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Redox control of nuclear glass

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Abstract

Vitrification is one of the recommended immobilization routes for nuclear waste, and is currently implemented on an industrial scale in several countries, notably for high-level waste. To optimize and extend the scope of nuclear waste vitrification, research is being conducted to specify suitable glass formulations and develop more effective processes. Vitrified nuclear waste often contains several multivalent species whose oxidation state can impact the properties of the melt and of the final glass. The redox control of nuclear glass is often advantageous: in many case it could improve the glass melting and increase the amount of waste in the final glass. In the glassmaking industry, the oxidation state of glass is optimized in order to improve the glass properties, notably refinement and colour. In this case the aimed redox state is obtained by the appropriate choice of raw materials. Redox control of nuclear glass is more complex because several redox species are contained in this glass. Furthermore, raw materials are partly driven by the chemical and physical properties of the waste that must be vitrified and specific constraints due to the active process. Different techniques of glass redox control developed for nuclear waste vitrification are reviewed.

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1. Introduction

Today, nuclear waste containment in optimized glass is a well-recognized solution considering the advantages it offers. Nuclear waste vitrification has been implemented on an industrial scale in France for more than 30 years. It is primarily used for containment of fission products that correspond to the category of nuclear wastes with the highest level of radioactivity. This solution is also employed by other countries which produce nuclear energy. Waste vitrification can guarantee a long term durability of the containment and drastically reduces the volume of the final waste in comparison with the option of non-reprocessing of spent fuels.

Waste vitrification is a constant subject of research intended to extend the range of waste consistent with vitrification in industrial performing processes. The innovations developed in this context concern vitrification technology and glass formulation. The innovations on glass formulations take into account the evolution of waste compositions and new types of waste for which vitrification has not been already considered. They also contribute to improving the performance of industrial processes.

Optimization of glass formulation obviously concerns the glass composition but also other parameters such as the physical form of additives, the melting temperature…The redox state of multivalent elements incorporated in the glass is one of these parameters. Thus redox control of multivalent elements in nuclear glass can also be one of these innovations.

The glass-making industry has developed methods to control the redox state of their glass in order to optimize its colour or to remove bubbles from the glass melt as explained by Muller-Simon et al. (1991). However, these methods are not directly applicable to nuclear waste vitrification because process constraints are different and redox couples in the glass are far more numerous in nuclear than in classic industrial glass. Using examples, the following presentation explains the techniques developed or under development in order to control redox of nuclear glass.

2. Interest for redox control of nuclear glass

Nuclear waste containment glass currently produced on an industrial scale is the result of formulation studies that optimize its composition. Even the melting temperature can be optimized if it is not imposed by process or glass composition. These optimisations on composition and temperature aim to obtain a glass formulation such as:

- the volume of waste is decreased,
- the melting conditions are compatible with available industrial processes,
- long term behaviour of containment glass is optimized (in terms of chemical durability, stability under radiation...).

The composition of glass containing radioactive wastes is often silicate or borosilicate. Many elements contained in this glass can exist into different redox states: Ce$^{4+}$/Ce$^{3+}$, Ru$^{4+}$/Ru$^{0}$, Fe$^{3+}$/Fe$^{2+}$/Fe$^{0}$, Zn$^{2+}$/Zn$^{0}$, Cd$^{2+}$/Cd$^{0}$, Cr$^{6+}$/Cr$^{3+}$/Cr$^{2+}$/Cr$^{0}$, S$^{6-}$/S$^{4-}$/S$^{0}$/S$^{2-}$, Ni$^{2+}$/Ni$^{0}$, Mn$^{3+}$/Mn$^{2+}$/Mn$^{0}$, Mo$^{6+}$/Mo$^{5+}$/Mo$^{4+}$/Mo$^{3+}$/Mo$^{0}$… These multivalent elements essentially come from the waste but they can also be included in additives. The redox states of these elements are determining in several ways as explained by Pinet et al. (2005):

- the solubility in glass of several elements usually contained in radioactive waste such as cerium, molybdenum and chromium depends on their redox state,
- corrosion of the inner furnace wall material can differ according to the redox state of glass melt,
- foaming phenomena in glass melt are often linked to its redox state,
- formation and sedimentation of metallic particles with negative effects on the process behaviour are linked to an over-reduced glass melt,
- physical properties of glass such as electrical conductivity, viscosity and thermal conductivity can also be affected by redox.

