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XVIII INTERNATIONAL SYMPOSIUM ON THE SIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT

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MODELING RELATIONS BETWEEN THE COMPOSITION AND PROPERTIES OF FRENCH LIGHT WATER REACTOR WASTE CONTAINMENT GLASS

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ABSTRACT

Models have been developed to calculate the density, molten-state viscosity and initial corrosion rate according to the chemical composition of glass formulations used to vitrify high-level fission product solutions from reprocessed light water reactor fuel. Developed from other published work, these models have been adapted to allow for the effects of platinoid (Ru, Pd, Rh) inclusions on the molten glass rheology.

INTRODUCTION

The density, viscosity and initial corrosion rate of a nuclear containment glass are directly related to the glass fabrication conditions (density and viscosity) or to its aqueous corrosion properties (initial corrosion rate). Controlling the density ensures that no glass overflow can occur from the canister as the material is cast. The viscosity is used to determine the casting rate and to ensure satisfactory flow inside the canister. The initial corrosion rate is indicative of the glass leaching resistance, although not necessarily of its long-term behavior.

A number of published models describe these properties [1-6], but none of them allow for the effect [6-8] of incorporating platinoid elements (Ru, Rh and Pd) which result in heterogeneous inclusions and significantly affect certain properties of the sodium borosilicate glass used in France [9] for LWR waste containment purposes, notably its rheological characteristics in the molten state and its microscopic homogeneity. Based on previously published work [1,2] we developed a model valid for glass without platinoids (WoP) and adapted it to glass containing platinoids (WP) at concentrations of up to 3%.

DENSITY

The density calculation module was based on the model described by SCHOLZE [1]. The glass density is determined using a barycenter relation:

$$d_g^{WoP} = \frac{100}{\sum_{components} \frac{m_i}{d_i}}$$

d_g^{WoP}	glass density
m_i	fraction of each component (wt%)
d_i	characteristic density of each basic glass component.

To allow for the overall changes in structural parameters due to the transition from pure oxides to oxides in the glass, the ds_{iO2} parameter for silica (the predominant glass component) was adjusted to 2.36 to fit the experimental results of a sensitivity study covering composition variations in over 80 glass samples without platinoids [10].

All the other d_i parameters were values for pure oxides taken from a data base [11].

Figure 1 compares the calculated and measured values for glass without platinoids after experimental characterization[10].

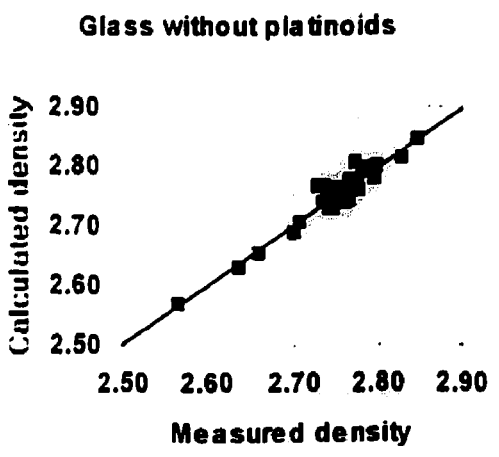

Figure 1 : Calculated versus measured results : model WoP.

The WoP model overestimated the density of glass containing platinoids at high concentrations [6] (Figure 2).

We therefore developed the WP model after experimental analysis of over 25 different glass compositions containing these elements at concentrations of up to 3%, using the following relation :

$$d_g^{WP} = d_g^{WoP} (p1\ \%RuO2 + p2\ \%Pd - p3\%Rh + q)$$

where :

% : weight percentage of each element

p1 = -0.003266

p2, p3 = -0.006526

q = 1.003852

The effects of rhodium and palladium were considered to be equivalent in view of their comparable densities [11] and similar behavior in the glass [6].

This formula traduce the structural perturbation product by platinoids in global glass.

The resulting parameter values included a second term q with a value near 1, corresponding to the glass without platinoids (within experimental error limits). In order to provide for perfect continuity between the models with and without platinoids, the p1 and p2 parameters were recalculated while maintaining q equal to 1 (p1 = -0.000608, p2 & p3 = -0.0065865, q = 1).

