
Glamor- or How We Achieved a Common Understanding on the Decrease of Glass Dissolution Kinetics Through International Cooperation

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The objective of the EC funded GLAMOR project was to achieve a common understanding of the processes that control the decrease of the dissolution rate of high-level waste glass in water when silica becomes saturated. Is affinity control or a protective layer dominating? The following steps were taken: (1) review literature, (2) select an experimental dataset and the models $r(t)$ and GM2003, and (3) apply the models to the datasets. The focus was on dissolution tests in pure water at different values of surface-to-volume ratio and pH. Some of the main conclusions are: (1) both affinity and protective layer concepts must be considered in the interpretation of the rate decreasing stage, (2) the residual dissolution rate observed beyond the silica saturation stage is far more important in view of the long-term performance of the glass, and deserves more attention in future R&D. In the GLAMOR final report, we also discussed in detail the modeling parameters, such as the silica saturation concentration, the silica diffusion coefficient in the gel, the silica retention factor in the gel, and the water diffusion coefficient in the diffusion layer.

Introduction

Since the early 1980s large research programmes have been performed worldwide to investigate the dissolution behaviour of candidate high-level waste (HLW) glasses in pure water or candidate repository waters [1]. It became soon clear that the dissolution rate of the glasses in pure water decreases with time. In a similar way detailed, more recent research on the dissolution of HLW glasses for prolonged (months to years) contact with mostly static geological disposal media also led to a consensus that the dissolution rate of the glasses decreases with time. Very low values of the dissolution rate are achieved under solution saturation¹ conditions, as expected for most geological environments [2-4]. This decrease results in longer lifetimes of the vitrified waste, and so contributes to greater long-term safety of geological disposal.

However, the understanding of the long-term dissolution rate and its precise value are poorly documented or known [5]. Two explanations for the decrease in dissolution rate have been considered. The decrease can arise as the solution concentration of H_4SiO_4 approaches a solubility limit thereby decreasing the driving force for the dissolution (affinity concept). In the second explanation, layers² that develop on

the surface of the glass act as transport barriers (= the protective layer concept). Both interpretations refer to concepts that were proposed as early as the 80's [6,7].

The European Commission sponsored Concerted Action GLAMOR³ was conceived to achieve a common interpretation for the decrease in dissolution rate of nuclear waste glasses observed in most experimental programmes. To achieve this goal, and following the recommendation of an International Topical Workshop held in 2000 [5], an international group of experts was brought together, to carry out a quite new kind of project. A set of existing experimental data and existing analytical models were selected. These models were then applied to the data by the European Union (EU) partners, and the entire project team discussed the results of the calculations, primarily focusing on a common interpretation of the processes responsible for the rate decrease. Another goal of GLAMOR was to gain a better understanding of the uncertainties of the values for the various parameters used in the analytical models.

An important aspect of GLAMOR was that we included international, non-EU experts in nuclear waste glass dissolution into the project, in order to have additional critical review within the project itself. GLAMOR ran from 2001 until 2004. A full report of the results of the project can be found in [8].

Background

The general scheme of glass dissolution in confined solution proposed by the Commissariat à l'Energie Atomique (CEA)

¹ In the context of this work, 'saturation' refers not to the overall concentration of solutes, but to those solutes that participate in the rate limiting step(s) from a kinetic point of view

² A general scheme of the surface or reaction layers formed upon glass dissolution consists of an outer precipitation layer consisting of amorphous and crystalline phases, next a porous "gel" layer, and an inner diffusion layer exhibiting a depletion of soluble elements such as B, Na, Li [1]

³ GLAMOR: = A Critical Evaluation of the Dissolution Mechanisms of High Level Nuclear Waste Glasses in conditions of Relevance for Geological Disposal

[10] was used as starting point of the GLAMOR project, see Figure 1. The main concern in GLAMOR is the rate drop stage in the left part of the graph, referred to as "diffusion/affinity".

