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Long-term dissolution rate of nuclear glasses in confined environments: does a residual chemical affinity exist?

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An experimental procedure based on static leach tests of a combination of glass powder and a finely polished monolith is proposed to determine the long-term corrosion rate of nuclear glasses in confined environments. Solution analyses and detailed characterization of the monolith surface with MeV ion-beam techniques show a drastic decrease of the corrosion rate with reaction progress. It is concluded that the residual affinity model, based on a control of the final rate by dissolved silica, cannot account for our observations.

1. Introduction

The aqueous corrosion of nuclear glasses is currently considered as the main phenomenon by which radiotoxic nuclides disposed in a deep-seated geological repository could eventually reach the biosphere. Therefore, a great deal of research effort has been devoted to the corrosion mechanisms of such glasses, in particular for estimating their dissolution rates under various experimental conditions [1, 2]. The most likely scenarios involve confined environments where the corrosive solution is only very slowly renewed; in such conditions, it is expected that the glass dissolution rate will markedly decrease with time as a result of the gradual "saturation" of the solution with reaction products, as suggested by many experimental results [3–6]. However, the time periods of interest (> 1000 y) largely exceed those directly accessible to experimentation, so that long-term extrapolations are extremely difficult. Moreover, true thermodynamic equilibrium cannot be reached in silicate glass/water systems because glass is a metastable phase. It is usually considered that, even for very long periods of time, a residual chemical affinity driving the corrosion reaction will persist [5–8]. This issue is still a matter of debate, because its consequence for glass durability may not be negligible.

In such a model [8], the dissolution rate of the glass is ruled by its major constituent and thus by the silica concentration in solution. When saturation is reached with respect to some silica-containing precipitated phase, a residual constant corrosion rate persists, which corresponds to the rate of silica transfer from the metastable glass to the stable secondary phase. However, such a steady state is difficult to evince by solution analysis, because silica concentration should, by definition, be constant, but is reflected by the residual release rate of mobile elements. In particular, alkalis and boron which do not participate in secondary-phase formation, are thought to allow assessment of the residual corrosion rate.

To overcome the intrinsic difficulty of measuring very low dissolution rates, previous authors have developed accelerated testing techniques based either on an increase of the leaching temperature or of the surface area of glass upon volume of solution (SA/V). The use of the first type of tests is limited, because temperature enhancement could involve a change in the kinetically ruling mechanism. This is illustrated by the varying apparent activation energy estimated in different temperature ranges [9]. We have ourselves shown, on both soda-lime glass and complex glasses, including a nuclear glass, that hydration of the network is ruled by $H^+ \rightarrow Na^+$ ion exchange below $\sim 100^\circ$ C and likely by permeation of molecular water above $\sim 150^\circ$C [10]. In addition, the temperature enhancement also involves a change in the nature of the stable secondary phases.

Similarly, classical high SA/V tests ($\geqslant 10\,\mathrm{cm}^{-1}$) necessitate the use of finely powdered materials [4, 11] which excludes the application to the solid of sophisticated surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Rutherford backscattering spectrometry(RBS), resonant nuclear reaction analysis (RNRA) etc. These tools are indispensable for identifying basic corrosion mechanisms. They also permit the measurement of extremely low rates such as those expected in near-equilibrium conditions, which are difficult to assess by the sole solution analyses. Indeed,

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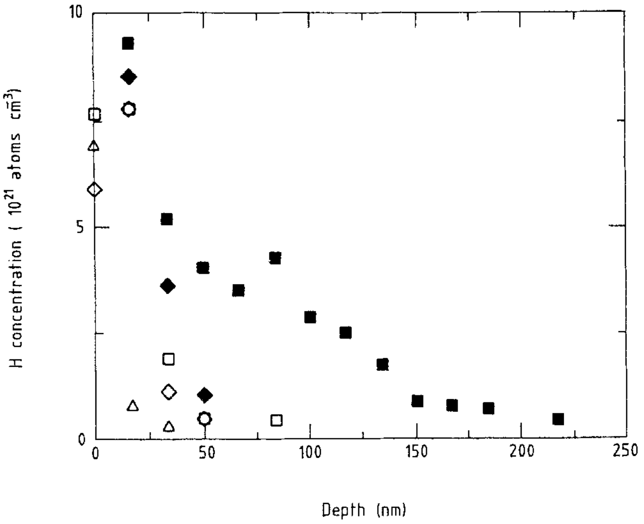