Figure 3 shows the result of the same calculation using the adjustment coefficients : the WP model correctly predicts the actual values without overestimation.

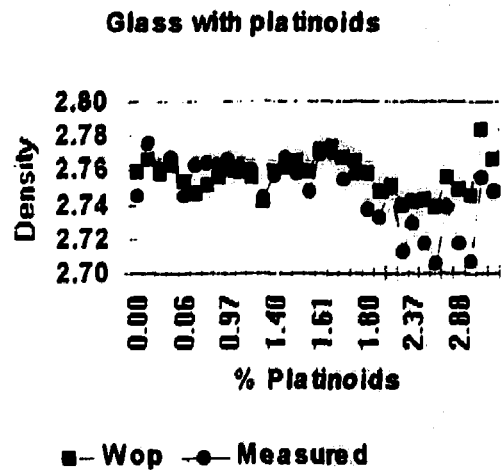

Figure 2 : Calculated versus measured results ; model WoP

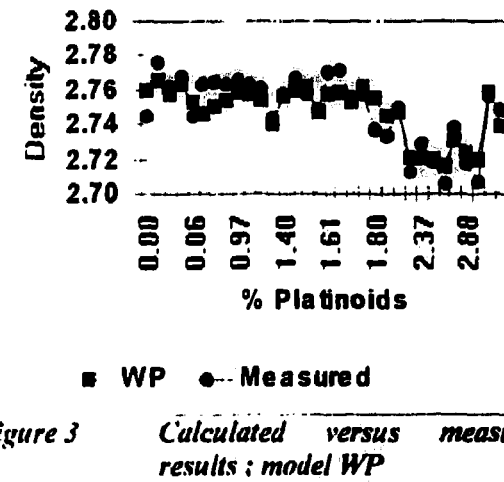

Figure 3 Calculated versus measured results ; model WP

VISCOSITY

In order to calculate the viscosity of glass without platinoids, we adapted the model described by FENG and BARKATT [2] based on thermodynamic and structural considerations. Using a VOGEL-FULCHER-TAMMANN formulation, the viscosity η is expressed as follows :

$$\text{Ln}\ \eta = A - \frac{B}{(T - T_0)}$$

A = a ΔHg+b

B = C ΔHg

To = e ΔHg+d

ΔHg : overall glass formation energy

a, b, C, d, e : adjustment coefficients.

The overall glass energy of formation, corresponding to the binding energy of all the glass components, is determined from the sum of the energies of formation of each oxide :

$$\Delta Hg = \sum_{i}^{oxides} x_i \Delta H_i$$

ΔHi : formation energy of oxide i in the glass

x_i : molar fraction of oxide i in the glass

The individual oxide formation energy values are calculated from the formation enthalpy of the pure oxide, modulated to allow for the role of each oxide in the glass structure (network former, modifier, etc.).

The oxide formation energy for **network formers** is calculated as follows :

$\Delta H_{former} = 2\Delta H_i^0$ | ΔH_i^0 : formation enthalpy of pure oxide i

The coefficient 2 corresponds roughly to the calculated ration between the binding energy and the enthalpy of formation [2] for elements such as SiO_2, Al_2O_3 or ZrO_2, which are the principal network formers in LWR containment glass.

For **network modifiers.** the formation energy is calculated from the formation enthalpy less an energy term corresponding to the mean binding energy created by the network formers :

$\Delta H_{modifier} = \Delta H_i^0 - Enet$ | $Enet = \sum_{i}^{formers} \frac{x_i \Delta H_i}{a_j x_j}$ | xj : molar fraction of element j; aj : number of bonds formed by each mole of oxide j.

For **"neutral" or intermediate oxides.** the formation energy is assumed equal to the formation enthalpy of the pure oxide :

$\Delta H_{neutral} = \Delta H_i^0$

B_2O_3 is a network former that nevertheless tends to diminish the glass viscosity in the process temperature range (1040–1150°C) because of peculiar behavior in the molten glass state [1]; consequently, a special formulation is used :

$\Delta H_{B2O3} = \Delta H_i^0 - 2Enet$

The formation enthalpy values for pure oxides at 25°C are taken from a data base [11].