Both affinity and protective layer concepts are currently coupled to describe the corrosion of complex glasses, since neither process alone can explain the complex process of nuclear waste glass dissolution. The scientific debate over the glass dissolution processes controlling the long-term dissolution has given different weights to both concepts for about two decades. The coupling of only affinity and protective layer concepts appears to be insufficient to describe long-term dissolution of glass beyond the time at which saturation with respect to silica occurs or the rate decrease illustrated in Figure 1. Other key processes such as water diffusion, ion exchange (inter-diffusion) and precipitation of secondary minerals (i.e., clays, zeolites, etc) may be important in the long-term and they may occur in parallel to glass matrix corrosion. However, their impact on the long-term dissolution is still poorly understood.

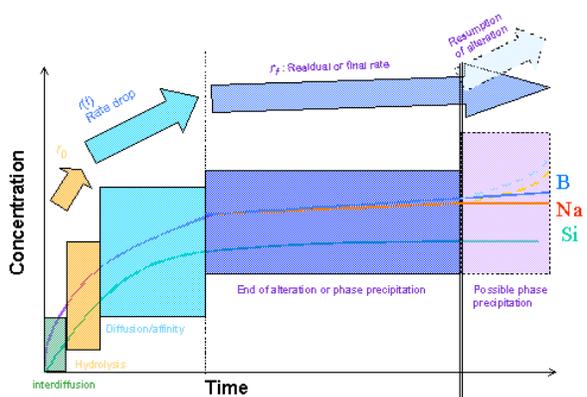


Fig.1 Schematic presentation of the predominant mechanisms of high-level waste glass dissolution in confined solution, represented by the glass matrix constituents Si, B, and Na. Note, the curves plotted do not necessarily correspond to real data, and both axes do not represent quantitative information.

Results

State-of-the-art on glass dissolution based on a literature review

An extensive literature survey was carried out of experiments showing a dissolution rate decrease, silica saturation and subsequent phenomena. Many of these results were obtained at high surface-to-solution volume (S/V) ratios with powdered glass samples, leading to reaction progress⁴ values as large as $10^4 - 10^5 \text{ g/m}^3$ (≥ 100 times values currently achieved in standard leach tests [15]). The review showed that:

- The rate decreasing stage before silica saturation is now currently interpreted as a combined effect of affinity-limited dissolution and kinetically-retarded dissolution from the alteration layer barrier [11, 12].
- There is an agreement that beyond the silica saturation stage dissolution continues, but there is no unanimous interpretation of the results in terms of kinetics [8]. These

“final” or “residual” dissolution rates may be ~ 5000 times lower than the initial dissolution rate in case of the French R7T7 glass SON68⁵ (residual rate $\sim 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 90°C) [8]. Different hypotheses are proposed for the final dissolution rate (e.g. [13]), such as water diffusion in glass, precipitation of secondary phases, and network hydrolysis.

The most important conclusion, however, was that the identification and interpretation of this final dissolution rate is definitely more important than the elucidation of the relative impact of the processes leading to the decrease of the dissolution rate before silica saturation, because that most strongly affects the lifetime of the HLW glass package.

Selection of experimental data and models

The GM2003 [12] and $r(t)$ [14] analytical models were selected. Both models consider a first order rate law and Si diffusion through the “gel” (the main reaction layer), although in $r(t)$ diffusion through the alteration layer is considered more rate limiting than in GM2003. The mathematics of both models are quite similar, and both use D_{Si} (Si diffusion coefficient through the gel) and C^* (Si saturation concentration in solution) as main fitting parameters. There are some other similarities as well, such as the forward and final dissolution rates that are used as fixed parameters, and differences. The strategies to fit the models to the data are different, for instance in $r(t)$ D_{Si} is an important fit parameter, whereas in GM2003 much less credit is given to D_{Si} , and a constant, high value for D_{Si} is chosen. For more details, see [8,9].

The datasets selected for GLAMOR covered S/V values between 50 and 200000 m^{-1} (the latter is 20000 times larger than the S/V in currently used standard leach tests [15]), solution free or fixed pH values from 2.5 to 11.5, glass composition (SON68, a high Al_2O_3 glass, and simple glass), solution composition (high purity water as reference; various chemicals added), temperature (50°C , 90°C , and 150°C), presence/absence of solids (clay), and flow rate (static as reference and 14.4 mL/d). Fifty experimental datasets were selected.

