass.

## INTRODUCTION

As the nuclear weapon arsenals of the United States and the Former Soviet Union are reduced, metric tonnage quantities of fissile material must be dispositioned [1]. One of the potential disposition options for U.S. weapons material is vitrification into a plutonium or uranium glass product [2]. The U.S. Department of Energy - Office of Technology Development has sponsored a program at the Savannah River Technology Center (SRTC) to develop suitable glass formulations for the long term safe storage of uranium and plutonium, as well as americium, neptunium and curium. These "actinide glasses" are the focus of this paper [3].

Three of the most important questions which must be answered for any actinide glass product are (1) what is the maximum actinide oxide loading, (2) what is the chemical durability, and (3) how can it be produced. The experiments described below were performed to provide a preliminary technical baseline on actinide solubility in glass and glass durability. Glass processing characteristics and limits will be discussed in subsequent publications.

This paper discusses the chemical composition and durability of two types of actinide glasses under development. One of the glasses is a commercial borosilicate composition developed in the 1930's for use as an optical glass [4]. This glass, referred to as the Löffler glass, was selected for study due to the very high (55 weight percent) lanthanide oxide content [5]. Lanthanides are commonly used as actinide surrogates [6]. There was, therefore, a high degree of confidence that this glass would be chemically compatible with high concentrations of actinides. The other glass is an iron phosphate. This glass was selected for study due to the combination of low melting point and high durability [7,8]. In the initial studies thorium and uranium were used as the actinides. Because of the low radioactivity of these elements, the glasses could be prepared and tested on the bench top.

The specific objectives of the initial study were to determine:

(1) maximum weight percent loading of thorium an uranium oxide in the borosilicate and phosphate glass,

(2) chemical durability of the glasses as a function of actinide loading,

Data obtained were used to determine initial frit compositions and processing parameters for the plutonium melts. The first plutonium glasses have been prepared and are being tested in the shielded cell and glovebox facilities at SRTC.

## EXPERIMENTAL

### Glass Fabrication

The initial glass samples fabricated were made from reagent chemicals. The batches were made in high-form alumina crucibles. Water was added to all reagent chemical batches to ensure proper mixing. The batch was allowed to dry overnight at 90°C prior to firing. The crucibles were then placed in a furnace and ramped to temperature no faster than 8°C per minute. The appropriate melt temperature was held for a period sufficient to ensure complete melting. The glass was then cast into a graphite mold and annealed. Glass frit was produced in the same manner except the melt was cast into water and then crushed into powder.

### Glass Durability Testing

Relative durability of the glasses discussed above was measured using the ASTM C-1285 standard nuclear waste glass durability test method, commonly referred to as the Product Consistency Test, or PCT [9]. The PCT protocol calls for crushed glass powder to be reacted with ASTM-I deionized water in a closed vessel [10]. The test conditions included:

- 10 milliliters ASTM-I $H_2O$ per gram 100-200 mesh glass powder,
- 90°C test temperature,
- 7 day test duration.

PCT leachates were analyzed for soluble glass constituents by Inductively Coupled Plasma - Emission Spectroscopy (ICP-ES). U and Th concentrations in the leachates were determined by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). Leachate solution pH was measured by a glass bulb electrode.

Relative glass durability was calculated from the PCT data. Normalized Loss ($NL_{[i]}$), a common expression of relative glass durability was calculated for each glass tested. $NL_{[i]}$ is a function of the concentration of a soluble glass constituent cation in the PCT leachate solution and the concentration of the cation in the glass. $NL_{[i]}$ is expressed in the units grams of glass dissolved per liter of leaching solution. The following relationship is used to calculate $NL_{[i]}$:

$$NL_{[i]} \equiv \frac{c_{[i]}}{(1000)f_{[i]}}$$

where

$c_{[i]}$ = concentration of "i" in solution (mg/L),

$f_{[i]}$ = weight fraction of "i" in glass.

### X-Ray Diffraction

X-Ray Diffraction was performed on all samples to identify any crystalline phases. Scanning Electron Microscopy was also performed as a complementary technique if crystalline phases were detected. None of the glass samples discussed above had any discernible crystalline character.

