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by

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Abstract

Chemical Compatibility of HLW Borosilicate Glasses with Actinides: Solubilities and Segregation Processes

During liquid storage of HLLW the formation of actinide enriched sludges is being expected. Also during melting of HLW glasses an increase of top-to-bottom actinide concentrations can take place. Both effects have been studied.

Besides, the vitrification of plutonium enriched wastes from Pu fuel element fabrication plants has been investigated with respect to an isolated vitrification process or a combined one with the HLLW. It is shown that the solidification of actinides from HLLW and actinide waste concentrates will set no principal problems.

The leaching of actinides has been measured in salt brine at 23° C and 115° C.

Zusammenfassung

Chemische Verträglichkeit von HLW-Borosilikatgläsern mit Aktiniden: Löslichkeiten und Segregationsprozesse

Während der Lagerung von flüssigen hochaktiven Abfallösungen wird mit der Bildung von Aktiniden-haltigen Niederschlägen gerechnet. Ebenso kann es während des Schmelzens von hochaktiven Gläsern zu einer Anreicherung von Aktiniden durch Schwerkraft kommen. Beide Effekte sind untersucht worden.

Daneben wird die Verglasung von plutoniumreichen Abfällen aus der Pu-Brennelementfertigung unter den Gesichtspunkten der direkten Verglasung oder der Verglasung zusammen mit den hochaktiven Abfallösungen untersucht. Es wird gezeigt, daß die Verglasung von Aktiniden aus hochaktiven Abfallösungen und Aktinidenabfallkonzentraten keine besonderen Probleme aufwirft.

Die Auslaugung von Aktiniden durch Salzlaugen ist bei 23° C und 115° C gemessen worden.

Résumé

Compatibilités chimiques des verres borosilicate à hautes activités avec des actinides: solubilités et procédés de segregations

Pendant le stockage des déchets liquides à hautes activités la formation de boue enrichie par des actinides est supposée. Egalement, pendant la fusion des verres à hautes activités les actinides peuvent être concentrés aux fonds des fontes. Les deux effets ont été étudiés.

Au delà la vitrification des déchets enrichis par le plutonium provenant des installations de fabrication des combustibles contenant de plutonium a été étudiée sous l'aspect d'une vitrification exclusive ou ensemble avec les déchets liquides à hautes activités. Il est démontré qu'il n'y a pas des problèmes concernant l'enrobage des déchets divers alpha dans les verres.

La lixiviation des actinides par des eaux salées a été mesurée à 23° C et à 115° C.

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1. Introduction

Borosilicate glasses are considered to be a suitable matrix for the immobilization of fission products and actinides from high level liquid wastes (HLLW). The high active vitrification products are representing the most effective barrier against any influences which might cause transition of activity onto the pathways to the biosphere:

- In the run of extensive time lapse irradiation experiments, it has been shown that borosilicate glasses are stable against long-term irradiation over millennia (1-4).
- It has also been demonstrated that borosilicate glasses are highly resistant to the attack of different leachants ranging from pure water to saturated salt brines which, eventually, are generated in the case of natural events and water penetration to the final disposal in salt deposits. Investigations on the leaching mechanism have provided additional information on the behaviour of actinides in the system glass/leachant, where the actinides have turned out to be bonded to high polymer siliceous molecules (5).

From the above mentioned criteria it is being suggested that borosilicate glasses are as well suitable for immobilizing actinide waste concentrates from fuel reprocessing and plutonium fabrication. In the frame of the experimental work reported below the various actinide enriched waste streams will be characterized with respect to the feasibility of their incorporation into borosilicate glass. The feasibility study is based on the concept of the solidification of HLLW combined with the α -bearing effluents, mainly those arising from the UO_2/PuO_2 -fuel element fabrication, into borosilicate glasses. Besides that, the isolated actinide enriched waste

forms are considered in view of extreme conditions and compositions which may occur upon vitrification.

With reference to previously published (5) data supplementary results on the leaching of plutonium, americium and neptunium by saturated salt brine, formed when water penetrates rock salt repositories, are provided. The leach rates as determined for the single actinide elements at ambient and boiling temperature are significantly different from each other, indicating that the earlier supposed leaching mechanisms (5) in saturated salt solutions have to be considered seriously and proven by further experiments. Some suggestions are set up from the evaluation of the investigations reported below.

2. General

First of all, experiments were carried out on HLLW and its vitrification products, as they contain besides large amounts of fission products also some actinides. These actinides can be enriched either in sludges formed during liquid storage of HLLW or during melting of HLW glasses by segregation processes:

- Besides some qualitative information there is, at the time being, no analysis available on the composition of sludges formed in HLLW storage tanks.

One fraction of the sludges will be due to dispersed undissolved nuclear fuel, another fraction will consist of phosphates esp. zirconium phosphate formed after degradation of residual dissolved tributyl-phosphate. A third fraction will consist of dispersed insoluble fission products or precipitating compounds due to the change of valency states

or to the decrease of the nitric acid concentration as a consequence of its radiolytic decomposition.

Following these considerations, homogeneous solutions of simulated full-level LWR-HLLW with 5 mole/l HNO_3 and 1 mole/l HNO_3 with the proper amounts of actinides have been prepared. Both solutions have been stored for several months until sludge formation was observed to reach equilibrium. Sludges and supernatants were analyzed.

- An increase of actinide concentrations in the glass melts from top to bottom by force of gravity has sometimes been considered.