Results of the joint modelling of the experimental results

The EU project partners applied both $r(t)$ and GM2003 models to all datasets [8]. The discussion of the outcome was organized along the assessment of the effect of S/V, solution pH, solution saturation and glass composition. Here, we focus on one experiment only, as it is informative to show the approach of GLAMOR.

The dissolution experiment was performed in deionised water at 90°C at a moderate S/V of 50 m^{-1} , which is close to the value of 10 m^{-1} used in the ASTM standard leach test [15], with monolithic SON68 glass samples. Some experimental and modeling results are shown in Figure 2. The results

⁵ SON68 (full code: SON 68 18 17 L1C2A2Z1) is a reference glass with a composition simulating the nominal composition of the Areva R7T7 glass produced at La Hague facility.

⁴ Reaction progress is the mass of glass dissolved per solution volume

	FIG 2, top r(t) (CEA)	FIG 2, lower r(t) (CEA)	Best fit with r(t) SCK•CEN	Best fit with GM 2003 SCK•CEN
Forward rate (g m ⁻² day ⁻¹)	$r_o=f(\text{pH})\sim 0.95$	$r_o=f(\text{pH})\sim 1.5$	$r_o=f(\text{pH})\sim 1.33$	0.7
Silica saturation (mg.L ⁻¹)	$C^*=16, C^*_{\text{tot}}\sim 25$	$C^*=35, C^*_{\text{tot}}\sim 66$	$C^*=16, C^*_{\text{tot}}\sim 25$	$K_{\text{SiO}_2}=25.05$
Si-diffusion coefficient (m ² s ⁻¹)	$D_g=5.0\ 10^{-14}$	$D_g=7.0\ 10^{-16}$	$D_g=5.0\ 10^{-14}$	$D_{\text{Si}}=2.6\ 10^{-13}$
Si-retention α (ppm ⁻¹)	0.023	0.031	0.022	0.022
Final rate, r_{fin} (g m ⁻² day ⁻¹)	$1.0\ 10^{-8}$	$1.0\ 10^{-8}$	$8\ 10^{-3}$	$8.0\ 10^{-3}$
Water diffusion coefficient $D_{\text{H}_2\text{O}}$ (m ² s ⁻¹)	Not considered	Not considered	Not considered	$5.0\ 10^{-21}$
K_{dB} (kg m ⁻³)	Not considered	Not considered	Not considered	100

Table 1. Summary of r(t) and GM2003 parameters⁶ used in the plots in Figures 2 and the best fit (not shown)

display a quite "simple" dissolution sequence: initial dissolution, rate decrease with the approach to silica saturation, and a "residual" dissolution afterwards. The modelling results shown were obtained with the r(t) model. Only the Si and B concentrations were calculated, as Si is the most important element in HLW glass dissolution and B is a soluble element from which the dissolution of the glass matrix can be inferred.

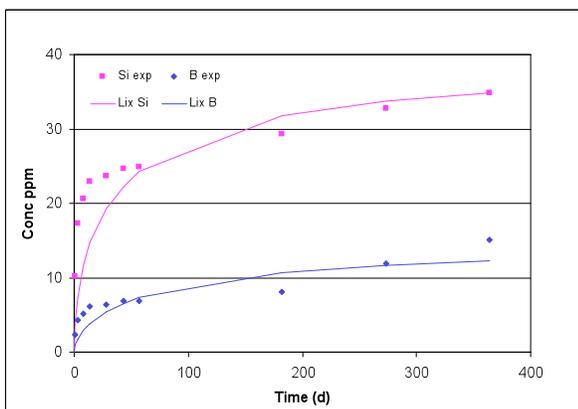
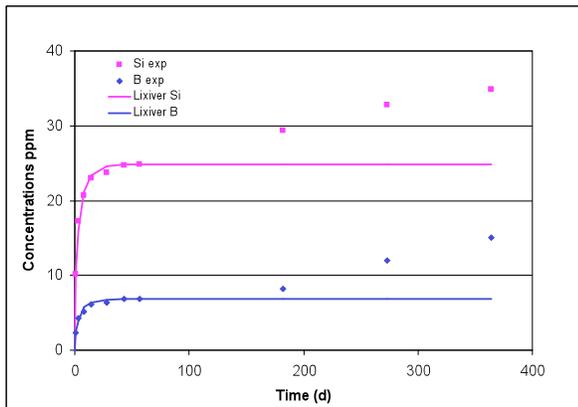


Fig. 2 Model fits with model r(t) with results from tests performed with SON68 at 50 m⁻¹ and 90°C in deionised water. The parameter values are listed in Table I.