## RESULTS

### Glass Production

Minor adjustments to the base Löffler glass composition were made in order to lower the melting point and liquidus temperature and raise the melt viscosity [11,12]. This was accomplished by reducing the total lanthanide oxide content and increasing the alumina, lead oxide, and silica fractions of the glass composition. The compositions of one series of glasses, which bracket the expected process parameters for actinide glass production, are given in Table 1. All glasses shown in Table 1, with the exception of Lan-22, were melted at 1425°C. Lan-22 was melted at 1460°C.

Table 1. Composition Range of Non-Radioactive Loffler Glasses Tested (oxide mole percent)

| Oxide | Lan-14 | Lan-17 | Lan-18 | Lan-19 | Lan-22 | Target |
|---|---|---|---|---|---|---|
| $SiO_2$ | 51.7 | 46.4 | 48.1 | 50.5 | 47.6 | 49.4 |
| $B_2O_3$ | 7.8 | 6.9 | 7.4 | 6.8 | 6.3 | 5.4 |
| BaO | 2.6 | 2.7 | 2.1 | 1.7 | 2.5 | 2.8 |
| $Al_2O_3$ | 16.9 | 19.9 | 18.5 | 17.3 | 18.4 | 18.0 |
| $La_2O_3$ | 9.9 | 5.7 | 9.9 | 10.3 | 9.0 | 5.8 |
| $Nd_2O_3$ | 0.0 | 7.6 | 3.6 | 3.5 | 6.6 | 6.7 |
| $CeO_2$ | 5.5 | 6.0 | 5.6 | 5.3 | 5.2 | 6.9 |
| PbO | 5.8 | 4.9 | 4.7 | 4.6 | 4.4 | 5.1 |

The next series of glasses consisted of uranium and thorium oxide added to the target glass composition shown in Table 1. Uranium and thorium oxide were substituted on a 1:1 molar basis for cerium and neodymium oxide. Melts containing 1, 5, and 9 mole percent (9 mole percent $\cong$ 20 weight percent) uranium oxide (calculation basis $UO_2$) and thoria ($ThO_2$) were successfully processed at 1425°C.

The base composition iron phosphate glass, as shown in Table 2 has a melting point $\cong$ 1100°C. No composition adjustment was necessary to the base glass prior to adding uranium or thorium oxide. Thorium and uranium oxide were substituted on a 1:1 molar basis for $Fe_2O_3$. Melts containing 10, 14, and 17 mole percent (17 mole percent $\cong$ 30 weight percent) actinide oxide were successfully processed at 1150°C.

Iron phosphate glass frits were made for plutonium processing. Frit and $PuO_2$ were mixed together and then heated to 1100°C (5 hours at temperature). Melts containing 10 and 17 mole percent $PuO_2$ were successfully processed. A frit composition (denoted Frit + Ba) developed for the plutonium glass melts is shown in Table 2.

Table 2. Composition of the Iron Phosphate Base Glass and Frit Glass (oxide mole percent)

| Oxide | Base | Frit + Ba |
|---|---|---|
| $P_2O_5$ | 55.0 | 66.3 |
| BaO | 0.0 | 3.6 |
| $Na_2O$ | 10.0 | 12.0 |
| $Fe_2O_3$ | 35.0 | 18.1 |

## Relative Glass Durability

The Löffler glasses are quite resistant to aqueous attack. The PCT experiments on the non-radioactive glasses (Table 1) show very uniform results. All six Löffler glasses tested were more durable than two common durable glasses - Vycor and fused silica. This is graphically represented in Figure 1. Table 3 lists the PCT leachate Si concentration for the Löffler glasses, fused silica and Vycor. Normalized Release, $NR_{[Si]}$, and the Glass ID's used in Figure 1 also shown in Table 3.