Therefore, experiments have been performed to study the actinide concentration increase as a function of the residence time at melting temperature. To achieve a high accuracy for the subsequent analytical determinations on the cooled down glass cylinders, the full-scale HLW glasses were doped with a more than one order of magnitude excess of plutonium and uranium.

Whereas these laboratory scale experiments are performed on initially homogeneous HLW glasses, the realistic conditions of HLW glass production are different, starting with an inhomogeneous mixture of HLW calcine and glass forming additives. It is therefore, that occasionally, sedimentation of some oxides like cerium and plutonium oxide has been observed in glass melting technology. This effect has not been investigated in the frame of the work reported here. But the effect may be attributed to the low dissolution rate of some oxides in glass melts, and has to be studied according to the special calcining and melting conditions applied in the individual technical process.

To obtain a figure of the solubility of actinides in borosilicate glass a base glass and two typical HLW glasses have been doped with high concentrations of actinides, esp. of plutonium, americium, neptunium and uranium. All glasses have been quantitatively analyzed by microprobe as well as second crystalline phases if any phase separation occurred due to oversaturation of the borosilicate glass melts. These experiments should render an account of a general waste management concept based on the immobilization of HLLW together with all α -bearing liquid or dispersible effluents from a LWR reprocessing and UO_2/PuO_2 recycle fuel production plant.

As one of these α -waste streams the incinerator ashes from the dry combustion of solid plutonium containing material seem to pose some problems with respect to vitrification. Therefore, the extreme composition of typical incinerator ashes has been vitrified with borosilicate glass without any blending with HLLW, as considered in the general concept mentioned above. Thus, the individual criteria for the solubility limits of incinerator ashes in borosilicate glass have been established.

The lixiviation of individual constituents of borosilicate glasses with water or diluted aqueous solutions has proven as independent on the respective concentration in the glass (5). But, a different behaviour must be expected for the leaching with saturated salt brines as has been shown by some preliminary leach test results (5). Extended experiments have been performed and, obviously, the leaching mechanism with saturated salt brines renders some striking aspects with regard to the leaching behaviour of the different actinides, esp. with respect to their valency states.

3. Experimental

3.1 Sludge Formation from HLLW

A full level simulated HLLW was prepared by mixing the corresponding nitrate solutions of the inactive fission product isotopes, technetium was substituted by manganese, and the actinides corresponding to a LWR-fuel burn-up of 33 GWd/t. The concentration of uranium and plutonium was equivalent to losses of 1 wt.-% each to the HLLW. The free nitric acid concentration amounted to 5 mole/l and the total concentration of fission products and actinides of the 2 l-batch was corresponding to 960 l HLLW/t spent fuel. 1 l of the batch was carefully denitrated by addition of formic acid to the boiling solution until the nitric acid concentration had decreased to 1 mole/l. Both, the 5 mole/l and the 1 mole/l nitric acid solutions of simulated HLLW were kept at boiling temperature for 10 hours, afterwards stored at ambient temperature for several weeks.

In the same manner simulated HLLW solutions were prepared, which contained an additional quantity of gadolinium nitrate corresponding to 15 kg of gadolinium per ton of spent fuel. The gadolinium should simulate the homogeneous poisoning of the dissolver acid in great reprocessing plants, where finally the gadolinium ends up in the HLLW.

The solutions were stirred during storage. About every 5 days samples were taken for analysis of the HLLW aiming at the determination of the equilibrium state for the sludge formation and possible adsorption processes. The equilibrium was reached after about 3 months.

The analytical measurements were performed on the supernatant and on the sludge after filtration (pore size of the filter: 0,1 μm):

- The ignition residues were obtained on a series of equal samples kept for various periods of time at 900^o C. From the graph - weight of residue/time of ignition - a real weight for the ignition residue could be extrapolated. This procedure was taking into account petty losses of material due to volatilization. Thus, an accuracy of $\pm 10 \%$ was achieved.
- The actinides were determined by two independent methods, γ -spectrometry and x-ray fluorescence, whereas molybdenum and zirconium were only analyzed by the latter method.

The analytical results are compiled in table 1:

As a result, it can be seen that no significant precipitation of actinides in the HLLW has occurred, but high amounts of Zr and Mo are present in the sludge.

3.2 Sedimentation of Actinides from Glass Melts

The sedimentation behaviour of actinides and cerium has been studied on two reference HLW borosilicate glasses containing 20 wt.-% and 30 wt.-% of HLW-oxides with the compositions listed in table 2. These glasses were doped with an additional quantity of 5 wt.-% uranium oxide and 1 wt.-% plutonium oxide to achieve a good analytical accuracy for these elements in the subsequent microprobe analysis. The doped specimens were grinded and remelted twice in order to obtain glass cylinders with a homogeneous distribution of the vitrified elements.

