

# A combined glass dissolution/diffusion experiment in Boom Clay at 30 °C



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## ABSTRACT

At the appropriate times, silica diffusion in clay is possibly the rate determining process for the dissolution of vitrified waste disposed of in a clay layer. For testing this hypothesis, combined glass dissolution/silica diffusion experiment are performed. SONG8 glass coupons doped with the radioactive tracer  $^{32}\text{Si}$  are sandwiched between two cores of humid Boom Clay, heated to 30 °C. Due to glass dissolution,  $^{32}\text{Si}$  is released and diffuses into the clay. At the end of an experiment, the mass loss of the glass coupon is measured and the clay core is sliced to determine the diffusion profile of the  $^{32}\text{Si}$  released from the glass in the clay.

Both mass loss and the  $^{32}\text{Si}$  diffusion profile in the clay are described well by a model combining glass dissolution according to a linear rate law with silica diffusion in the clay. Fitting the experiments to this model leads to an apparent silica diffusion coefficient in the clay between  $7 \times 10^{-13} \text{ m}^2/\text{s}$  and  $1.2 \times 10^{-12} \text{ m}^2/\text{s}$ . Previously determined values from diffusion experiments at 25 °C are around  $6 \times 10^{-13} \text{ m}^2/\text{s}$  (In-Diffusion experiments) and  $2 \times 10^{-13} \text{ m}^2/\text{s}$  (percolation experiments). The maximal glass dissolution rate for glass next to clay is around  $1.6 \times 10^{-7} \text{ g glass/m}^2 \text{ s}$  (i.e. 0.014 g glass/m<sup>2</sup> day). In undisturbed clay, the measured silica concentration is around 5 mg/L. Combining these values with the previously measured (In-Diffusion experiments) product of accessible porosity and retardation factor, leads in two ways to a silica glass saturation concentration in clay between 8 and 10 mg Si/L.

Another candidate for the rate determining process of the dissolution of vitrified waste disposed in a clay layer is silica precipitation. Although silica precipitation due to glass dissolution has been shown experimentally at 90 °C, extending the model with silica precipitation does not lead to much better fits, nor could meaningful values of a possible precipitation rate be obtained.

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## 1. Introduction

In Belgium the disposal of vitrified radioactive waste in Boom Clay is considered. Safety studies require to estimate the release rate of radionuclides from the host glass and their transport rate in Boom Clay. Experiments have shown that many of the radionuclides dissolve congruently with the glass.

Dissolution of glass next to clay is described by a model (Pescatore, 1994) according to which at large times the glass dissolution rate is controlled by the transport parameters of dissolved silica in Boom Clay: the apparent diffusion coefficient  $D$  and the product  $\eta R$  of the diffusion accessible porosity  $\eta$  and the retardation factor  $R$ . The values of these parameters have been measured by diffusion experiments (Aertsens et al., 2003; Aertsens et al., 2008) confirming silica retardation in Boom Clay. Both dissolved silica and clay are negatively charged, so initially silica sorption

on clay was not expected. Possible mechanisms explaining it have been put forward (De Cannière et al., 1998).

The silica transport parameters in Boom Clay and the Pescatore model are validated by experiments where  $^{32}\text{Si}$  doped glass dissolves next to clay. This allows to determine not only the glass mass loss as a function of time, but also the  $^{32}\text{Si}$  diffusion profile in the clay. The combination of both types of measurement makes it possible to verify if the  $^{32}\text{Si}$  profile in the clay can indeed be coupled to the glass mass loss. If so, all parameters of the Pescatore model can be measured. Because at 90 °C silica precipitates have been observed next to a dissolving glass in contact with clay (Pozo et al., 2007), a precipitation term is added to the Pescatore model. An overview of possible precipitation mechanisms is given by Gin et al. (2001). The Pescatore model does not describe the precipitation of secondary phases (especially phyllosilicates) on the glass surface, which can form a sink for silica released from the glass (Frugier et al., 2008).

This paper starts by describing the experiment. From the Pescatore model, two approximate expressions for the  $^{32}\text{Si}$  profile in the clay are derived. Two extensions of the Pescatore model

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are derived: one taking into account the finite size of the clay, and one taking into account silica precipitation in the clay. These models are used afterwards to fit the experimental data.