Thorium and uranium bearing Löffler glasses are also quite resistant to aqueous attack. The PCT results show little or no difference between the durability of actinide bearing and non-radioactive compositions. Also, uranium and thorium oxide appear to have identical effects on glass durability. There is no difference between the durability of glasses with 1 percent and 5 percent actinide oxide content. Glasses with 9 mole percent actinide oxide were slightly less durable. These results are displayed in Figure 2. It should be noted the relative durability of the Löffler glasses is approximately 3 orders of magnitude better than the standard for high-level waste glass [13,14].

The iron phosphate glasses are also quite resistant to aqueous attack. PCT experimental results indicate the iron phosphate glass to be approximately 2 orders of magnitude more durable than the standard for high-level waste glass. Thorium and uranium bearing glasses have similar PCT response up to the 20 weight percent actinide oxide concentration. Both thorium and uranium have a negative effect on the durability of the iron phosphate glass beyond 20 weight percent oxide loading. Beyond twenty weight percent, uranium glasses are appreciably less durable than thorium glasses. These data are graphically represented in Figure 3. The leachate solutions are also significantly more acidic as the uranium oxide content increases beyond 20 weight percent. These data are graphically represented in Figure 4.

Table 3. Durability Data From Löffler Glasses, Fused Silica, and Vycor

| | Vycor | Silica | Target | Lan-14 | Lan-17 | Lan-18 | Lan-19 | Lan-22 |
|---|---|---|---|---|---|---|---|---|
| ppm Si | 54.3 | 26.4 | 1.12 | 2.00 | 3.25 | 1.12 | 2.24 | 1.34 |
| $NL_{[Si]}$ | 0.121 | 0.057 | 0.010 | 0.015 | 0.030 | 0.010 | 0.019 | 0.011 |
| Glass ID* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

* Denotes the ID used on the x-axis of Figure 1.