These glass cylinders (80 mm long) were melted again in a platinum crucible and kept at melting temperature (1175^o C) for 25 hours. After cooling of the glass cylinders three sections were analyzed in the electron microprobe:

Table 1 Composition of Sludges Formed during Storage of HLLW - Experimental Results

compound	kind of HLLW ^{*)}			
	5 M HNO ₃	5 M HNO ₃ with Gd-Poisoning	1 M HNO ₃	1 M HNO ₃ with Gd-poisoning
	precipitated compounds in wt.-% of their initial content in the HLLW			
AmO ₂	< 0.1	< 0.1	< 0.1	< 0.1
NpO ₂	< 0.1	< 0.1	< 0.1	< 0.1
PuO ₂	< 0.1	< 0.1	< 0.1	< 0.1
UO ₃	≤ 0.1	≤ 0.1	0.6	0.6
ZrO ₂	16.5	16.5	38.2	31.7
MoO ₃	58.2	59.0	84.2	81.6
	relative ignition residues of sludge/sludge and supernatant (wt.-%)			
ignition residue at 900° C	20.8	15.2	17.6	12.0
	precipitated compounds in wt.-% of the total of sludge compounds			
AmO ₂	< 0.01	< 0.01	< 0.01	< 0.01
NpO ₂	< 0.01	< 0.01	< 0.01	< 0.01
PuO ₂	< 0.01	< 0.01	< 0.01	< 0.01
UO ₃	≤ 0.1	≤ 0.1	0.7	0.8
ZrO ₂	7.2	7.0	19.6	17.0
MoO ₃	26.5	26.2	45.3	46.0

*) HLLW from the reprocessing of spent LWR-fuel:
 - burn-up: 33.000 MWd/t (6)
 - U and Pu losses to HLLW: 1 wt.-%
 - concentration: 960 l/t HM
 - optional Gd-content, introduced as homogeneous poison into the dissolver acid: 15 kg Gd/t HM

Table 2 Composition of Reference HLW Borosilicate Glasses

component	composition (wt.-%)	
	HLW glass 98 - 20 %	HLW glass 98 - 30 %
<u>base glass:</u>		
SiO ₂	40.2	35.1
TiO ₂	3.3	2.9
Al ₂ O ₃	1.1	1.0
B ₂ O ₃	10.8	9.5
CaO	2.2	2.0
Na ₂ O	21.9	19.1
<u>fission products</u> ¹⁾ :		
SrO	0.498	0.498
BaO	0.760	0.760
Cs ₂ O	1.360	1.360
Rb ₂ O	0.175	0.175
TeO ₂	0.380	0.380
MoO ₃	2.470	2.470
Ru	1.060	1.060
Rh	0.187	0.187
Pd	0.635	0.635
instead of TcO ₂ : MnO ₂	0.526	0.526
CdO	0.045	0.045
ZrO ₂	2.360	2.360
Y ₂ O ₃	0.282	0.282
Ld ₂ O ₃	0.710	0.710
Ce ₂ O ₃	1.600	1.600
Nd ₂ O ₃ ²⁾	2.900	2.900
Pr ₂ O ₃	0.670	0.670
<u>corrosion products:</u>		
Fe ₂ O ₃	1.870	1.870
Cr ₂ O ₃	0.530	0.530
NiO	0.290	0.290
<u>actinides:</u>		
UO ₂	0.516	0.516
NpO ₂	0.412	0.412
(Am,Cm)O ₂	0.115	0.115
PuO ₂	0.015	0.015
<u>Gd neutron poison:</u>		
Gd ₂ O ₃	-	10.0

1) the fission product composition corresponds to spent LWR-fuel with a burn-up of 33 GWd/t (6)

2) Nd₂O₃ content comprises (wt.-%): 2.23 Nd₂O₃ + 0.46 Sm₂O₃ + 0.06 Gd₂O₃ + 0.05 Pm₂O₃ + 0.10 Eu₂O₃

- bottom section: 0 - 10 mm height
- middle section: 35 - 45 mm height
- top section : 70 - 80 mm height

One representative set of results of the quantitative electron microprobe analysis is listed in table 3. A detailed description of the analytical procedure is given in chapter 3.5.

From the results (table 3) of the sedimentation experiments it is demonstrated that no significant actinide enrichment processes take place during melting of HLW glasses for periods of 25 hours.

For these experiments it can be supposed that the glass melts have not been stirred neither by thermal convection nor by gas evolution or other physical and chemical effects which are involved under realistic technological conditions:

Conditions for an undisturbed sedimentation process are at least indicated by the complete sedimentation of dispersed particles of the noble metals, which, normally, are homogeneously distributed in the HLW glasses in consequence of their low particle size being in the range of some μm :

Figure 1 shows the noble metals in the bottom section of the glass cylinders.

3.3 Solubility of Actinides in Borosilicate Glass

To obtain a figure of the solubility of actinides in borosilicate glasses a base glass 98 and two reference HLW glasses, 98-20 % and 98-30 % as listed in table 2, have been doped with high concentration of actinides. The procedures and the results of the microprobe analysis can be summarized as follows (8):

- 1) the glasses doped with 5 wt.-% AmO_2 are still vitreous, no crystalline phase is observed
- 2) the glasses doped with 3 wt.-% UO_2 are still vitreous, no crystalline phase is observed

Table 3 Vertical Distribution of Some Elements in Glass Cylinders Held in the Molten State for 25 Hours at 1175° C (Viscosity < 50 Poise)

specimen position	concentration (wt.-%)*			
	UO ₂	NpO ₂	PuO ₂	Ce ₂ O ₃
top	5.18±0.12	0.29±0.01	0.92±0.03	2.53±0.08
middle	5.19±0.09	0.28±0.01	0.95±0.01	2.57±0.15
bottom	5.10±0.12	0.26±0.01	0.93±0.02	2.49±0.06
theory	5.49	0.39	1.01	1.50

* The concentration values and their standard deviations are tabulated without any correction factors which should be considered when the real concentrations are wanted. Nevertheless, the directly measured values are well within the range of the theoretical values.