As for the density, the adjustment coefficients a = –0.0180, b = –11.567, C = –22.742, d = –0.5355 and e = 156.32 were evaluated from experimental measurements [10]. Figure 4 compares the calculated and measured results for glass without platinoids.

LWR waste containment glass without platinoids is a Newtonian fluid in its process temperature range (1050–1100°C); after incorporation of platinoid elements, its behavior becomes that of a Bingham fluid [9, 15].

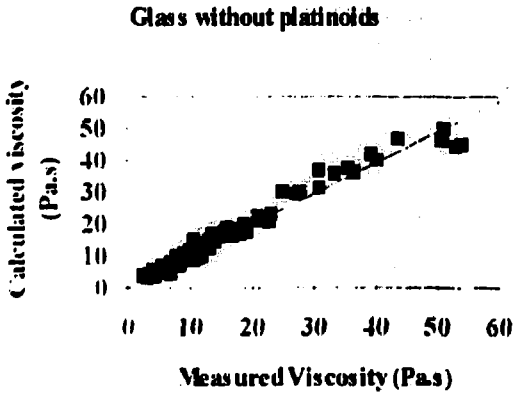

Figure 4 Calculated versus measured results : model WoP

The rheographic plot for this type of fluid [12] corresponds to a straight line that does not intersect the origin, and the fluid behavior is described by its Y-intercept τ (shear threshold) and slope α (viscosity parameter). These values were evaluated using the following relation :

$\alpha_\varphi^{WP} = \eta_\varphi^{WoP}$ (r1 %RuO2 + r2 %Pd + r3 %Rh + s) | r1 = 0.3129; r2, r3 = -0.0133; s = 1.05

The r2 and r3 coefficients were assumed equal for the same reasons as in the density calculation : r1 and r2, r3 were evaluated to fit the platinoid glass behavior.

The resulting parameters were such that s was nearly equal to 1, and the effect of RuO_2 (r1) was considerably greater than for Pd and Rh. The relation was therefore simplified to allow only for the percentage of RuO_2 and in which s was adjusted to 1 in order to ensure a continuous transition between the models with and without platinoids :

$\alpha_\varphi^{WP} = \eta_\varphi^{WoP}$ (r %RuO2 + 1) | r = 0.336

The resulting r parameter yielded a satisfactory fit with the experimental data (Figure 5).
Considering the predominant effect of RuO_2 in assessing τ, we used the following relation :

$\tau = m\ \%RuO2$ | $m = 14.048$

The result (Figure 6) is considered satisfactory.

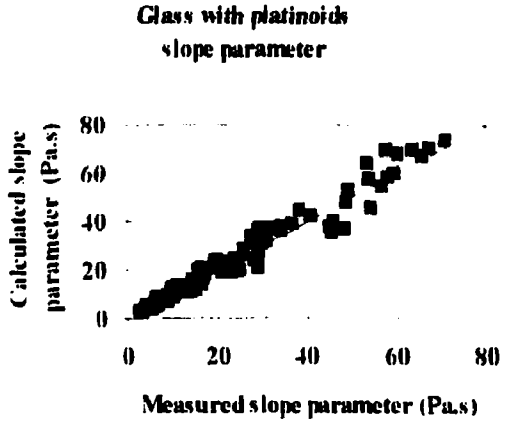

Figure 5 *α : Calculated versus measured results : model WP*

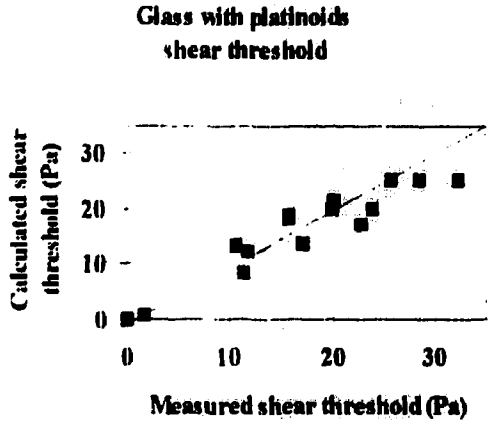

Figure 6 *τ ; Calculated versus measured results : model WP*

INITIAL CORROSION RATE

The "initial corrosion rate" (Ro) corresponds to the daily mass leach rate of a glass specimen exposed to flowing water under Soxhlet conditions at 100°C.