3. General parameters affecting redox state of glasses

Pinet et al. (2006) showed that the parameters affecting the ratio between the concentrations of the reduced and the oxidized elements of a redox couple $M^{(m-n)+}/M^{m+}$ can be identified by equalizing the potentials of the two redox equations for the $M^{m+}/M^{(m-n)+}$ and $O_2/O^{2-}$ couples. The role of the solvent, and in particular of the $O^{2-}$ ions in the redox equilibrium, can be better illustrated by writing the redox equation for the $M^{m+}/M^{(m-n)+}$ couple, for which the standard oxidation-reduction potential is $E_{0M}$, as follows:

$$MO_x^{(2x-m)-} + ne^{-} \rightleftharpoons MO_y^{(2y-m+n)-} + (x-y)O^{2-}$$

$$E_{0M}$$ (1)

The redox ratio $\frac{\text{Red}}{\text{Ox}}$ follows the relation:

$$\log \frac{\text{Red}}{\text{Ox}} = \frac{nF}{2.3 \cdot RT} E_{0M} - \log \alpha + \left( y - x + \frac{n}{2} \right) \log a(O^{2-}) - \frac{n}{4} \log f_{O_2}$$

(2)

where $f_{O_2}$ is the oxygen fugacity in the glass and $a(O^{2-})$ is the activity of the $O^{2-}$ ions in the glass.

$$\alpha = \frac{\gamma_{MO_x^{(2x-m)-}}}{\gamma_{MO_y^{(2y-m+n)-}}}.$$ $\gamma_{MO_x^{(2x-m)-}}$ is the activity coefficient of $MO_x^{(2x-m)-}$ ion in the glass, and $\gamma_{MO_y^{(2y-m+n)-}}$ is the activity coefficient of $MO_y^{(2y-m+n)-}$ ion in the glass.

$$E_{0M} = -\frac{\Delta G^0}{nF} = -\frac{\Delta H^0}{nF} + T \frac{\Delta S^0}{nF}$$

From Equation (1), the major factors affecting the redox state are as follows:

- **Oxygen fugacity $f_{O_2}$**: Increasing $f_{O_2}$ results in greater oxidation of the polyvalent elements in the glass. Equation (2) clearly shows a first-order linear relation with a slope of $n/4$ between $\log(f_{O_2})$ and $\log([\text{Red}] / [\text{Ox}])$; this relation was also often observed experimentally by Schreiber et al. (1987). The oxygen fugacity is measured in the molten glass using electrochemical methods previously described by Baucke (1991) et Claes et al. (1985). The measurement is based upon the potential difference between an iridium working electrode and a zirconia reference electrode immersed in a glass melt which is given by the following relation: $\Delta E = \frac{RT_{glass}}{4F} \ln \left( \frac{f(O_2)}{P(O_2)^{ref}} \right)$, where $T_{glass}$ is the glass melt temperature, $R$ is the molar gas constant, $F$ is the faraday constant, $f(O_2)$ is the oxygen fugacity in the glass melt and $P(O_2)$ is the oxygen partial pressure in the zirconia reference electrode.

- **Temperature $T$**: The influence of the temperature on the redox state is not clear from Eqn(3). It has been noted experimentally that higher temperatures are conducive to reduced states. From a theoretical standpoint, the sign of the standard enthalpy of the oxidation reactions ($\Delta H^0 < 0$) on the Ellingham diagram indicates that the oxidation reactions are exothermic. The Van’t Hoff law relative to the temperature effect on the direction of an exothermic reaction confirms the observed experimental results, i.e. that the redox equilibria are shifted toward the reduced species at higher temperatures.
Glass basicity $a(O^2-)$. The effect of the glass basicity on the oxidation state of its constituents depends theoretically on the sign of the $(y-x+n/2)$ term, which in turn depends on the environment of each of the two elements of the redox couple. From a practical standpoint, Schreiber et al. (1987) indicate for all redox couples, with the possible exception of $\text{Cu}^{2+}/\text{Cu}^+$, that an increase in the basicity favours the oxidized states. It is difficult to measure the $O^2-$ ion activity. Different techniques have been proposed as electrochemical measurements by Abdelouhab et al. (2008). Glass basicity depends first on its composition, and Duffy et al. (1976) and Baucke et al. (1994) propose that it can be characterized by its optical basicity, $\Lambda$. Different works as Duffy (1996) and Pinet et al. (2006) highlight linear relations between glass basicity, $\Lambda$, and $\log([\text{Red}]/[\text{Ox}])$.