## 2. Description of the experiment

SON68 glass coupons with a thickness of 2 mm and a diameter of 16 mm were doped with the radioactive tracer  $^{32}\text{Si}$ , leading to a specific glass activity  $\rho_{\text{Bq, glass}} = 1.24 \times 10^5 \text{ Bq/g glass}$ . The glass samples were sandwiched between two cores of humid Boom Clay with a length of typically about 2 cm each and pressed into a percolation cell with a diameter of 20 mm (see Fig. 1). After the saturation of the clay by percolation with clay water, the valves at the inlet and outlet were closed and the cells were heated to 30 °C. Possible voids around a glass coupon caused by the different diameters of the glass and the clay are unlikely because of the swelling capacity of the clay. Due to glass dissolution,  $^{32}\text{Si}$  is released from the glass and diffuses into the clay.

After stopping the experiment, the glass weight (mass) loss (subscript  $_{\text{WL}}$ ) per surface unit  $Q_{\text{WL}}$  (unit: g glass/ $\text{m}^2$ ), was measured. Then the clay core was sliced to determine the  $^{32}\text{Si}$  diffusion profile. Therefore, the clay slices were dried, and after secular equilibrium of  $^{32}\text{Si}$  with its daughter  $^{32}\text{P}$ , in each slice the activity was measured with a Packard Auto-Gamma 5650 NaI(Tl) counter. The ratio  $Q_{\text{Bq}}$  (unit: g glass/ $\text{m}^2$ ;  $_{\text{Bq}}$  refers to activity):

$$Q_{\text{Bq}} = \frac{B_{\text{Bq, clay}}}{S \rho_{\text{Bq, glass}}} \quad (1)$$

with  $B_{\text{Bq, clay}}$  the total activity (unit: Bq) in clay and  $S$  the contact surface (unit:  $\text{m}^2$ ) provides another estimate for the glass mass loss. The mass loss  $Q_{\text{Bq}}$  based on the amount of  $^{32}\text{Si}$  in the clay, is larger than the weight loss  $Q_{\text{WL}}$  because during the dissolution of glass next to clay, clay components are integrated in the outer part of the glass alteration layer. This process decreases the weight loss  $Q_{\text{WL}}$ , but it hardly changes the mass loss  $Q_{\text{Bq}}$  based on  $^{32}\text{Si}$  because there is almost no  $^{32}\text{Si}$  in the clay next to the glass (initially the  $^{32}\text{Si}$  content in the clay is zero, due to glass dissolution this content slowly rises in the vicinity of the glass/clay interface). Since the mass loss  $Q_{\text{Bq}}$  based on  $^{32}\text{Si}$  is larger than the weight loss  $Q_{\text{WL}}$  ( $Q_{\text{Bq}} > Q_{\text{WL}}$ ), the specific glass activity based on weight loss  $\rho_{\text{Bq, WL}}$  (unit: Bq/g glass), defined as

$$\rho_{\text{Bq, WL}} = \frac{B_{\text{Bq, clay}}}{S Q_{\text{WL}}} = \frac{Q_{\text{Bq}}}{Q_{\text{WL}}} \rho_{\text{Bq, glass}} \quad (2)$$

is larger than the specific glass activity  $\rho_{\text{Bq, glass}}$ .

In similar experiments with undoped SON68 glass, only the weight loss is measured. At the end of such an experiment, a few milliliter of Boom Clay water was pressed through the clay core for analysis. The samples were not filtered, and analyzed by ICP–AES, ICP–MS and ion chromatography, leading to a clay water composition at the end of the experiment. This clay water composition has also been determined for blank tests, where real Boom

Clay water (taken from the Underground Research Lab, where the temperature is around 13 °C) was percolated through a clay core at 30 °C.

The experiments with  $^{32}\text{Si}$  doped SON68 were stopped after 887 days, 1227 days, 1570 and 1890 days.

## 3. Models

The Pescatore model (Pescatore, 1994) for dissolution of glass next to clay is used to derive two approximate expressions for the  $^{32}\text{Si}$  concentration in the clay. Then the model is extended by taking into account the finite size of a clay core. In a second extension, a precipitation term is added.