To calculate the "initial corrosion rate" of glass without platinoids, we adapted the model described by FENG and BARKATT [2] based on the same thermodynamic and structural considerations as the viscosity model

The binding energy of the glass components is the predominant factor controlling the dependence between the physical parameter and the glass composition. The initial corrosion rate is related to the overall glass energy of formation by the following relation :

$$\text{Ln } TL = \text{Ln } TL_0 - a\,\Delta H_g$$

where :

ΔHg	overall glass formation energy
TL_0	adjustment coefficients

Figure 7 (in which $a = 0.0204$ and $TL_0 = 7.4641$) compares the calculated and measured results for a glass composition without platinoids.

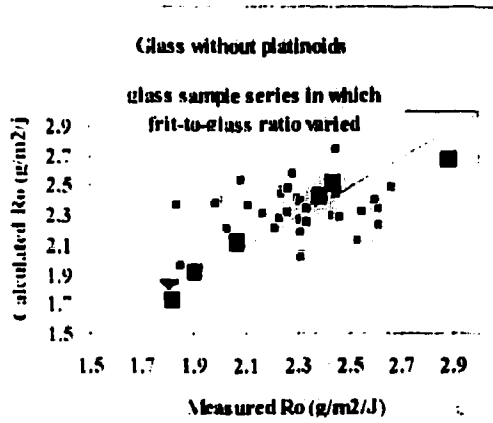

Figure 7 *Calculated versus measured results ; model WoP*

The pure oxide formation enthalpy values are the same as those used for the viscosity ; the glass formation energy calculation differs in only one respect : when calculating the initial corrosion rate, B_2O_3 was considered as a simple "neutral" oxide.

Considering the scattered results due to the experimental error margin (20–25%) and the slight variation recorded for the experimental initial corrosion rate measurements according to the glass chemical composition, no satisfactory relation could be determined for the entire sample population. The adjustment coefficients were therefore calculated only for the glass sample series in which the frit-to-glass ratio varied [10], i.e. the series for which the corrosion rate variation versus the glass chemical composition was the most significant.

When applied to a few specimens containing platinoids for which the initial corrosion rate had been measured under Soxhlet conditions at 100°C, the WoP model provided a satisfactory fit with the experimental data

In Figure 8 the error bars correspond to the mean estimated experimental error.

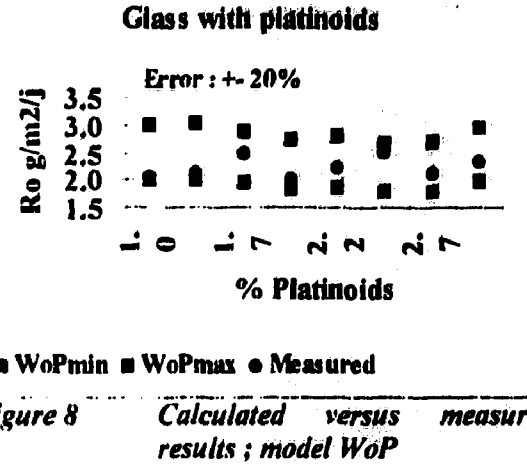

Figure 8 *Calculated versus measured results ; model WoP*

DISCUSSION

The absolute value of the deviation between the experimental results and the values calculated by the model was determined for each sample :

$Ej = |Vmj - Vcj|$

Ej : absolute value of deviation for sample j
Vmj : measured value for sample j
Vcj : calculated value for sample j

The result can be used to assess the numerical accuracy of the models (Table I).

- Although the deviations for the glass density exceeded the experimental error (0.15%) they remain acceptable considering the error liable to affect the glass composition analysis.
- For the viscosity, the calculated deviations were on the same order of magnitude as the experimental error (± 10 or 15%).
- The deviations on the initial corrosion rate were lower than the experimental error (± 20%).

Table I. *Deviations between calculated and measured values for models with platinoids*

Density deviation		Viscosity deviation				Initial corrosion rate deviation	
		α		τ			
Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
0.3%	0.3%	9%	7%	13%	9%	10%	8%

Density

The parameters from the regression used to adjust the WoP model to fit the glass containing platinoids seem to indicate that palladium had a significantly greater effect than ruthenium.

