EFFECT OF PLATINOIDS
ON FRENCH LWR REFERENCE GLASS PROPERTIES

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ABSTRACT

Nine samples of the "R7T7" glass composition selected to vitrify fission product solutions in France were prepared with added platinoid elements (ruthenium, rhodium and palladium) in soluble form and as insoluble metal particles in solution, and their major properties were measured. Regardless of the initial form when added to the glass the platinoids always formed the same heterogeneous inclusions in the final glass: RuO_2 precipitates which were often found as aggregates, and polymetallic (Pd, Rh & Te) inclusions.

The particles tended to settle in the molten glass. The viscosity increased by about 20% at 1100°C. The mechanical properties and short-term leach rates were not significantly affected. Crystallization increased by a factor of 2 or 3 in heat-treated glass specimens but did not exceed a few volume percent. However, as the short-term leach rate did not significantly increase, the glass properties were very satisfactory.

INTRODUCTION

LWR fuel irradiated to a mean burnup of 33 000 MWd·t^{-1} are reprocessed at La Hague 3 years after removal from the reactor. The reprocessing solutions are mixed and vitrified one year later. The vitrification feed solution contains platinoid elements (ruthenium, rhodium and palladium) either as insoluble metallic particles or as soluble salts. Under normal conditions the elements in the fission product solutions are suitably digested, but not so with the platinoids which have been shown to form heterogeneities in the glass [1,2,3,4]. The composition and properties of the R7T7 reference glass without platinoid additives has been widely documented [5]. The following discussion covers the effect of platinoid inclusions on the properties of nonradioactive R7T7 laboratory glass specimens.

GLASS SPECIMEN COMPOSITIONS

The inactive R7T7 laboratory reference glass composition (without platinoid additives) is indicated in Table I. This composition is identified as Specimen 0 in the following text. The fission product and actinide oxide breakdown is indicated in Table II.

Nine R7T7 glass compositions were prepared with platinoid additives in various forms that may be considered in three categories (refer to Table III):

• Four specimens with insoluble platinoids in the form of very fine metallic particles, with RuO_2 + Rh + Pd concentrations increasing from 0.84 wt% to 2.85 wt% (specimens 1 to 4).
• A specimen with soluble platinoids as salts in the fission product solution (specimen 5).
• Four specimens containing both soluble and insoluble platinoids (specimens 6 to 9).

It may be noted that the total platinoid reference concentration in the glass is 1.54 wt% of RuO_2 + Rh + Pd.

GLASS FABRICATION

Glass specimens were prepared using a batch process in a cylindrical Inconel 601 melting vessel inside an electric furnace with five heating zones. The zones are heated progressively during the procedure. The lowest zone heats the casting nozzle.

The feed streams consisted of the fission product solution and glass frit. When soluble platinoids were present, they were added as salts: ruthenium nitrosyl nitrate $RuNO(NO_3)_3$,

rhodium nitrate $Rh(NO_3)_3 \cdot 2H_2O$, and palladium nitrate $Pd(NO_3)_2 \cdot 4H_2O$, with a reference concentration of 3.31 g·l^{-1} (Ru+Rh+Pd). The aqueous suspension of insoluble platinoids, with a reference concentration of 2.58 g·l^{-1} (Ru+Rh+Pd), was prepared from Ru, Rh or Pd electrodes eroded by an immersed electric arc; the individual particles were minute (0.3–0.6 μm) but tended to agglomerate.

The mixture was fed to the melting vessel in 100 cm³ batches. After drying and calcining, the mixture was melted and refined for 3 hours at 1150°C, and the glass was cast into cylindrical graphite molds. Argon was bubbled through the melt at a rate of about 5 l·h^{-1} during the first two hours of refining to improve the glass homogeneity.

Platinoid volatility was unavoidable during the fabrication process, but was difficult to quantify. The final glass therefore contained smaller amounts of the platinoids than expected, as indicated by the analysis results in Table III.