E abs⁺



Ru



Rh

20 μm

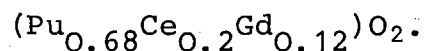
Segregation of Noble Metals from Borosilicate Glass Melt

Figure 1: Typical electron microprobe picture from the bottom section of the glass melts.

- 3) the glasses doped with 5 wt.-% PuO₂ consist of two phases, a crystalline and a vitreous one.

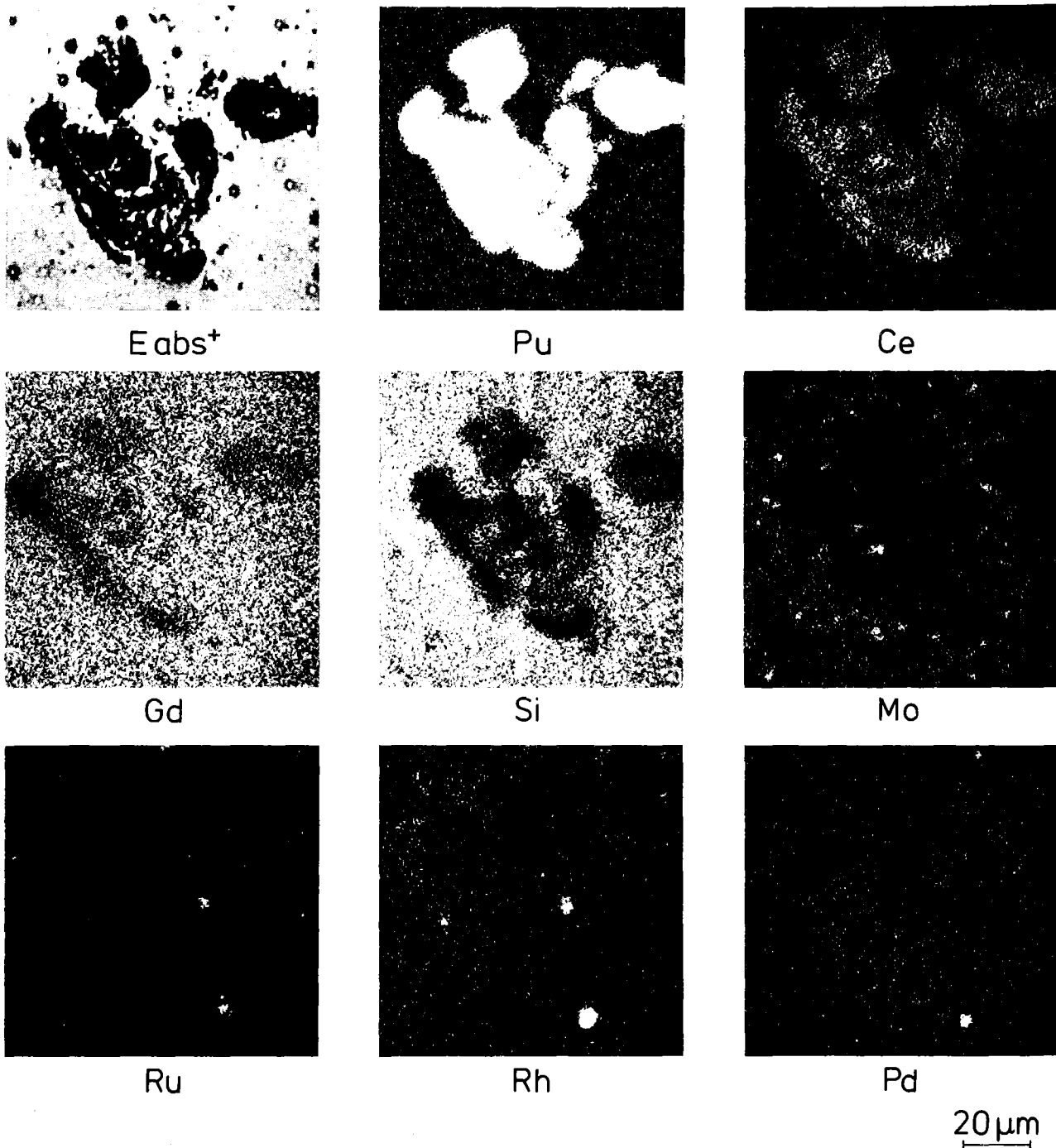
Case 3, the plutonium doped glasses, consequently, have been investigated in detail. Obviously, the three types of glasses have limited solubilities for PuO₂. From the quantitative analysis of the vitreous and crystalline phases in the electron microprobe the following results are obtained:

- 1) the homogeneously dissolved quantity of PuO₂ in the base glass 98 is limited to 4.6 wt.-%. The second crystalline phase consists of PuO₂
- 2) the homogeneously dissolved quantity of PuO₂ in the HLW glass 98-20 % (composition see table 2) is limited to 4.4 wt.-%. The second crystalline phase consists of PuO₂
- 3) the homogeneously dissolved quantity of PuO₂ in the HLW glass 98-30 % (composition see table 2) amounts to 1.2 wt.-%. The second crystalline phase consists of a compound with the average composition:



In the microprobe picture (figure 2) the distribution of the elements in the second phase can be seen.