This point is perhaps the consequence of the morphology of each kind of platinoid inclusions. In the glass inclusions, ruthenium is found as RuO_2, while palladium and rhodium are found in metallic form but associated with tellurium [6.8]

Viscosity

The parameters, obtained in Wop model for glasses containing platinoids, confirm the predominant role of RuO2 and the negligible effect of Pd (Rh) which can be observed in experimental data (Figures 9, 10).

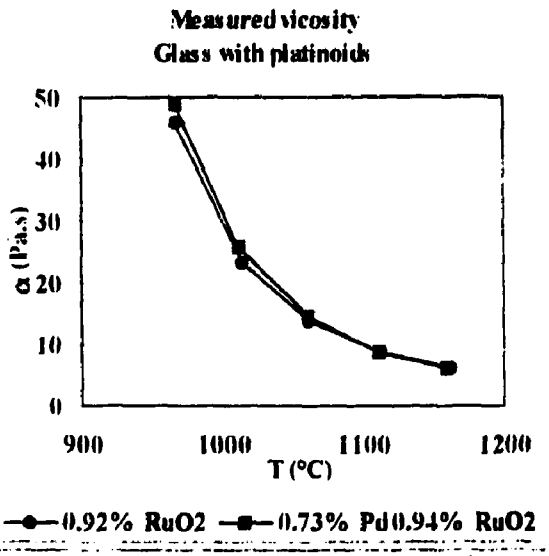

Figure 9 *Viscosity ; experimental data ; glasses with platinoids*

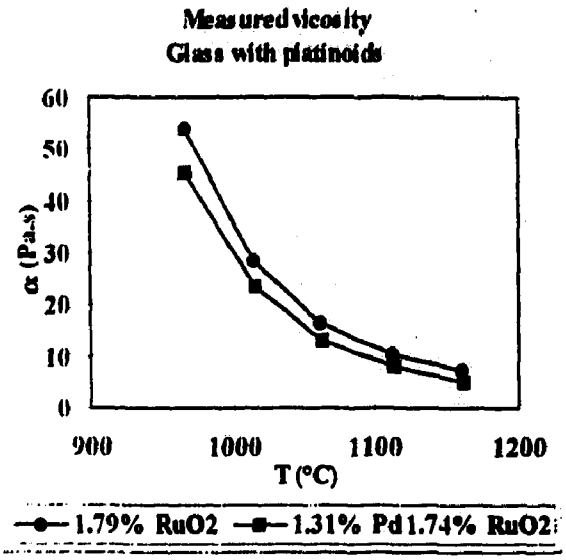

Figure 10 *Viscosity ; experimental data ; glasses with platinoids*

The formula used appears to be consistent with the Einstein-Smoluchowsky equation [12, 14] concerning the viscosity of solutions containing particles in suspension :

$\eta = \eta_s (2.5\,\Phi + 1)$

η	viscosity of solution containing particules in suspension
η_s	viscosity of solution without particules
Φ	volume concentration of particles in suspension

The Y-intercept is near 1 and the slope parameter depends on the percentage of ruthenium oxide, which forms the largest inclusions. In the type of glass considered here [6], Pd and Rh are found as small spherical particles, while RuO_2 forms larger clusters in a variety of shapes: polyhedral, spherical, rod-like and aligned.

Initial Corrosion Rate

The close correlation between the experimental results and the values calculated by applying the WoP model to glass containing Ru, Pd and Rh suggests that the presence of platinoid elements has very little effect on the initial corrosion rate.

This type of model, which has already been used to calculate the initial corrosion rate of nuclear containment glass (from the boron release), has proven useful over a wide range of compositions [2, 13].

CONCLUSION

Based on models described in the literature [1, 2] for French light water reactor waste containment glass, representative physical and statistical models have been ajusted to calculate the glass density, viscosity (in the glass process temperature range of 1040–1150°C) and initial corrosion rate (under Soxhlet conditions).

These models are applicable to glass formulations in which the chemical composition fluctuates around the LWR reference glass [9], and have been adapted to glass containing up to 3% platinoid elements (Ru, Pd, Rh).

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