Melt composition. In addition to its influence on the basicity, the composition no doubt also affects the activity coefficient ratio.

4. Review of main techniques available to control redox state of nuclear glass

Glass redox control in the glassmaking industry is achieved using techniques adapted empirically to each furnace. In many vitrification implemented processes, redox of glass is governed by supplying the raw materials in their oxidized or reduced forms on the glass melt surface in order to obtain the aimed redox state of the glass. The final glass redox results from the combination of the heating system of the furnace, coke addition, gas bubbling and raw materials. In these cases, controls can be performed after production; this permits a certain feedback in the management of the process.

In the case of nuclear waste vitrification, specific constraints need to be considered. Consequently, appropriate redox control techniques need to be developed. In this regard, the following specific criteria can be mentioned:

- limited additional uncertainties about glass redox and composition are expected,
- glass quality requirements must be fulfilled,
- reliable techniques are sought because no feedback is expected,
- soft reducing or oxidizing agent is preferred to minimize exothermic reactions and target a more precise value of oxygen fugacity,
- reducing or oxidizing agents compatible with glass specification are preferred because limited additional uncertainties about glass composition are expected.

To meet this objective, preliminary stages to vitrification can be implemented: the oxidation of chemical elements of the waste can be performed by combustion or calcination for example. The main drawback of this technique is the addition of a stage in the process. Nevertheless, it is often a necessary but relevant solution to oxidize reducing wastes as organic waste. As for example, to achieve this objective, a new and simplified equipment, using thermal oxygen plasma coupled with a cold crucible melter, is being developed at the Valrho-Marcoule nuclear center (France): SHIVA, for Advanced Hybrid System for Incineration and Vitrification. Thus, treatment of different simulated organic waste has been tested on this inactive prototype by Lemont et al. (2010).

Another solution consists in adding oxidizing or reducing agents during the melting of the glass as explained by Muller-Simon et al. (1991). An appropriate choice of the physicochemical form of raw materials that are necessary to make the glass can also give them an oxidizing or reducing power as nitrates, sulphates, sulphur, oxides, coke... In this way, within the framework of waste vitrification, special glass frit additives containing multivalent species have been developed. Multivalent species contained in this “redox power glass frit” are reduced or oxidized according to the considered application. Once in the furnace, the multivalent elements contained in the “redox power glass frit” react with elements coming from the waste stream and oxidation and reduction reactions are performed in the glass melt until a globally optimised redox state of the glass is reached. The use of “redox power glass frit” permits the control of redox with no additional supply of materials compared to a vitrification process in which additives are introduced as glass frit. The use of “redox power glass frit” means the addition of a sufficient quantity of one or several multivalent elements in glass. These additions slightly modify the final composition of glass and can possibly modify the properties of glass. The choice and quantity of multivalent element added to the glass frit is
firstly based on thermodynamic data. These thermodynamic data concern equilibrium of redox couple in nuclear glass melt. They have been the subject of several previous publications by Pinet et al. (2000, 2006, 2009). Nevertheless secondary oxidation and reduction reactions involving surrounding gas can shift the final redox equilibrium. These reactions are limited by kinetics depending on the size of the glass frit, and flow rate of gas.