Figure 1 Hydrogen depth profiles of the nuclear glass leached at 120° C for 16 h in (■) pure water, or in powder-reacted solutions: contact times (◆) 4 h, (□) 8 h, (◇) 28 h, (△) 52 h.

MeV ion-beam analytical techniques allow, for instance, easy detection of an elemental depletion on a very shallow depth (~ 50 nm), whereas the correlative amount released in solution corresponds to an undectable increment. In contrast, polished glass slabs are appropriate for a detailed characterization with these techniques, but hardly allow the exploration of systems with SA/V superior to $10\,cm^{-1}$ and consequently the study of high degrees of reaction advancement, i.e. corresponding to equivalent long periods of time.

2. Experimental approach

In order to conciliate these two antagonist constraints, we associated in the same dissolution experiment, a fine glass powder allowing a large SA/V value (easily superior to $200\,cm^{-1}$) and a centimetre sized monolith of the same material especially prepared for solid characterization. An additional advantage of this approach is to check the progress of the dissolution reaction by introducing a new untreated monolith at different stages of the reaction, for a given timespan. Minute modifications of the surface composition can then be detected by combining various surface analytical techniques. It should be noted that the introduction of this probe in powder-reacted solution does not significantly modify the SA/V value of the experiment ($< 0.1\%$).

This approach has been applied to the French reference nuclear glass (R7T7) leached in teflon-walled autoclaves with initially pure deionized water at 120° C. Direct opening of the autoclaves to introduce the monolith was not feasible and it was decided to cool the system at 90° C in a thermostatically controlled bath for a few minutes. The chosen SA/V was $200\,cm^{-1}$, the surface area of the powder being measured by the BET method. The glass monoliths were introduced after a time of powder–solution interaction ranging from 4 h to 30 d and leached for times from 16 h up to 36 d. They were subsequently analysed with Rutherford backscattering spectrometry, using a 1.8 MeV He beam, and resonant nuclear reaction analysis based on the $^1H(15N, \alpha\gamma)12C$ reaction induced by a 6.3 MeV 15N beam, to provide the depth profiles of, respectively, transition plus heavy elements and hydrogen. These two types of depth profiles are very useful for weighting the degree of glass corrosion through the thickness of the hydrated layer and the amount of surface-accumulated hydrolysable elements [12, 13]. Complementary solution analyses of boron, silicon, sodium and lithium with ionic chromatography and weight loss measurements were performed.

3. Results and discussion

Typical results pinpointing a "saturation" effect are illustrated by Figs 1 and 2 which show the marked difference in behaviour between a monolith leached at

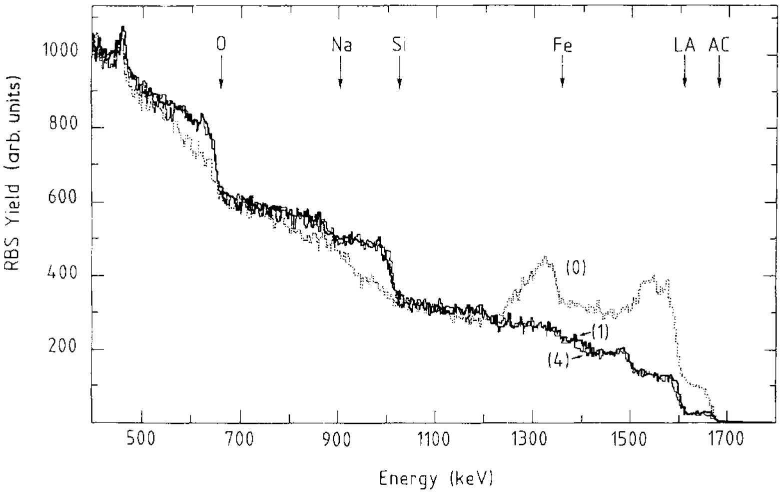

Figure 2 RBS spectra of the nuclear glass leached at 120° C for 16 h in (0) pure water, or in powder-reacted solutions for (1) 4 h and (4) 52 h; for sake of clarity, only two spectra are presented.