RESULTS

Platinoid Form in the Glass

The glass specimens were observed by optical microscopy and submitted to SEM–EDS and X-ray diffraction analysis. Regardless of whether the platinoids were introduced into the glass in soluble or insoluble form, the same types of heterogeneities were always observed in the final glass:

• RuO_2 particles forming isolated rodlets and aggregates that sometimes contained rhodium (Figure 1, item 2).

Table I. French LWR Reference ("R7T7") Glass Composition

Oxide	wt%	Oxide	wt%
SiO_2	45.5	Li_2O	2.0
B_2O_3	14.0	ZrO_2	1.0
Na_2O	9.9	Cr_2O_3	0.5
Al_2O_3	4.9	NiO	0.4
CaO	4.0	P_2O_5	0.3
Fe_2O_3	2.9	F.P. oxides	11.25
ZnO	2.5	Act. oxides	0.85

Table II. Fission Product and Actinide Oxides

Oxide	wt%	Oxide	wt%
TeO_2	0.23	La_2O_3	0.90
Cs_2O	1.42	Ce_2O_3	0.93
SrO	0.33	Nd_2O_3	1.59
ZrO_2	1.65	Pr_2O_3	0.44
MoO_3	1.70	CdO	0.03
MnO_2	0.72	SnO_2	0.02
CoO	0.12	Sb_2O_3	0.01
NiO	0.33	UO_2	0.52
BaO	0.60	ThO_2	0.33

Table III. Platinoid Concentration (wt%) in the Nine R7T7 Glass Specimens

Glass Specimen	Nominal Platinoid (RuO_2 + Rh + Pd) Concentration (wt%)	Platinoid Distribution		Mean Platinoid Concentration (wt%) in Final Glass (Analysis Results)
		Soluble	Insoluble	
0*	0			
1	0.84	0%	100%	0.81
2	1.19	0%	100%	0.98
3	1.76	0%	100%	1.28
4	2.85	0%	100%	2.02
5	0.92	100%	0%	(not determined)
6	1.68	50%	50%	1.52
7	1.25	75%	25%	0.82
8	1.67	100%	0%	1.22
9	1.67	75%	25%	1.64

- Spherical polymetallic Pd-Rh-Te particles from 1 to 30 μm in diameter containing no oxygen (Figure 1, item 1).
- Chromite crystals (Fe, Ni, Cr, Zn), also found in the glass not containing any platinoids [5]; their presence can probably be attributed to corrosion of the steel melting vessel.

Image analysis revealed that virtually all the ruthenium, rhodium and palladium were present in the glass as RuO_2 + Rh + Pd heterogeneities.

Homogeneity

The glass specimens appeared homogeneous to the naked eye, but often showed a dull finish char-

Figure 1. SEM Image of Platinoid Inclusions (x2700)
① Pd - Rh - Te   ② RuO_2

acteristic of microcrystallization. Optical microscopic observation clearly revealed the heterogeneous platinoid distribution (Figure 2), notably small RuO_2 particles forming aggregates up to 1 mm in diameter in the specimens with the highest platinoid concentrations. Glass samples were taken at the beginning, middle and end of the casting step to obtain representative specimens of the glass at the bottom, middle and top of the melting vessel. Platinoid chemical analysis results are indicated in Table IV for compositions 6, 7, 8 & 9. Note that the platinoid concentration tended to rise rather uniformly from top to bottom, indicating that the platinoids settled in the melt. These results are consistent with those reported by other laboratories [3,4].

Specific Gravity

The specific gravity increased with the platinoid content, as shown in Table V for samples 1, 2, 3 and 4 taken in the middle of the casting operation.