From the experimental results it is demonstrated, that rather high quantities of actinides are homogeneously dissolved in borosilicate glasses. The solubility limits are by orders of magnitude above the average concentrations which are introduced from the HLLW into the glasses.



Segregation of Pu Enriched Phase from
Borosilicate Glass Melt

Figure 2: Electron microprobe picture from the second crystalline phase precipitated from glass 98-30 % doped with 5 wt.-% plutonium oxide.

3.4 Vitrification of Alpha-Bearing Waste

As can be seen from the preceding paragraphs, borosilicate glass is also a suitable matrix for the immobilization of alpha-bearing waste in view of the actinide solubility upon vitrification.

Anyhow, there are still remaining some other problems to be solved, when different types of α -bearing wastes are considered to be vitrified:

- 1) The concentrated supernatant from the precipitation of plutonium-oxalate normally contains a high concentration of americium and residual plutonium. This waste stream can easily be combined with the HLW without further treatment. Or, this stream can be recycled to the input feed tank of the reprocessing plant for Pu recovery, and only the Am content of the HLLW will increase.
- 2) Other liquid wastes from plutonium fuel production plants contain larger quantities of acids like hydrochloric, hydrofluoric and sulfuric acid. These compounds have to be considered with respect to their limited compatibility with glass and possible corrosion effects in the vitrification plant.

For the borosilicate glasses 98-20 % and 98-30 % (composition see table 2), the solubilities of anions are limited to 1.1 wt.-% Cl^- , 1.3 wt.-% SO_4^{2-} and 1.5 wt.-% F^- . If any corrosion problems can be solved during glass melting it will be possible to vitrify the liquid waste from a plutonium fuel fabrication plant together with the HLLW of a commercial reprocessing plant since the ratio of HLLW and α -bearing liquid waste is about 10 for equivalent plant capacities.

- 3) Incinerator ashes from the dry combustion of solid waste also contain a large amount of chloride, which may segregate from the glass melt. In one campaign, the combustible

waste from 28 drums from the EUROCHEMIC plant has been treated in the incineration facility at Marcoule for establishment and comparison of the plutonium balance before and after incineration of the waste material (7).

These ashes, containing about 10 wt.-% plutonium oxide have been vitrified in borosilicate glass. With up to 15 wt.-% of incinerator ash melted with 85 wt.-% of the base glass 98 (table 2) a homogeneous final product was obtained. At higher amounts of ash a second crystalline white phase appeared on the top of the melt consisting predominantly of alkali chloride.

The vitrification of α -bearing waste together with the HLW arising from a plutonium-fuel fabrication plant and a reprocessing plant with an equivalent plutonium output can be realized on the basis of the experimental results reported above. It is taken into account that the concentrated plutonium containing wastes do amount only to approximately 10 % of the total of HLW.

3.5 Electron Microprobe Analysis

All the experimental information mentioned in paragraphs 3.2 - 3.4 is based on electron microprobe investigations:

A shielded Cameca Ms 46 electron microprobe was employed at an acceleration voltage of 13 kV with beam currents of 20, 50 and 100 nA. The composition of the plutonium containing inclusions in the glass 98-30 % doped with 5 wt.-% PuO₂ (paragraph 3.3) was determined using the standard analytical procedure in which k values ($k = I/I_0$, where I is the characteristic line intensity from the specimen and I₀ is that from the pure standard) are obtained for each constituent and then corrected for atomic number effects, x-ray absorption and x-ray fluorescence using a ZAF programme. In this work the programme of Tong (9) was used.

The amounts of actinide oxides and fission products dissolved in the borosilicate glasses were determined by direct measurement against a number of glass standards each of which contained a known amount of one of the oxides under investigation.

The glass standards contained only a small amount of either an actinide oxide or a fission product oxide. For example, the U_3O_8 glass standard contained 10 wt.-% oxide, the Ce_2O_3 standard 5 wt.-%, the NpO_2 standard 4 wt.-% and the PuO_2 standard 2 wt.-% oxide. The amount of an oxide which could be usefully added to the borosilicate glass to produce a standard was restricted by its solid solubility limit. Precision analysis required that the oxide was uniformly dissolved throughout the glass and that not segregate phases were formed.

The low oxide concentrations in the glass standards resulted in poor x-ray counting statistics which can be a source of inaccuracy in the analysis. Such errors, however, are judged to be small and the worst case were probably of the order of the standard deviation which resulted from point to point variations in the measured concentration.