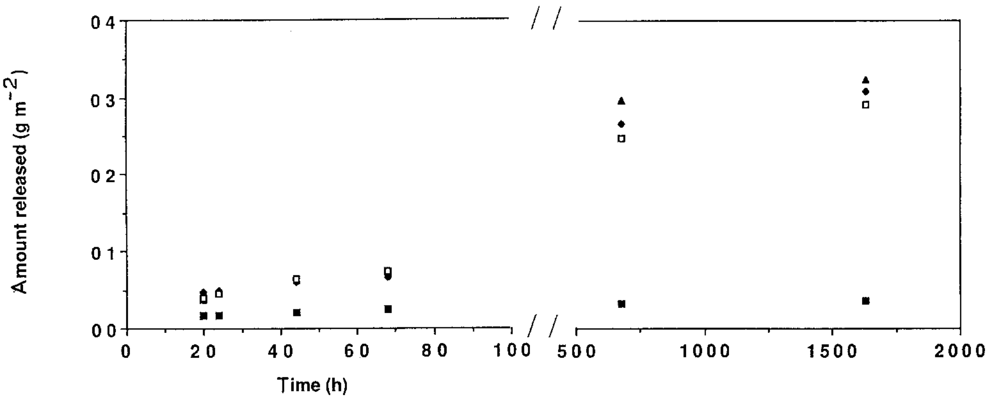

Figure 3 Amounts of (■) silicon, (◆) boron, (▲) lithium and (□) sodium released in solution as a function of time for short- and long-term experiments.

120° C with deionized water and those leached in powder-reacted solutions for equivalent short duration of 16 h. In deionized water, one notes first a hydration over a thickness ~ 200 nm with a maximum hydrogen concentration ~ 10 × 10^{21} atoms cm^{-3}, and second a marked superficial accumulation of iron, lanthanides and actinides (uranium and thorium). The neat shift of the silicon edge on the RBS spectrum would suggest that the surface-accumulated heavy elements are in the form of hydroxides. These features are quite typical of surface modifications occurring during nuclear glass dissolution [3, 5, 14].

In contrast, in powder-reacted solutions, both hydration and elemental accumulation are drastically and continuously reduced, with increasing reaction progress. Neither the weight loss of the monolith nor its contribution to elemental release are measurable. From this short-term experiment, we find that the hydration rate, initially of ~ 10 nm h^{-1}, is reduced by an order of magnitude after a powder-solution interaction of 52 h. Data on solution analyses are reported in Fig. 3 which clearly indicate that a steady state with respect to silica is already reached after 52 h, whereas sodium, lithium and boron continue to be released. Note that the corresponding leach rates are continuously decreasing, which is not in favour of the residual affinity model.

However, these short-term results do not allow us to decipher whether the persistence of hydration, as well as the corresponding release of mobile elements, is actually attributable to a residual affinity of the glass corrosion, or rather to the fact that the solution was not at true saturation with respect to silica. The long-term runs allow discrimination between these two hypotheses. Indeed, the data reported in Fig. 4 show no marked difference in the hydrogen depth profiles, for similar leach times of the monolith, whatever the duration of powder-solution interaction (compare the data of samples 4 and 6, on the one hand, and 5 and 7, on the other). This fact, together with solution analyses, demonstrates that near-saturation of the solution in silica is already reached within a few days under these experimental conditions. For the longest contact time of 36 d (sample 7), the hydration rate fell to a value of 0.1 nm h^{-1}, i.e. was reduced by two orders of magnitude compared to the rate in deionized water. In the corresponding RBS spectrum, the accumulation of heavy elements is restricted to a small peak due to lanthanides (Fig. 5). Note that at the end of this experiment, the release rates for mobile elements are of the same order as those measured in a more classical experiment with a one-year duration [11]. This illustrates the usefulness of our approach in simulating long durations of leaching.