The top graph shows a fit for the first two stages, the lower graphs for the later stage. Obviously none of these fits is suited to fit the entire duration of the test. The parameter values used in these plots are shown in Table I, together with the parameter values for the best fit modelling with r(t) and GM2003 (not shown). From the modelling results on the tests at different S/V, the following observations can be made:

- The key parameters used in the models are C* and D_{Si} to calculate the Si release, α to relate B with Si, and the residual rate (r_{fin}). Some of the modelling parameters are correlated with each other: D_{Si} with α , and D_{H2O} with K_{dB} [8]

The decrease in the dissolution rate before Si saturation is modelled by optimizing the D_{Si} and C* values [8]. The major difference between the top and lower graphs in Figure 2 is the choice of different values for C* and D_{Si}, which clearly strongly affects the quality of the fit in the rate decreasing stage. Adjusting the value for the residual rate (Table I) generates the best fit for the entire data set.

Modelling data similar to those in Figure 2, but at S/V of 200000 m⁻¹ revealed another problem. Soluble elements such as B and Na reached very high concentrations in solution of ≥ 3000 mg/L and Si concentrations up to 350 mg/L. This latter value cannot be explained by considering amorphous silica as the only solubility controlling phase for Si, as the solubility of SiO_{2(am)} is ~ 100 mg/L at pH ~ 9.4 . In reality we have to account for the formation of NaHSiO₃ complexes at high pH [16], leading to higher "total" Si concentrations at saturation in agreement with the experimental results.

New Programs

In recent years, the US Department of Energy has renewed interest in the reprocessing of used nuclear fuel. In Fuel Cycle Research and Development program, glass is the baseline technology for the disposal of radionuclides from reprocessing. In the waste form development part of the program, an international effort has been started with the same goal as GLAMOR and many of the same participants. The starting point of this program is the point at which the GLAMOR project ended. To date, a workshop was held in Seattle, WA, USA and less formal meetings have been held, usually in conjunction with other technical meetings. The results of this DOE program are to be documented in forthcoming publications.

Conclusions

The GLAMOR project has shown that mechanistic analytical models are able to produce reasonable fits to experimental data of the dissolution rate decrease in experiments with simulated high-level waste glasses. Beyond the saturation stage that follows the rate decrease, however, there is less agreement between the modelling predictions and the experimental data. This is because additional phenomena or processes occur, that have not yet been taken into account in the present models.

The methodology chosen in GLAMOR to let various EU and international experts work with the same models and datasets was very fruitful. It enabled us to achieve a common understanding on some aspects of the glass dissolution mechanism that have been the subject of long-time debate, such as:

- It is agreed that both affinity and protective layer concepts must be taken into account. However, some uncertainties still exist, for instance, on the conditions under which diffusion of dissolved Si through a surface layer is rate limiting.
- There is a consensus that a residual ("final" but not necessarily constant with time) dissolution rate exists beyond the rate decrease, at least in the pure water and closed systems considered in GLAMOR. This residual rate significantly controls the long-term release from the glass, and it should become an input parameter in the safety assessment calculations for a geological disposal site. Various processes have been proposed to account for this residual rate: water diffusion, ion-ion-exchange reactions, network hydrolysis, and precipitation of secondary phases. More efforts should be devoted to document and understand the processes behind this residual rate under standard conditions (pure water), but as well in repository waters loaded with near- or far-field solids.

A general recommendation of GLAMOR is that the uncertainties on the various modeling parameters (mainly C^* , D_{Si} and r_{fin}) should be further reduced, in order to reduce the uncertainties of the model predictions over disposal timescales. These efforts should be coupled with continued efforts to better understand the various dissolution processes, in particular those controlling the final dissolution rate.

Acknowledgements

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