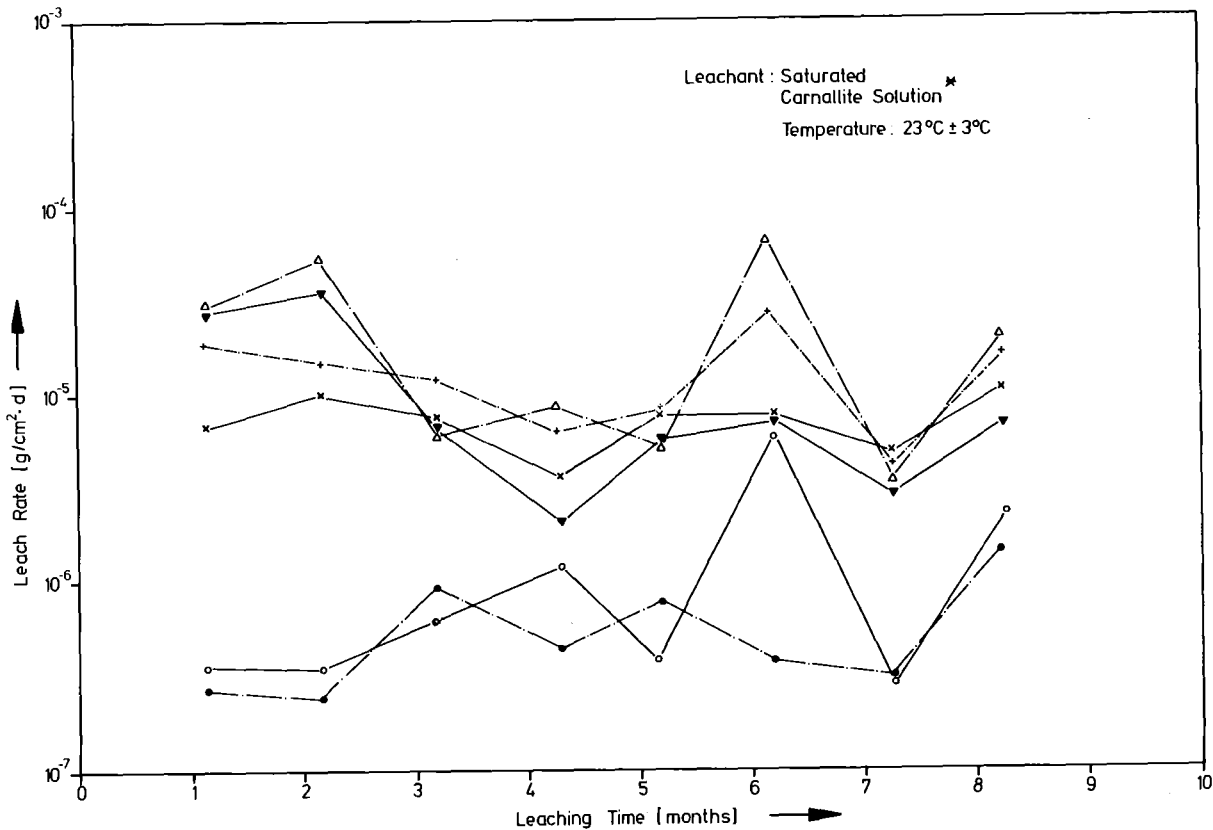
Borosilicate glass is an insulator and hence prior to electron microprobe analysis both the HLW glass specimens and the glass standards were coated with a conducting layer of aluminium about 150 Å thick.

4. Actinide Leaching Rates

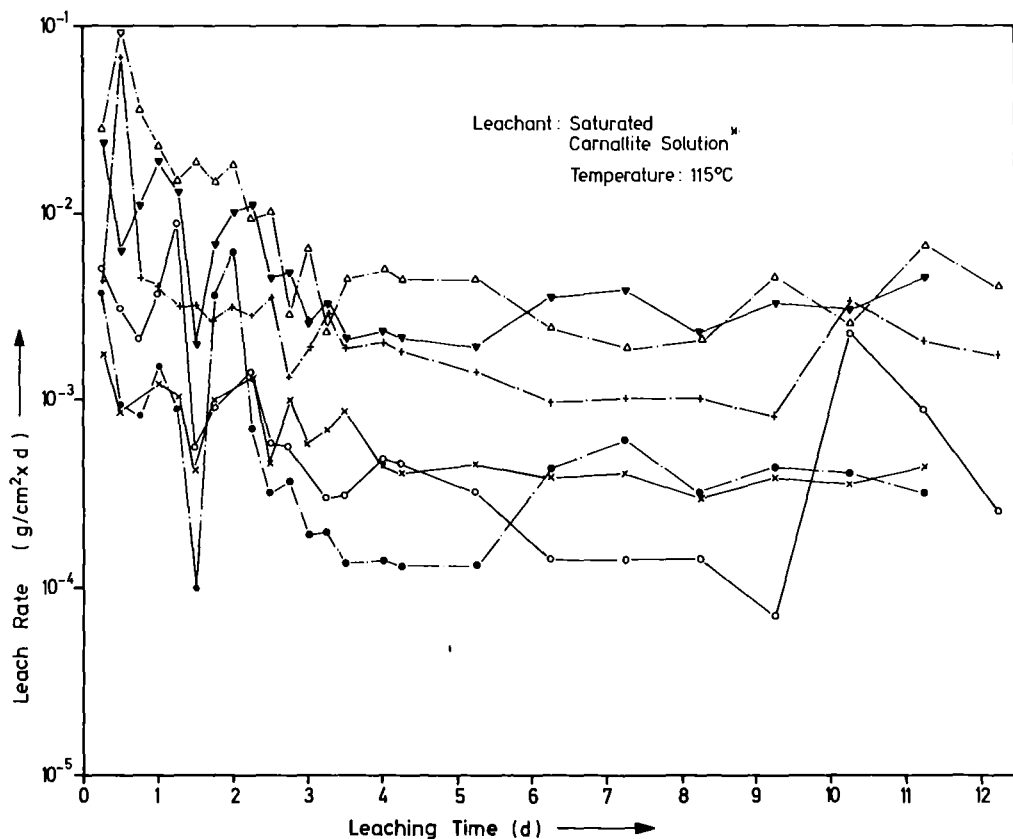
It has, previously, been reported (5) on extensive leach test experiments with various leachants at ambient temperature. In the frame of these experiments there was missing information on the leaching behaviour at high temperatures and on the long-term durability of the glasses against saturated "carnallite" brine occurring as an equilibrium brine (5) when water is penetrating salt deposits.