The steady decrease, with increasing leach time, of the release rates of mobile elements cannot be explained by a residual corrosion of the glass governed by silica. In addition, the observation of a residual hydration of the glass supports the idea that ion exchanges involving alkalis still persist. In our judgement, the decrease

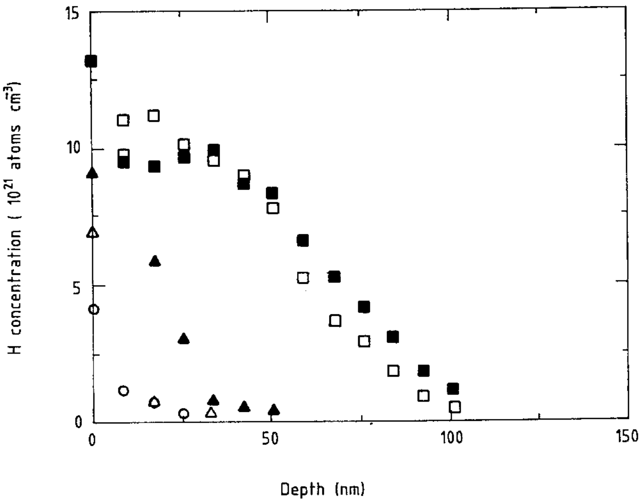

Figure 4 Hydrogen depth profiles of the nuclear glass (○) untreated, and leached at 120° C for 16 h in powder-reacted solutions (contact time (△) 52 h, (▲) 32 h) or leached for 32 d in powder-reacted solutions ((□) 52 h, (■) 32 d).

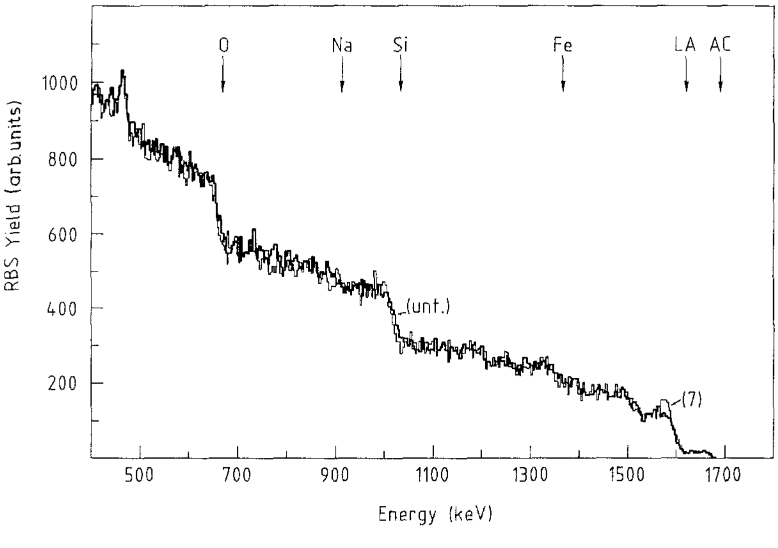

Figure 5 RBS spectra of the nuclear glass either untreated (unt.) or (7) leached at 120° C for 32 d in a solution previously reacted for 32 d with powder.

in hydration and release rates can be explained by the progressive accumulation of alkalis in solution. The independent behaviour of mobile elements with respect to silica is exemplified by our observation of a drastic decrease of the release rate of sodium, when glass leaching is performed in concentrated NaCl solution [10, 14]. Such a phenomenon, which occurs since the very beginning of the leach tests (i.e. far from silica saturation), even leads to a backward sodium penetration into the near-surface region of the glass. All our observations suggest that, even if the concept of residual affinity is still considered, it should not be limited to silica, but should be extended to the other major glass constituents. Therefore, the residual glass corrosion rate, if any, would be attained when the solution is "saturated" with respect to every major constituent. Because alkalis and boron are still released at a measurable level in our longest leach runs, it is likely that "saturation" has not yet been reached for these elements and that the corresponding leach rates will keep on decreasing.

