

Analysing Rhenium volatilization with viscosity of nuclear waste glass melts

Ojovan, M.I.* (1,2), Xu, K. (1), Yang, D.(1).

(1) State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, China;

(2) School of Chemical, Materials and Biological Engineering, The University of Sheffield, UK;

* lead presenter m.ojovan@sheffield.ac.uk

Vitreous materials in form of both homogeneous glasses and glass composite materials incorporating crystalline disperse phases within a durable glass matrix are currently the most reliable wasteforms effectively used on industrial scale for nuclear waste immobilisation.

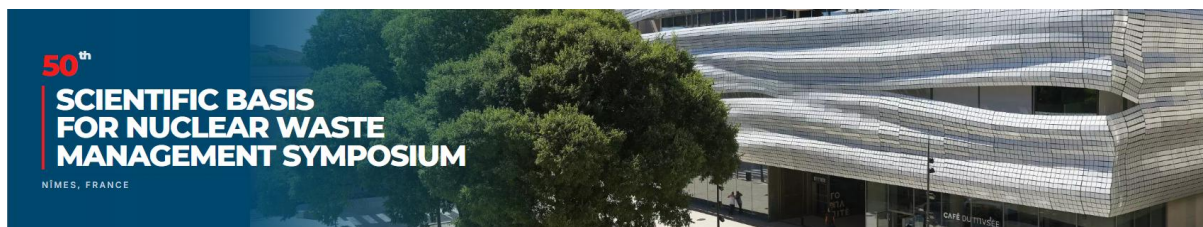
Understanding radionuclide volatilization behavior is crucial for improving vitrification efficiency along with modelling viscous flow on melting and solidification.

This study utilized the non-oxidizing volatilization (NOX) model which integrates Fick's law (the effective diffusion coefficient D ($\text{cm}^2 \cdot \text{s}^{-1}$)), reaction kinetics (the reaction rate k (s^{-1})), and partition coefficient α (the fraction of direct volatilization, dimensionless), characterizing the relationship between reaction and diffusion [1]. It describes the total carryover from the surface of glass melt M ($\text{g} \cdot \text{cm}^{-2}$) via relationship:

$$M = C_0 [\alpha(1 - \exp(-kt)) + 2(Dt/\pi)^{1/2}],$$

where C_0 is the concentration of nuclide (e.g. Re, Tc) in the melt. The analysis of loss of Rhenium (as a simulant of radioactive Technetium [1,2]) from borosilicate glass melts as a function of melt viscosity has revealed that a reduction in viscosity from ~ 15.9 to ~ 5.2 Pa·s increased Re volatilization by $\sim 40\%$ over 8 h at 1200 °C. The NOX model effectively described the volatilization from molten glass across a wide range of melt viscosity. Re volatilization was governed by its diffusion with the effective diffusion coefficient, which increased from $\sim 1.5 \cdot 10^{-8}$ to $\sim 1.5 \cdot 10^{-7}$ $\text{cm}^2 \cdot \text{s}^{-1}$ as melt viscosity decreased. The NOX model showed a steady Re reaction rate $k = 1.6 \cdot 10^{-4}$ s^{-1} . The partition coefficient α quantifying the relative contribution of direct volatilization from the glass melt versus interfacial reaction systematically ranged from 0.49 to 0.79 in the ISG-modified glass melts. This observation indicated the dominance of direct volatilization from the glass melt as the glass melt viscosity decreased. For example, the direct reaction mechanism ($\alpha > 0.63$) dominated Re volatilization in low viscosity glass melts ($\eta < 10$ Pa·s). In this case, Re diffusion mainly involved direct binding with alkali ions to form volatile species that evaporated from the glass melt. The analysis shows that the viscosity of the melt affects Re diffusion and volatilization. The modified Stokes–Einstein calculations revealed that the average effective radius of Re ($2.1 \cdot 10^{-11}$ m) was $\sim 60\%$ smaller than its theoretical radius ($5.6 \cdot 10^{-11}$ m), suggesting the combination of Re with the Na^+ and K^+ ions to form volatile species such as KReO_4 or NaReO_4 which could escape from the glass melt.

Most novel data revealed the effect of Sulfur on the volatilization of Re in the glass melt during vitrification. The presence of S in the melt promotes Re volatilization in the glass melt. Most Re volatilizes within 1h of heat treatment and the mass of Re loss M increases with the



addition of S. Using the NOX model, it was revealed that Re effective diffusion coefficient D increases significantly with the increase of S/Re ratio, indicating that S facilitates Re diffusion in the melt thus promoting its volatilization. The addition of S is also increasing the partition coefficient α indicating on increased role of reaction kinetics at higher S contents. The reaction constant k remains almost unchanged with S addition $k \approx 8.4 \times 10^{-4} \text{ s}^{-1}$.

The temperature-dependent viscosity η (Pa·s) of both glasses and melts was fitted using the DDO model, describing viscosities in a wide range of temperatures including the temperatures where the activation energy of flow was variable (non-Arrhenian range) [3,4]:

$$\eta(T) = A \cdot T \cdot \exp(H_m/RT) [1 + B \cdot \exp(H_d/RT)],$$

where T is the temperature (K), H_m and H_d are the configuron (broken chemical bond) motion enthalpies and formation enthalpies respectively, coefficients A and B represent pre-exponential factors related to the configuron entropies of motion and of formation respectively, and R is the universal gas constant. The DDO model provides results coinciding with well-known and widely-used VFT model within the temperature range where the activation energy of viscous flow Q(T) varies from its high value at temperatures close to glass transition temperature T_g to its low value in the high temperature range where the viscosity deviates from the Arrhenian law [3]. However, the VFT fails to describe the viscosity behaviour in both vitreous state (below T_g) and high temperature molten state where the viscosity approaches Arrhenian laws with constant activation energies high and low correspondingly [3,4]. The DDO model fitting results for the temperature dependent viscosity behavior molten glass enabled calculation of thermodynamic parameters of configurons in ISG-modified glasses [3]. This revealed that the low (Q_H) and high temperature (Q_L) activation energies of viscous flow of ISG-modified glasses and ISG-modified glass melts are as follows $Q_H = (265 - 288) \text{ kJ/mol}$ and $Q_L = (140 - 158) \text{ kJ/mol}$.

Thus, we successfully demonstrated the possibility to analyze Re volatilization and viscosity of nuclear waste glass melts using NOX and DDO models respectively.

References:

1. C. Niu, M.I. Ojovan, K. Xu. Rhenium volatilization from molten glass: Relationship between volatilization and melt viscosity. *J. Am. Ceram. Soc.* **109**, 5, e70750 (2026).
2. D. Kim and A. A. Kruger. Volatile species of Technetium and Rhenium during waste vitrification, *J. Non-Cryst. Solids*, **481**, 41–50 (2018).
3. M.I. Ojovan, K.P. Travis, R.J. Hand. Thermodynamic parameters of bonds in glassy materials from viscosity-temperature relationships. *J. Phys.: Condensed Matter*, **19**, 415107, 1-12 (2007).
4. P. Hrma, P. Ferkl, A.A. Kruger. Arrhenian to non-Arrhenian crossover in glass melt viscosity. *J. Non-Cryst. Solids*, **619**, 122556 (2023).