Figure 3 shows the results of additional investigations following the published procedures and experiments (5): The leaching rates of the actinides are increasing considerably from about 10^{-6} g/cm².d at ambient temperature to about 10^{-3} g/cm².d at 115^o C in saturated "carnallite" brine.

The appearance of the surface of the glass specimens after leaching periods of several months is shown in figures 4 and 5. Obviously, a continuous corrosion of the HLW glasses takes place as indicated earlier (5).

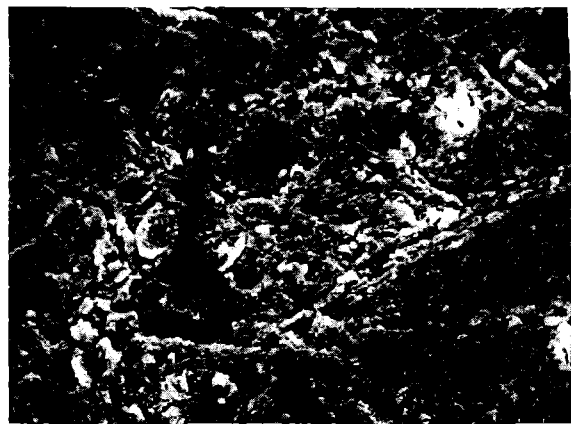
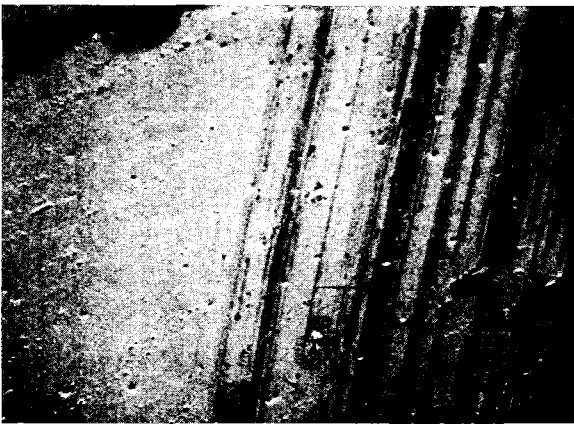
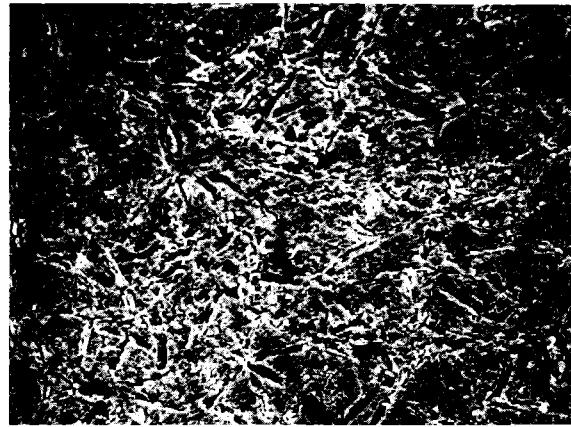
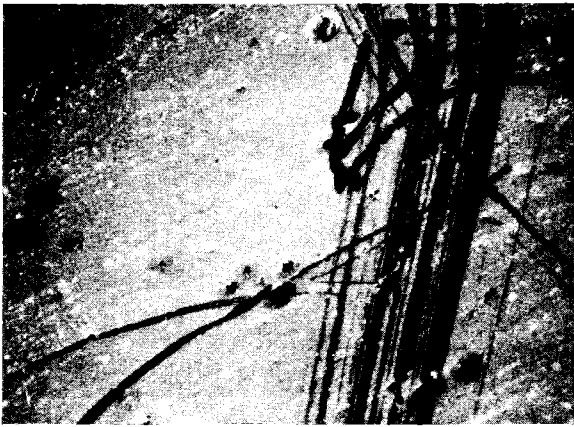
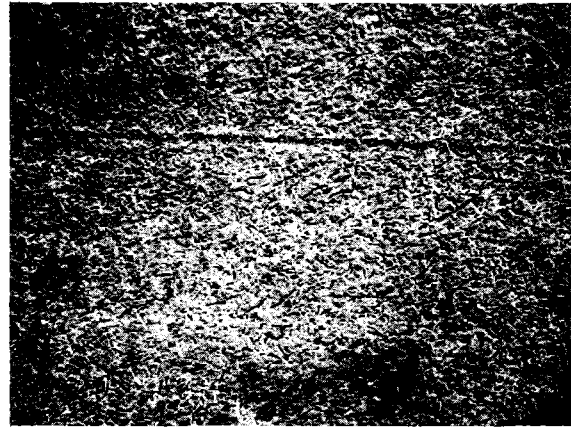


② VG 98+20 wt.-% Fission Products ③ VG 98+20 wt.-% Fission Products+10 wt.-% Gd₂O₃
 ●-●- Am ②, ▼-▼- Np ②, x-x- Pu ②, ○-○- Am ③, △-△- Np ③, +--+ Pu ③



② VG 98+20 wt.-% Fission Products ③ VG 98+20 wt.-% Fission Products+10 wt.-% Gd₂O₃
 ●-●- Am ②, ▼-▼- Np ②, x-x- Pu ②, ○-○- Am ③, △-△- Np ③, +--+ Pu ③

