

EDITORIAL OPEN

Simplifying a solution to a complex puzzle

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Approximately 20,000 tons of borosilicate glass have been produced worldwide so far, for confining high-level radioactive waste generated from the reprocessing of commercial or defense nuclear fuels. The ability of glass structure to incorporate elements throughout the periodic table into a mechanically strong and chemically durable material—with the added convenience of straightforward and mature production processes—makes vitrification the best demonstrated technology for waste immobilization. In particular, the longevity of this material is a critical parameter in limiting the exposure of the biosphere to confined radionuclides, and research has been conducted for decades to study the long-term behavior of these materials and to assess the safety of various disposal concepts.^{1,2}

Chemical alteration of glass by groundwater, and to a lesser extent radiation damage to the glass structure, are expected to control the fate of radionuclides confined in glass, determining how long they can be held within the glass structure.¹ Research has shown that glass durability is not only material dependent, but is also strongly influenced by extrinsic parameters, such as the chemistry of the surrounding solution (such as groundwater), solution renewal rate, temperature, and near field compositions. Although progress has been made in deciphering many of the fundamental processes that control glass corrosion, questions remain regarding the non-linear response of corrosion with glass composition, the role that glass surface layers play in dissolution kinetics, and the evolution of secondary phases over time, to name a few. Yet, all these factors must be understood if successful models are to be built for simulating and predicating the long-term effectiveness of glass for waste immobilization.

In order to provide a common benchmark to relate results generated by different research groups using various experimental tools, including probes from multi-scales, and modeling approaches, it was decided to formulate a common glass that would be studied by all collaborators.³ This decision was made during the 4th International Workshop on Glass Corrosion held in Savannah, GA, USA (May 2011). This glass, called the International Simple Glass (ISG), has the following composition (mol%): 60.2SiO₂, 16.0B₂O₃, 12.6Na₂O, 3.8Al₂O₃, 5.7CaO, and 1.7ZrO₂. The main oxide components of this glass are common to most boroaluminosilicate glasses for nuclear waste immobilization, and the elemental ratios are the same as those of SON68 glass (the inactive reference glass of the French R7T7 glass produced by Areva at La Hague), which is arguably the most studied nuclear waste glass to date. To achieve homogeneity between glass samples, a 50 kg batch of ISG was produced in May 2012 by MoSCI Corporation (Rolla, MO, USA). From May 2012 to May 2018, 55 ingots of ~500 g (Fig. 1) were distributed to 23 laboratories from seven countries, and ~20 scientific papers have been published in the literature so far at the time of writing. *et al.* Historically a similar composition was studied at CEA at the end of the 1990s, providing sound arguments in favor of this glass as a good compromise between simplification and representativeness.⁴

Although 'simple' based on its number of constituents compared to actual nuclear glass composition, this glass is still complex from a fundamental point of view. Six cations means tens of different A–O–A or A–O–B (where A and B represent different cations) linkages with variations in bond lengths and bond angles. It is thus not surprising that its structure remains incompletely known and only a combination of spectroscopic and computational modeling approaches can shed light on its short-range and medium-range structural orders.⁵ Additionally, the structure, and properties of ISG, depend on how fast the glass is quenched.⁶ Limiting the reference glass to six cations, however, has enabled the possibility of modeling the glass structure with molecular dynamics.⁵ Such models can be utilized to evaluate potential gel structures, examine diffusion, and determine the relative reactivity of certain structural units.^{7–9}

In contact with water, the glass matrix first dissolves by ion-exchange and hydrolysis of covalent bonds. The rate of these processes is mostly glass composition, temperature, and pH dependent.¹⁰ As corrosion proceeds in a solution with appreciable quantities of glass-sourced ions, amorphous alteration layers are formed from the surface of the corroding glass.¹¹ This alteration layer (or layers), can either be formed by precipitation of dissolved species or by in situ reorganization of the Si-rich and Al-rich skeleton left behind from the release of the most mobile species (mainly B and Na), depending on the alteration conditions.^{12–18} In silica-rich solution and pH < 10, the alteration layers can act as a transport barrier for key ions, effectively acting as a passivating layer like those on corrosion-resistant metals thereby reducing the glass dissolution rate by several orders of magnitude. Interestingly, alteration layers are not specific to ISG or aluminoborosilicate. A recent review has detailed the commonalities and differences observed between the passivation films formed on silicate glasses, ceramics, and metals, and brought forward ideas that delve deep into the mechanisms of degradation of these materials.¹⁹ For example, the amorphous nature of the films coating both glasses and ceramics allows the incorporation of many exogenous elements supplied by the environment.²⁰ This can affect the structure, properties, thermodynamic stability, and the transport of products and reactants. Although noticed, these effects cannot yet be predicted by existing kinetic models.

Further, although the Ostwald rule of stages predicts these amorphous films will transform into crystalline phases, the timing and processes behind this transition are still unsolved questions. It is known, for instance, that iron or iron corrosion products,²¹ as well as cementitious environments,²² or Mg-rich solutions can trigger the formation of secondary phases, which, in turn, can accelerate glass corrosion.^{23–25} The impact of radiation and other decay-related effects on corrosion properties is also poorly understood. Under self-irradiation, silicate glasses undergoes structural modifications, but the impact of these modifications on long-term durability is variable.²⁶ The forward rate of dissolution is not affected, but the impact on the alteration layers is less clear.

The mechanisms and kinetics of glass degradation are both complex and non-linear. No individual research group will be able to answer all these demanding questions singlehandedly, and it is thus vital that the community works together. ISG provides a

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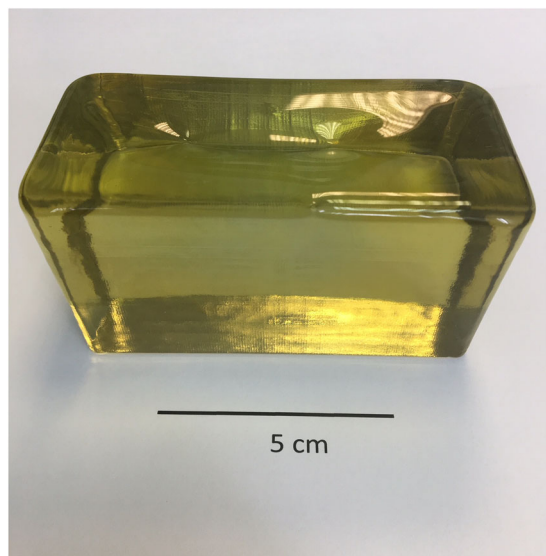


Fig. 1 Ingot of 500 g of International Simple Glass (ISG) glass produced by MoSCI corporation

uniform material on which different groups can exert their specific expertise to contribute to a common understanding of glass degradation. Toward this goal, this collection of papers in *npj Materials Degradation* on ISG²⁷ shows that focusing on a reasonably complex glass is a good way to make progress in the understanding of basic alteration processes. This is a prerequisite for improving predictive models, and for subsequently making informed choices of the best environments for final disposal of vitrified nuclear wastes, as well as the optimal compositions to use. While the puzzle of waste immobilization will not be simple to solve, ISG does provide a common starting point for piecing together understanding.

AUTHOR CONTRIBUTIONS

S.G., J.R., S.K., and J.D. contributed equally to this editorial.

ADDITIONAL INFORMATION

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