In spite of these difficulties, our data can be used to estimate an upper limit of the durability of the nuclear glass, at 120° C in static conditions. By assuming a constant rate of 0.1 nm h^{-1} over a disposal period of 10 000 years, the corresponding maximum thickness of hydrated glass would be ~ 0.9 cm, compared to the ~ 30 cm diameter of the nuclear glass rod. In the hypothesis of a closed system, the actual value would even be lower as the trend is a steady decrease of the hydration rate with time, but our estimate could correspond to an attack in a slowly renewed solution. Moreover, the release rate of transuranic elements is necessarily even much lower, because the hydrated layer acts as a very efficient trap for these highly hydrolysable elements. Such an evaluation only intends to illustrate the likely good durability of the nuclear glass in these hypothetical conditions, and should not be extrapolated without caution to actual disposal conditions.

4. Conclusion

This work shows that the hypothesis of a residual affinity, only ruled by the silica activity in solution and controlling the long-term durability of complex silicate glasses like nuclear ones, is questionable. Indeed, we think that, whenever valid, such a concept should at least be extended to all major glass components and particularly to alkalis. Our results indicate that, in a confined medium, the estimated upper limit of the residual corrosion rate is already extremely low.

We have also shown the versatility of this experimental approach which can easily simulate corrosion times at least one order of magnitude longer than those attainable with previously proposed experiments. In addition, such an approach permits the use of the surface analytical techniques, necessary for the identification of the basic mechanisms of glass corrosion.

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References

1. J. E. MENDELL, Final report of the defense high-level waste leaching mechanisms program, PNL-5157, (Pacific Northwest Laboratory, 1984).
2. B. C. BUNKER, *Mater. Res. Soc. Symp. Proc.* **84** (1987) 493.
3. A. BARKATT, B. C. GIBSON, P. B. MACEDO, C. J. MONTROSE, W. SOUSANPOUR, M. A. BOROOMAND, V. ROGERS and M. PENAFIEL, *Nucl. Technol.* **73** (1986) 140.
4. L. R. PEDERSON, C. Q. BUCKWALTER, G. L. McVAY and B. L. RIDDLE, *Mater. Res. Soc. Symp. Proc.* **15** (1983) 47.
5. D. M. STRACHAN, *Nucl. Chem. Waste Management* **4** (1983) 177.
6. B. GRAMBOW and D. M. STRACHAN, *Mater. Res. Soc. Symp. Proc.* **26** (1984) 623.
7. E. MOUCHE and E. VERNAZ, *ibid.* **112** (1988) 703.
8. B. GRAMBOW, *ibid.* **44** (1984) 15.
9. E. Y. VERNAZ, J. L. DUSSOSOY and S. FILLET, *ibid.* **84** (1987) 555.
10. J.-C. DRAN, G. DELLA MEA, A. PACCAGNELLA, J.-C. PETIT, L. TROTIGNON, *Phys. Chem. Glasses* **29** (1988) 249.
11. JSS Project phase V, final report, "Testing and modelling of the corrosion of simulated nuclear waste glass powders in a waste package environment", Technical report 88-02 (1988).

12. B. C. SALES, C. W. WHITE, G. M. BEGUN, L. A. BOATNER, *J. Non-Cryst. Solids* **67** (1984) 245.
13. J.-C. PETIT, J.-C. DRAN, G. DELLA MEA, C. BROUSSE, A. PACCAGNELLA and P. A. MANDO, *Nucl. Instrum. Meth. Phys. Res.* **B32** (1988) 498.
14. J.-C. PETIT, G. DELLA MEA, J.-C. DRAN, M.-C. MAGONTHIER, P. A. MANDO, A. PACCAGNELLA and A. STEFANINI, *Geochim. Cosmochim. Acta*, (1990) in press.

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