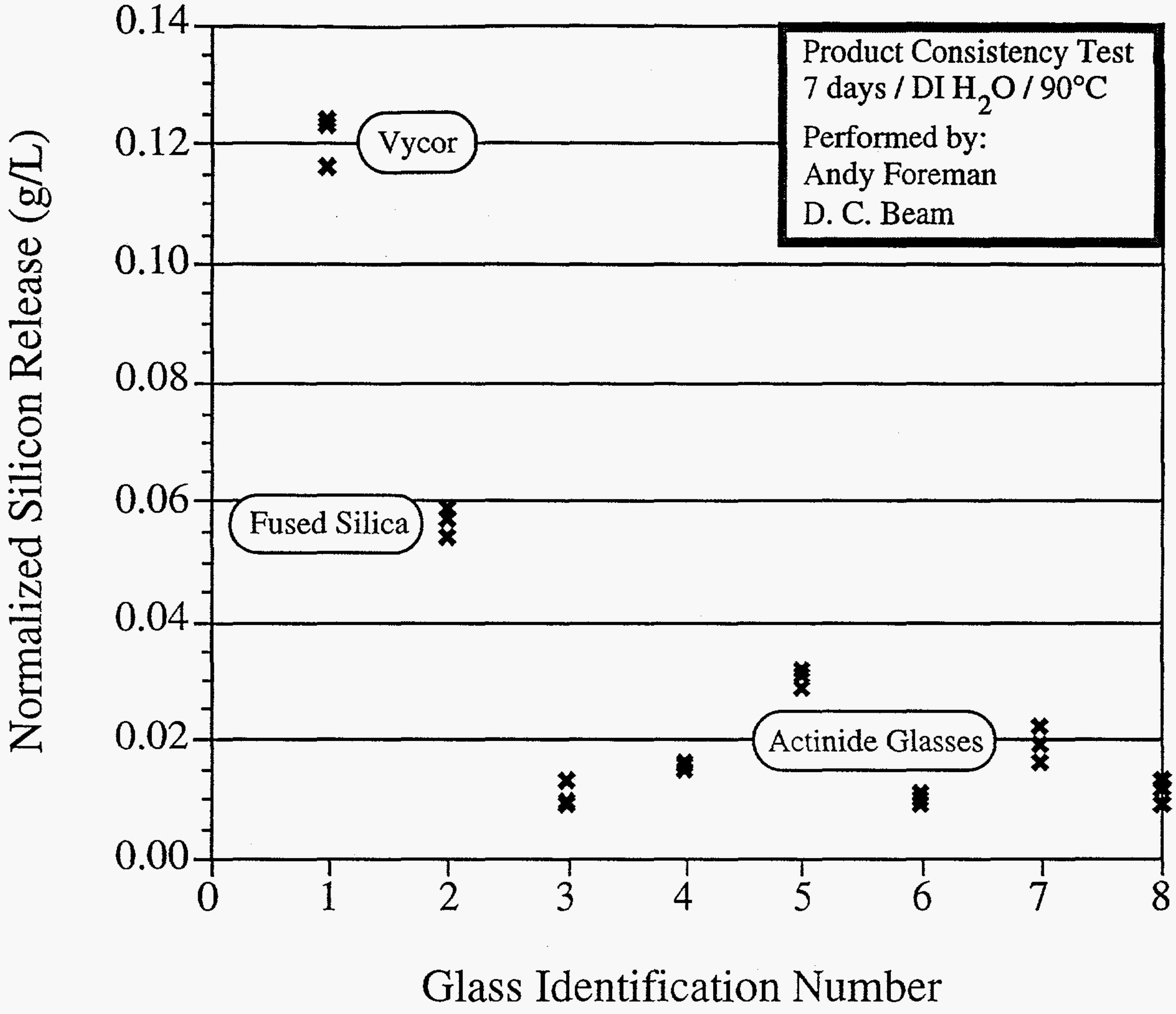

Figure 1. Relative Durability of Löffler Glass as determined by the Product Consistency Test