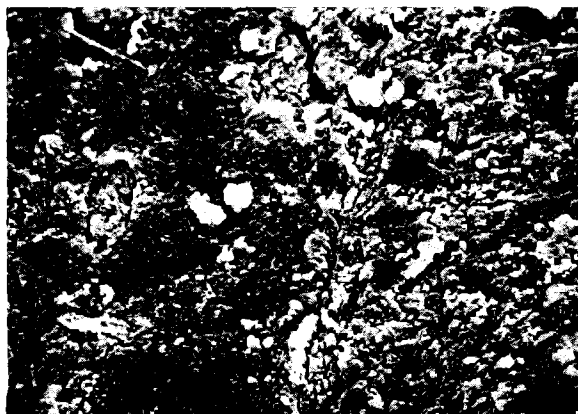
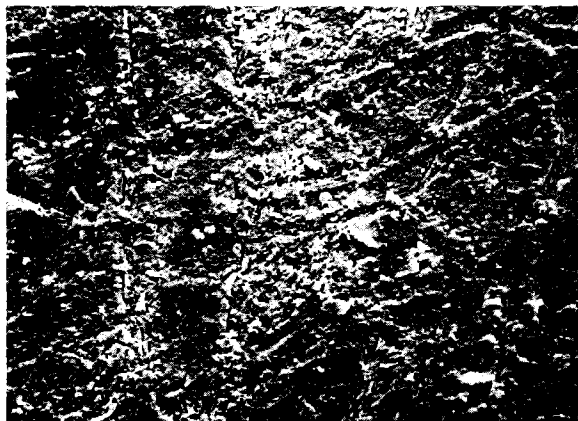
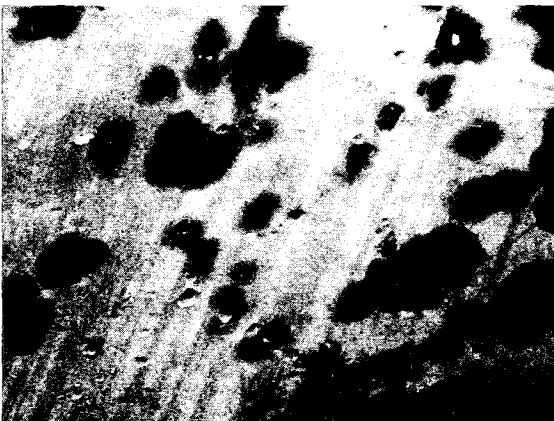
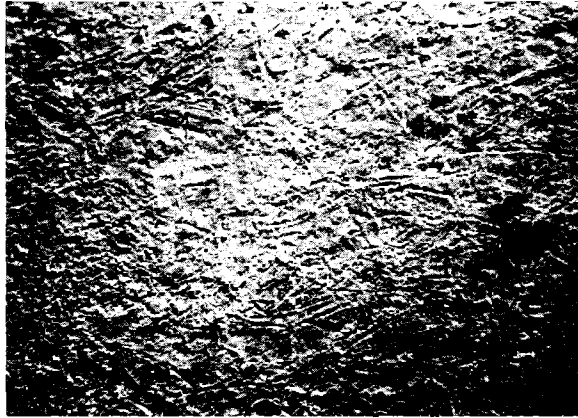
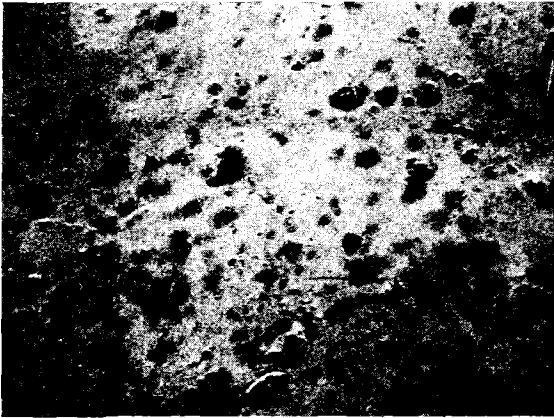
Figure 3: Leach rates for actinides leached from HLW borosilicate glasses with saturated "carnallite" brine at 23°C and 115°C.



23° C

115° C

Figure 4: Surface structure of HLW glass 98-20 % leached with saturated "carnallite" brine at 23° C and 115° C (magnifications: 80, 300, 800).



23° C

115° C

Figure 5: Surface structure of HLW glass 98-30 % leached with saturated "carnallite" brine at 23° C and 115° C (magnifications: 80, 300, 800).

5. Summary and Conclusions

From the experimental results reported above it is illustrated that borosilicate glasses are a suitable matrix for the solidification of HLLW and alpha-bearing wastes as well.

The ever possible amounts of actinides, which will be vitrified from the different waste streams are in any case quite below their solubility limits in the glass. But, the composition of the the waste material with respect to constituents others than actinides is important and may cause problems.

When high temperatures for the final disposal have to be taken into account special hazard considerations must be regarded, since the leachability of the actinides increases with increasing temperature considerably as shown by the experiments performed in saturated "carnallite" brine media. But it must be mentioned that not only the leaching rate but the complete system of mechanisms involved in the special disposal evaluation must be considered, as leaching mechanism and kind of leachant, chemical form of actinides in the leachant, migration and dispersion effects, adsorption and ion exchange processes in geological formations on the pathways to the biosphere.

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