In this regard, tests have been performed at the lab-scale to define a technique for controlling redox of borosilicate glass melted in an in-can process. In such a process, the metal of the canister can act as a reductant. Thus, according to the type of metal of the canister and the melting duration, reduction of the melt may occur. In order to prevent this reduction, different amounts of Fe₂O₃ were added to the borosilicate glass simulating the waste containment glass under consideration. The glass used for the corrosion tests was borosilicate glass with Fe₂O₃ content varying from 3.6 up to 12.6 wt %. The glass contains mainly SiO₂, B₂O₃, Na₂O, Li₂O, CaO, Al₂O₃, Fe₂O₃ and a small amount of ZnO and SO₃. This glass is inactive glass. The viscosity of this glass at 1100 °C is around 40 dPa.s. Initial value of log(fo₂) at 1200°C is between -1 and 0. These tests consist in static immersion tests in which 400 g of crushed glass were introduced in a metallic crucible and then melted at 1100 °C under air atmosphere in an electrical resistance heated furnace for 8 h 30 for short lasting tests or 96 h for long lasting tests. The crucible was 100 mm in diameter, 150 mm in height, 3 mm thick and the glass melt height was about 20 mm. Metals tested are 310S alloy and inconel 601. Oxygen fugacity measurements after corrosion tests showed that the glass is reduced (fo₂ around 10⁻⁸ atm.) if the initial iron oxide glass content is lower than 3.8 wt %. At the same time, it appears that the glass remains in an oxidized state (fo₂ ≥ 10⁻² atm.) if the initial iron oxide glass content is higher than 4.7 wt %. These results do not differ according to the two durations and the two type of metals tested. These results are in good agreement with those obtained on a pilot scale in figure 1.

![Figure 1: Plot of oxygen fugacity at 1100°C after corrosion tests versus initial iron oxide content (wt %) of the glass melt by Hugon et al. (2010).](image)

In accordance with the same principles, the efficiency of a reduced glass frit has also been tested favourably in order to avoid foaming in glass melt due to their too high level of oxidation as explained by Pinet et al. (2005).
As explained previously, the redox state of glass melt depends mainly on its oxygen fugacity. Considering thermodynamic equilibrium between glass melt and surrounding gas, the oxygen fugacity in glass melt and partial oxygen pressure in gas surrounding glass melt should evolve toward the same value. Generally kinetic phenomena drastically limit this equilibrium because the ratio between the total mass of the glass melt and its interface with gas is too low considering the diffusion of redox carrier elements in glass melt as described by Magnien et al. (2008). Results obtained by Cochain et al. (2009) estimate redox diffusivity of borosilicate glass at melt temperature is around $10^{-10}$ m$^2$.s$^{-1}$. It means that in case of diffusion controlled redox kinetics, it takes hours to oxidized or reduced a layer of glass of few millimeters thick. This value is consistent with previous results published by Shreiber et al. (1986). As previously mentioned, surrounding gas generally does not predominantly impact redox equilibrium of glass. Nevertheless, it is still possible to markedly modify the redox state of glass by bubbling gas into the glass melt at a sufficient flow rate with an appropriate oxygen pressure. Several experiments carried out at the CEA Marcoule have brought to light the possible effect of gas bubbling. The following experiment performed on a lab scale highlights this phenomenon. In this case, 800 grams of non radioactive simulated glass was remelted in a rhodium-platinum crucible heated by joule effect at 1200°C in air (figure 2). The initial oxygen fugacity of the glass melt at 1200°C, $f_{O_2}$, is 0.55 atm. The oxygen fugacity is almost not changed even after having remelted the glass at 1200°C for 5 hours without any bubbling of gas. A bubbling flow rate of around 40 NL/h of argon leads to a decrease of the oxygen fugacity of glass according to time. After 2 hours of such bubbling, the oxygen fugacity seems to be stabilized at a value of about 0.04 atm. The glass is then slightly reduced. A bubbling of air for two hours at the same flow rate in such reduced glass leads to a reoxidation of this glass. After two hours of bubbling with air, the oxygen fugacity measured at the melting temperature, i.e. 1200°C, is 0.14 atm., which is close to the oxygen partial pressure in air.

![Figure 2](image-url)

**Figure 2:** Change in the redox state of glass according to bubbling of gas – case of 800 g of simulated nuclear glass melted at 1200°C.

5. Conclusion

Controlling of redox of nuclear glass may often have advantages. In the present process, redox of nuclear glass is roughly controlled by the oxidation of the waste one stage before vitrification. In certain cases a more accurate control of redox may be worthwhile. New techniques from those implemented in the glass-making industry need to be developed to control the redox state of glass in vitrification for nuclear waste containment. The constraints in
term of reliability and additional supply are more severe. Multivalent elements should be added to the melt in order to control the redox of glass. This is one of the preferred techniques to control the redox of glass but gas bubbling optimization could also work. The determination of parameters concerning the nature and the quantity of additives necessary for controlling the redox state of nuclear glass is based both on thermal and kinetic data.

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