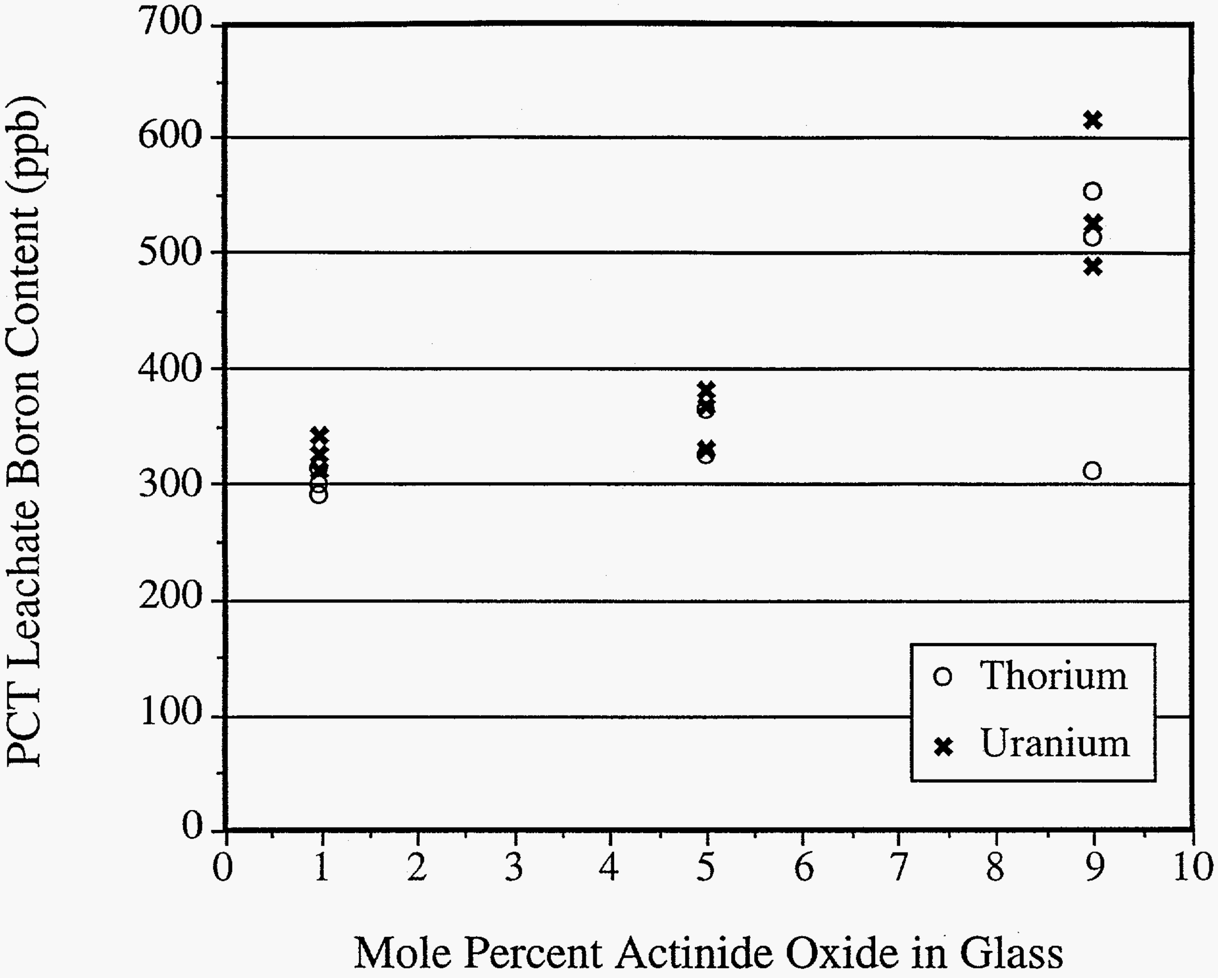

Figure 2. Effect of Actinide Oxide Content on Löffler Glass Durability

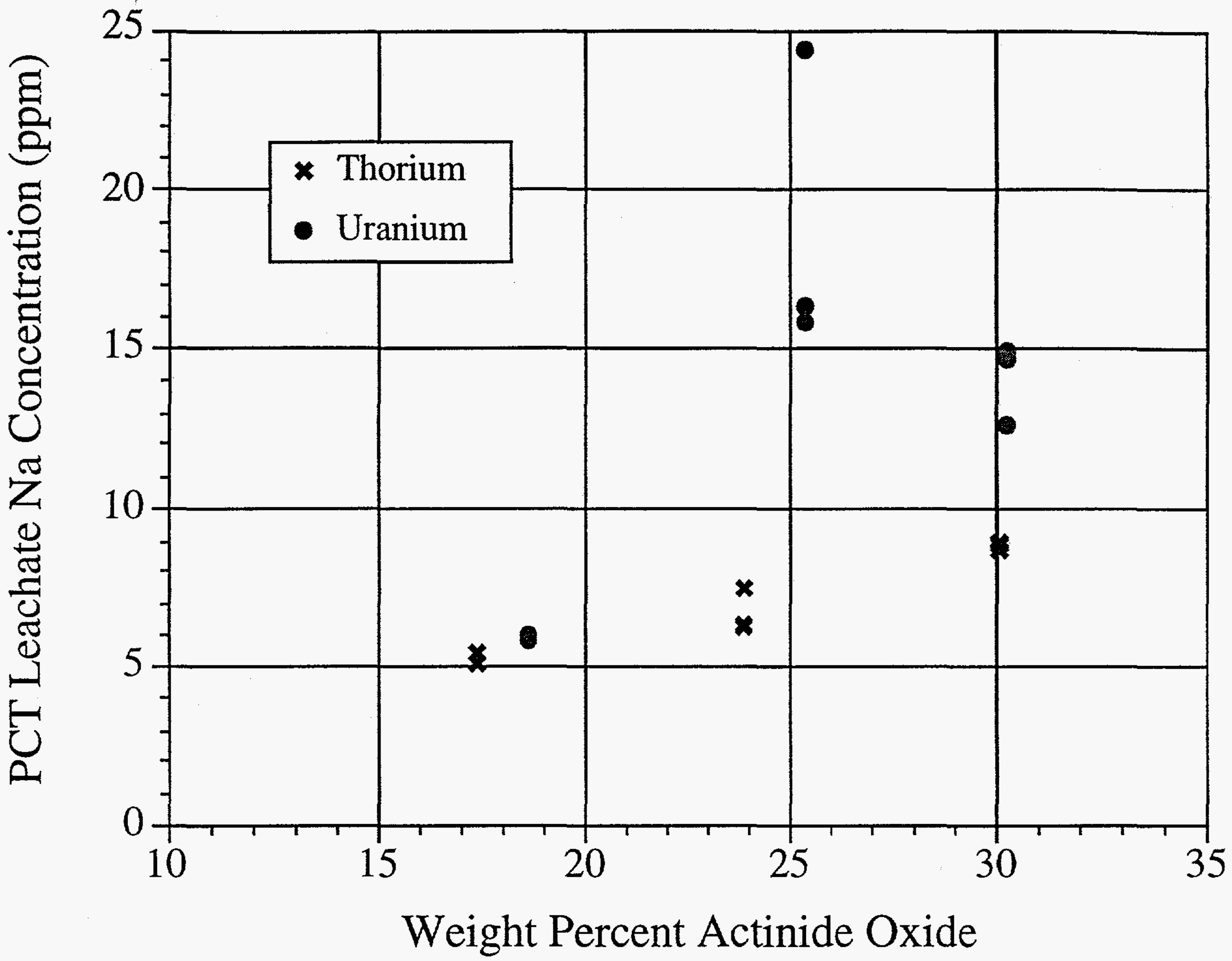

Figure 3. Effect of Actinide Oxide Loading on Iron Phosphate Glass Durability

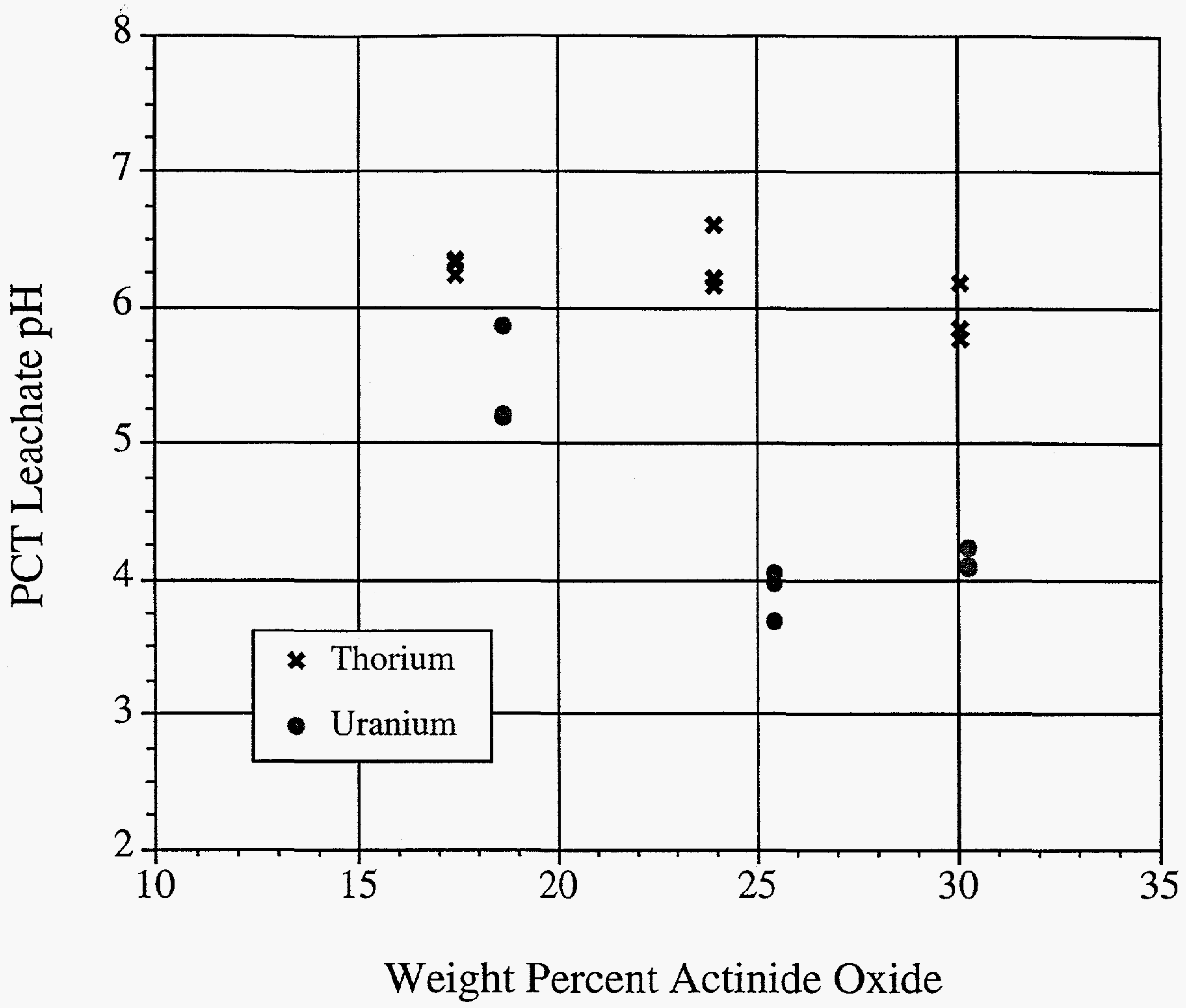

Figure 4. Acidity of Iron Phosphate Glass Leachate Solutions

## DISCUSSION

The Löffler and iron-phosphate glass compositions with high concentrations of actinides. Also, both glasses are extremely resistant to aqueous corrosion. Interestingly, the Löffler and iron phosphate glass are completely different chemically. The base compositions share no common oxides. Löffler glasses are processed at temperatures consistent with commercial borosilicate glasses. Iron phosphates are processed at temperatures 300°C lower, in the range of high-level waste glasses. It is felt, therefore, that these glasses may be used for different actinide vitrification missions - in the manner of complimentary products. The Löffler glass has been selected as the optimum glass formulation for vitrification of SRS americium and curium [11]. This glass is compatible with existing commercial melters and appears well