Dissolution rate equations for basaltic glasses. Comparison with experimental data

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With the concept of a geological repository, the long term behaviour of nuclear glasses must be assessed. For this purpose, computer codes were developed. The kinetic parameters and alteration mechanisms used in these codes have been determined on the basis of short term experiments on the nuclear glass R7T7. One way to validate these models is to use them to predict the long term behaviour of volcanic glasses which have been subject to alteration processes over geological time. Modelling the long term behaviour of basaltic glasses, considered as natural analogues of nuclear glasses, needs the incorporation of their dissolution kinetic laws. Many data have been published concerning silicate mineral dissolution [1]. In the Transition State Theory (TST), dissolution rates are expressed in terms of a thermodynamic parameter (chemical affinity) and of a kinetic one (catalyses or inhibition). Grambow suggested in 1985 [2] that the kinetic dissolution of nuclear glasses was controlled by the desorption of a surface silica complex. However, few data are available on the kinetic dissolution laws of basaltic glasses. A kinetic approach was published by Berger *et al.* [3] on the basaltic glass's dissolution under hydrothermal conditions. Daux *et al.* [4] proposed a kinetic law for basaltic glass at 90°C. However, the application of Grambow's law on basaltic glasses has never been performed. In this study, we will firstly discuss the validity of Grambow's law, then secondly Daux's law, based on experimental dissolution of a synthetic basaltic glass at 90°C. New results on the experimental dissolution of the basaltic glass with silica-rich solutions are presented as well as discussion on the specific role of the dissolved silica.

Experimental dissolution

A synthetic Li-doped basaltic glass (1 wt.% Li) was leached in the laboratory at 90°C under different reaction progress (near and far from equilibrium). Experimental release rates were calculated from the normalized weight losses of Na. Under initial conditions, a release rate of 0.7 $g.m^{-2}.d^{-1}$ was obtained. This value is in agreement with the literature data. A compilation of initial release rates with temperature gives an activation energy for the dissolution of the basaltic glass of 66 kJ/mol. This activation energy is similar to the value determined for R7T7 glass, suggesting comparable dissolution mechanisms. The release rate decreases with the reaction progress, and near equilibrium it is four orders of magnitude lower than the initial rate.

Comparisons between experimental release rates and theoretical values (deduced from kinetic laws proposed in the literature) are used to validate rate equations.

Dissolution kinetic laws of the basaltic glass

Applying the transition State Theory, Grambow in 1985 [2] considered that nuclear glass dissolution was controlled by the desorption of a silica complex in solution. The dissolution rate is then expressed in terms of the single silica activity in solution, at 90°C:

$$V = k^{+} \times [H^{+}]^{n} \left(1 - \frac{[H_4SiO_4^0]}{[H_4SiO_4^0]_{sat}}\right)$$

where V = dissolution rate ($mol/cm^2/s$); $[H^+]$ = H^+ activity in solution (mol/l); $[H_4SiO_4°]$ = orthosilicic acid activity in solution (mol/l); $[H_4SiO_4^0]_{sat}$ = orthosilicic acid activity at saturation (mol/l).

This law is applied to this work to calculate the dissolution rates of a basaltic glass at a temperature of 90°C. The parameters 'k^+' and 'n' are based on Guy's study [5] – $k^+ = 3.7410^{-15}$, $n = -0.44$ – and $[H_4SiO_4^0]_{sat}$ is determined from the current dissolution experiments carried out near equilibrium conditions.

Leaching of a synthetic basaltic glass at 90°C using a mixed flow-through system was performed by

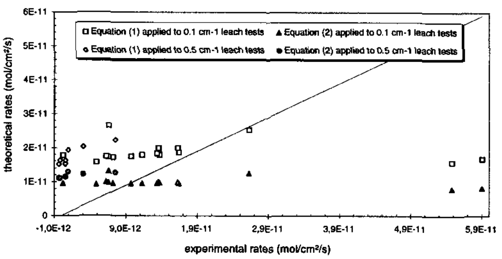

FIG. 1. Comparison between experimental and theoretical rates based on Grambow and Daux's law.

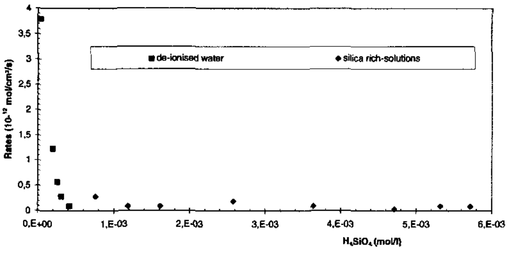

FIG. 2. Evolution of release rates in terms of the orthosilicic acid molality in solution (mol.l^{-1}) in an open system.

Daux *et al.* [4]. A kinetic law was proposed to describe the basaltic glass dissolution. This law expressed the release rate in terms of chemical affinity, taking into account silica, aluminum and iron activities in solution:

$$V = V_0 \times \left\{ 1 - \frac{[H_4SiO_4]\,[Al(OH)_4^-]^{0.36}\,[Fe(OH)_3]^{0.18}\,[OH^-]^{0.36}}{8.2 \times 10^{-5}} \right\} \quad (2)$$

with $\quad v_0 = 4.29 \times 10^{-15} \times [H^+]^{0.39}$

Theoretical dissolution rates of the basaltic glass were determined applying equations (1) and (2) and using experimental chemical data. Calculations were carried out using the geochemical code KINDIS [6] which determines the activities in solution from the total concentrations of elements and the pH of the leachates.

Results

Theoretical dissolution rates were compared with experimental release rates of the synthetic basaltic glass (Fig. 1). The results are:

- aluminum and iron can be considered as inhibitors to the reaction ; theoretical rates deduced with Daux's law are in fact closer to experimental rates than those obtained when applying Grambow's law, - nevertheless, the two laws are not in agreement with the experimental results, particularly at high reaction progress.

Chemical affinity expressed in terms of a single silica activity or a combination of silica, aluminum and iron activities cannot account for the diminution of the measured release rates. New results obtained on the nuclear glass R7T7 suggest that a specific role of silica could in part explain the diminution of the dissolution rates [7].

A specific effect of silica?

To show the possible effect of silica on the diminution of the dissolution rates, experiments of basaltic glass in silica-rich solutions in an open system were performed. The silica concentrations in the leachates fluctuated from 5.3×10^{-4} to 4.5×10^{-3} mol.l^{-1}. A comparison of release rates in de-ionised water and those in silica-rich solutions demonstrate that release rates are not directly dependant on the concentrations of aqueous silica (Fig. 2). A specific effect of silica cannot explain decrease in the dissolution rate observed in the previous statistic experiments (four orders of magnitude with respect to the initial dissolution rate).

Conclusion

The experimental results presented are not in agreement with the current kinetic laws (Grambow and Daux's law). A specific silica effect has been experimentally determined but it only results in a diminution of the dissolution rate by a factor lower than 100 compared to the initial dissolution rate. To explain the experimentally determined diminution in the dissolution rates of four orders of magnitude, other contributing factors need to be taken into account, such as bulk chemistry effect (affinity expression) or a diffusion barrier.

References

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