### 3.1. The model in an infinite system

The behavior of dissolved silica in clay is described by the diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - k(C - C_0) \quad (3)$$

with  $C(x, t)$  the concentration of silica in the pore water accessible for diffusion (unit: g Si/ $\text{m}^3$ ),  $t$  time,  $D$  the apparent diffusion coefficient of silica in the pore water of the clay (unit:  $\text{m}^2/\text{s}$ ),  $x$  the distance to the fixed glass/clay interface (where  $x = 0$ ),  $k$  the precipitation rate (unit: 1/s) and  $C_0$  the background silica concentration in the clay pore water (unit: g Si/ $\text{m}^3$ ). Glass dissolution is assumed to be congruent and caused by the dissolution of its main component, silica. Silica is supposed to dissolve according to a linear rate law:

$$J(x = 0, t) = \alpha \left( 1 - \frac{C(x = 0, t)}{\gamma} \right) = -\eta R D \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (4)$$

with  $J(x = 0, t)$  the flux of dissolving silica at the glass surface (which is chosen at the origin) (unit: g Si/ $\text{m}^2 \text{ s}$ ),  $\alpha$  the maximal silica dissolution rate (unit: g Si/ $\text{m}^2 \text{ s}$ ),  $\gamma$  a constant characterizing the saturation of glass silica in water (unit: g Si/ $\text{m}^3$ ),  $\eta$  the clay porosity accessible for diffusion and  $R$  the silica retardation factor in clay. The silica concentration in the clay is  $C_0$  ( $C(x > 0, t = 0) = C_0$ ). According to the linear rate law (4), the net silica dissolution rate  $J(x = 0, t)$  is the difference between two processes: silica dissolution at a constant rate  $\alpha$  and the adsorption of silica from the pore water of the clay on the glass alteration layer (with rate  $-\alpha C(x = 0, t)/\gamma$ ).

The solution of (3), (4) without precipitation ( $k = 0$ ) is (Pescatore, 1994)

$$C(x, t) = C_0 + \gamma \left( 1 - \frac{C_0}{\gamma} \right) F_{\infty}(x, t) \quad (5)$$

with

$$F_{\infty}(x, t) = \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) - \exp(hx + h^2 Dt) \text{erfc} \left( \frac{x}{2\sqrt{Dt}} + h\sqrt{Dt} \right); \quad h = \frac{\alpha}{\eta R D \gamma} \quad (6)$$

The function  $F_{\infty}(x, t)$  is dimensionless, while the unit of  $h$  is  $\text{m}^{-1}$ .

Expressions (5) and (6) are used for deriving expressions for the tracer silica bulk concentration  $C_{\text{b, Bq}}(x, t)$  (unit: Bq/ $\text{m}^3$ ), measured in our experiments. In case of no adsorption of silica from the clay pore water on the glass alteration layer, the tracer silica bulk concentration  $C_{\text{b, Bq}}(x, t)$  is the product of the excess silica bulk concentration  $\eta R(C(x, t) - C_0)$  (unit: g Si/ $\text{m}^3$ ) and the specific silica activity  $\rho_{\text{Bq, glass}}/f_{\text{Si}}$  (unit: Bq/g Si), where  $f_{\text{Si}} = 0.21$  (unit: g Si/g glass) is the silica weight fraction in the glass. Introducing the notations

$$\gamma_{\text{WL}}^* = \eta R \frac{\gamma}{f_{\text{Si}}} \left( 1 - \frac{C_0}{\gamma} \right); \quad \alpha_{\text{WL}} = \frac{\alpha}{f_{\text{Si}}} \left( 1 - \frac{C_0}{\gamma} \right) = \alpha_{\text{WL}} \left( 1 - \frac{C_0}{\gamma} \right) = h D \gamma_{\text{WL}}^* \quad (7)$$

with  $\gamma_{\text{WL}}^*$  (unit: g Si/ $\text{m}^3$ ) the excess glass bulk concentration needed to saturate the clay with respect to the glass silica saturation  $\gamma$ ,

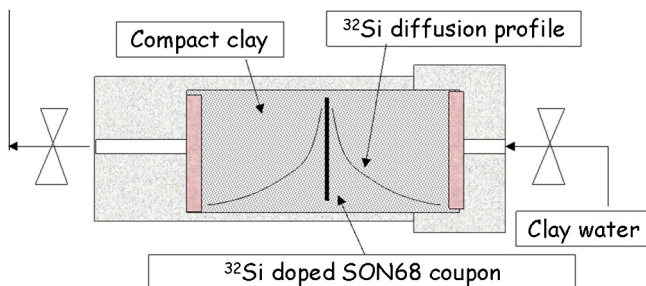


Fig. 1. Set-up of the combined glass-dissolution/silica diffusion experiment.

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