Viscosity

A coaxial-cylinder viscometer was used for these measurements. This method is applicable to Newtonian fluids. Analysis of the shear modulus suggests that the particle-laden glass can be considered a Newtonian fluid, but this must be confirmed. Under these conditions the presence of platinoids in the glass increases the viscosity by about 20% at 1100°C.
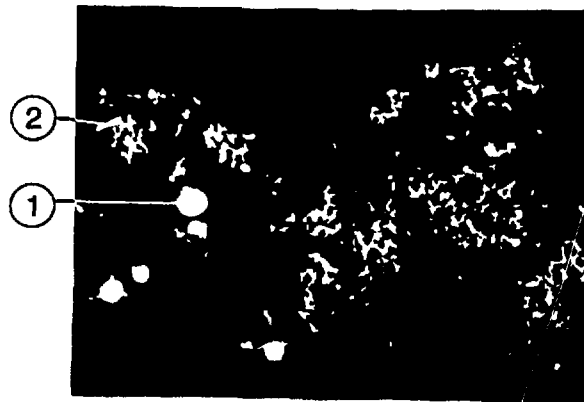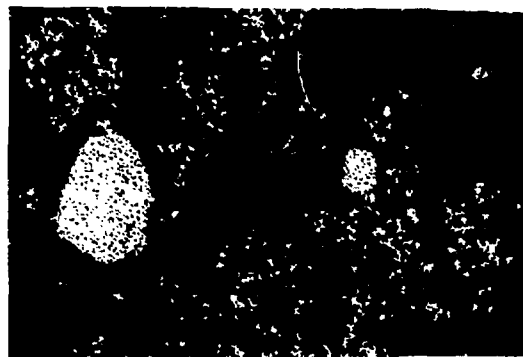

Figure 2. Optical Micrograph of Platinoid Heterogeneity (x550)

Table IV. Platinoid Concentration (wt%) versus Glass Height in Melting Vessel

Specimen Position	Glass Specimens			
	6	7	8	9
Top	n.d.	0.81	1.12	n.d.
Middle	1.51	0.72	1.20	1.45
Middle	1.46	0.79	1.23	1.56
Middle	1.53	0.85	1.22	1.55
Bottom	1.57	0.93	1.29	1.93

Table V. Glass Specific Gravity versus Platinoid Concentration

Glass Specimen	Specific Gravity	Platinoid Content (wt%)
1	2.769	0.81
2	2.788	0.98
3	2.791	1.28
4	2.823	2.02

Mechanical Properties

Young's modulus, the K1c stress intensity factor and the biaxial flexure strength were measured for glass samples 1, 2, 3 and 4. The results are indicated in Table VI, together with the values measured for R7T7 glass without platinoids (Specimen 0 in Table III). Given the uncertainty margin on these parameters, the addition of platinoids does not appear to affect earlier conclusions regarding glasses with heterogeneous inclusions [7]: the presence of such inclusions has no detrimental effects on the glass mechanical properties.

Table VI. Mechanical Properties

Glass Specimen	Young's Modulus 10^{10} N·m^{-2}	K1c Stress Intensity Factor MN·m$^{-3/2}$	Biaxial Flexure Strength N·m^{-2}
0	8.5 ± 0.6	0.91 ± 0.03	5.1 ± 0.3
1	8.4 ± 0.9	0.86 ± 0.03	5.8 ± 0.4
2	8.4 ± 0.3	0.86 ± 0.03	5.5 ± 1.2
3	8.4 ± 0.8	0.81 ± 0.06	5.6 ± 0.5
4	8.3 ± 1.9	0.79 ± 0.10	6.1 ± 0.4

Alterability

Glass alterability was measured according to standard procedures: i.e. Soxhlet (dynamic) and static leaching for 28 days in water at 100°C [6]. The mean normalized mass loss values are indicated in Table VII.

The platinoid concentrations in solution were extremely low – below the inductively coupled plasma spectroscopy detection threshold. The presence of platinoid elements therefore does not affect the chemical corrosion resistance of the glass.

Thermal Stability

Thermal stability was evaluated by heat-treating the glass under conditions designed to maximize crystallization in order to produce large crystals for easier observation and identification, and to duplicate the maximum actual crystallization liable to occur at any point in the glass inside the canister. The heat treatment conditions were determined during a prior crystallization study, and all

Table VII. Leach Test Results

Glass Specimen	28-Day Leach Rate (10^{-4} g·cm^{-2}d^{-1})	
	Soxhlet	Static
0	2.1	0.51
1	1.91	0.47
2	1.58	0.51
3	1.83	0.46
4	1.36	0.42
5	2.21	0.50
6	1.96	0.55
7	1.8	0.59
8	2.03	0.56
9	2.09	0.53

Figure 3. Crystalline Phases
in Heat-Treated Glass
(×1300)

① Complex phosphate
② Calcium silicate
③ Chromite
④ Cerium oxide

the glass specimens were submitted to the same treatment: nucleation for 5 hours at 550°C followed by 100 hours of crystal growth at 780°C.