suited for mass production. It is completely compatible with lanthanide neutron poisons (Gd, Sm, Eu) and, certainly, boron. The use of dual neutron poisons in the frit and glass compositions has obvious safety benefits.

The iron phosphate does not have the same degree of compatibility with lanthanide neutron poisons as the Löffler glass, but is easily processed in low temperature furnaces. Moreover, the glass appears to be fairly tolerant of fluoride and reducing agents. For this reason, the iron phosphate is being proposed for disposition of heterogeneous, sub-critical masses of plutonium by direct vitrification. This should significantly lessen the number of pretreatment processes which must be developed to handle existing U.S. plutonium inventories.

## CONCLUSIONS

There are four principal conclusions.

1) The solubility of thorium and uranium oxide in a representative Löffler borosilicate glass is approximately 9 mole percent (20 weight percent).

2) The durability of the Löffler borosilicate glass is extremely high, equivalent or better than fused silica. Thorium and uranium oxides have identical effects on Löffler glass durability.

3) The solubility of plutonium, uranium, and thorium oxide in the iron phosphate glass is approximately 17 mole percent (30 weight percent).

4) The durability of the iron-phosphate glass is considerably better than the standard for high-level waste glass. Glasses with high concentrations of uranium are slightly less durable than corresponding thorium bearing glasses.

The Löffler composition is the recommended glass composition for vitrification of SRS Am and Cm. The original composition has been tailored to be more compatible with the tetravalent actinide oxides and existing commercial melter systems. Based on the processability and extremely high chemical durability, it is concluded that this glass should also be considered for vitrification of metric tonnage quantities of weapons plutonium and uranium.

The iron phosphate glass has extremely high chemical compatibility with actinide oxides. It also has a high chemical durability and can be easily processed on the crucible scale. Based on these data, this glass should be considered suitable for disposition of small, heterogeneous sources of plutonium and uranium.

## ACKNOWLEDGMENT

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