Scanning electron microscope observations, energy-dispersive X-ray analysis, X-ray diffraction and image analysis were used to determine and quantify the crystalline phases. The same crystalline phases developed to a different extent in each of the glass specimens (Figure 3):

- Platinoids already observed in the untreated glass (see above).
- Chromite crystals ($FeCr_2O_4$) containing iron, chromium, nickel and zinc: two types of crystals with different morphological characteristics were observed in variable amounts, but never exceeding 1 vol%.
- Complex silicate crystals rich in silicon and calcium, generally containing iron, nickel and chromium: this phase could not be identified by X-ray diffraction, and was found in variable amounts, from minute concentrations up to 7 vol% in specimen 8. No correlation was observed with the platinoid concentration; the abundance of this phase appears to be related to the presence of chromites, a phenomenon previously observed in the glass without platinoids [8].
- Calcium molybdate crystals identified by X-ray diffraction as powellite ($CaMoO_4$): this phase was more highly developed in the presence of platinoids, but did not exceed 2-3 vol%, and the crystals were smaller than in glass without platinoids.
- Crystals enriched in cerium oxide and also containing thorium and uranium; this phase remained limited to less than 1 vol% and could not be identified by X-ray diffraction.
- Complex phosphate crystals enriched in phosphorus, silicon, calcium and the lanthanides: these crystals were rarely observed, and only in minute quantities, and could not be identified by X-ray diffraction.

All these crystalline phases (except for the phosphates) have already been observed in glass containing no platinoids [5].

The presence of platinoids in the glass increases crystallization by a factor of 2 to 3, but never exceeding a few volume percent. The molybdate phase reaches 2-3% and the silicate phase can reach appreciably higher levels, but this appears to be related to the presence of chromites rather than platinoids. Moreover, the chromite concentration in the glass fabricated in an industrial facility is expected to be lower than in a laboratory glass.

The mechanical properties and alterability of heat-treated glass specimens are indicated in Tables VIII and IX. No significant differences were observed between the treated and untreated glass. However, 28-day alterability tests are indicative of the short-term corrosion rate, and further investigations will be necessary to determine whether the long-term rates are affected.

Table VIII. Mechanical Properties of Heat-Treated Glass Specimens

Glass Specimen	Young's Modulus 10^{10} N·m^{-2}	K1c Stress Intensity Factor MN·m$^{-3/2}$	Biaxial Flexure Strength N·m^{-2}
0	8.9 ± 0.4	0.99 ± 0.03	7.3 ± 0.6
1	8.6 ± 0.4	0.97 ± 0.03	5.6 ± 1
2	8.6 ± 1.6	0.99 ± 0.02	4.8 ± 0.8
3	8.5 ± 0.8	0.92 ± 0.05	5.7 ± 0.7
4	8.6 ± 1	0.96 ± 0.04	6.3 ± 0.9

Table IX. Leach Test Results for Heat-Treated Glass Specimens

Glass Specimen	28-Day Leach Rate (10^{-4} g·cm^{-2}·d^{-1})	
	Soxhlet	Static
0	2.18	0.53
1	1.75	0.53
2	2.02	0.48
3	1.80	0.45
4	1.23	0.45
5	1.83	0.52
6	1.94	0.56
7	1.78	0.57
8	1.48	0.54
9	1.93	0.53

CONCLUSION

Glass samples containing platinoids are heterogeneous at microscopic scale. They contain RuO_2 precipitates that are often agglomerated, as well as polymetallic Pd-Rh-Te inclusions that tend to settle in the molten glass. Together with the higher viscosity, this phenomenon could affect glass casting properties.

While crystallization is more significant in glass containing platinoids, the mechanical properties and short-term leach rate are not adversely affected. Provided their long-term behavior is unaffected, the properties of these glass samples appear to be acceptable for disposal purposes.

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