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The effect of clay on the dissolution of nuclear waste glass

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Abstract

In a nuclear waste repository, the waste glass can interact with metals, backfill materials (if present) and natural host rock. Of the various host rocks considered, clays are often reported to delay the onset of the apparent glass saturation, where the glass dissolution rate becomes very small. This effect is ascribed to the sorption of silica or other glass components on the clay. This can have two consequences: (1) the decrease of the silica concentration in solution increases the driving force for further dissolution of glass silica, and (2) the transfer of relatively insoluble glass components (mainly silica) from the glass surface to the clay makes the alteration layer less protective. In recent literature, the latter explanation has gained credibility. The impact of the environmental materials on the glass surface layers is however not well understood. Although the glass dissolution can initially be enhanced by clay, there are arguments to assume that it will decrease to very low values after a long time. Whether this will indeed be the case, depends on the fate of the released glass components in the clay. If they are sorbed on specific sites, it is likely that saturation of the clay will occur. If however the released glass components are removed by precipitation (growth of pre-existing or new secondary phases), saturation of the clay is less likely, and the process can continue until exhaustion of one of the system components. There are indications that the latter mechanism can occur for varying glass compositions in Boom Clay and FoCa clay. If sorption or precipitation prevents the formation of protective surface layers, the glass dissolution can in principle proceed at a high rate. High silica concentrations are assumed to decrease the dissolution rate (by a solution saturation effect or by the impact on the properties of the glass alteration layer). In glass corrosion tests at high clay concentrations, silica concentrations are, however, often higher than the silica concentrations in equilibrium with the glass surface ($C^*_{\mathrm{Si,saturation}}$) that are found in absence of clay. Nevertheless, the glass dissolution proceeds at relatively high rate. $C^*_{\mathrm{Si,saturation}}$ seems to be increased by the presence of clay. To understand this, more knowledge is necessary concerning the fate of the released silica and the silica speciation in solution.

1. Introduction

In a nuclear waste repository, the waste glass will be in contact with solids. Many experiments have demonstrated that this can have an important impact on the dissolution rate of the waste glass. In a normal evolution scenario, the solids will consist of the engineered barrier materials of the near field (metals and their corrosion products, and possibly backfill materials). Upon contact with the repository environment, the near field materials will gradually alter due to the contact with the host rock (the far field). In the case of high level waste glass and deep geological disposal, the alteration will be enhanced by the high temperature and pressure. Frequently considered host rocks are tuff stone, granite, salt, and clay. The host rock can influence the near field, e.g. by migration of reducing or complexing species from the far to the near field. For this reason, it is important that we study the impact of both near field materials and host rock on the glass dissolution rate. In this paper, we discuss the effect of clays as backfill material and host rock. We focus on Boom Clay, which is a potential host rock in Belgium, and FoCa clay, which is a backfill clay (a Ca-bentonite), studied in Belgium and in France.

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2. General

In any environment, three major processes limit directly the pristine glass alteration kinetics, i.e. hydrolysis of the glass network, recondensation of hydrolysed network bonds, and ion exchange [1]. These processes give rise to the formation of an *alteration layer*, which is (partially) depleted with regard to the more soluble glass components.

The glass dissolution rate tends to decrease with time in most conditions. Two important hypothetical mechanisms are assumed to be responsible for this:

(1) as the solution approaches silica saturation, the dissolution rate decreases; often it is assumed that this decrease follows the first-order rate equation

$$r = r_0(1 - C_{\mathrm{Si}}/C^*_{\mathrm{Si,saturation}}),$$

where r is the dissolution rate, r_0 is the forward rate, C_{Si} is the H_4SiO_4 concentration in the bulk solution (if transport processes are neglected) or at the interface between glass and alteration film, $C^*_{\mathrm{Si,saturation}}$ is the H_4SiO_4 concentration at saturation (in equilibrium with the glass surface [2]).

(2) in conditions close to saturation, the glass surface layer can become protective [3–5].

On the short term, the presence of solids will prevent the decrease of the glass dissolution rate, if these solids act as a pump, removing silica or other glass components from the solution. The effect of clays on the glass dissolution rate depends on their mineralogical composition. Certain clays offer sorption sites for leached glass components, thereby increasing the glass dissolution rate. Because of the removal of the principal glass formers (Si, Al) and of relatively insoluble glass components (Ca, Zr, rare earths...) from the glass surface, the release of soluble glass components (Na, B,...) is also increased. Moderate sorption of silica on clay has been demonstrated for at least two repository relevant clay types, i.e. Boom Clay [6] and FoCa clay [7]. A first glass dissolution model including silica sorption was proposed by Curti [8].

The increased dissolution rate in the presence of sorbing solids is explained by two effects: (1) the decrease of the silica concentration in solution increases the driving force for further dissolution of glass silica (according to the first-order rate law), and (2) the transfer of Si, Al etc.... from the glass surface to the clay makes the surface layer less protective.

Protective surface layers are only formed in certain conditions (high SA/V, presence of elements in the glass such as Si, Al, Zr, and Ca). Tests by Jegou [3] with glass *in absence of solids* have suggested that such surface layers can be very protective, by slowing down the diffusion of reactive species (water). This effect can cause a decrease of the initial dissolution rate by several orders of magnitude, whereas saturation of the solution can explain only a decrease by a factor 10. So, the protective properties of the alteration layer can explain very low dissolution rates that cannot be explained by saturation of the solution. There is evidence that protective layers can be formed also *in the presence of clay* [3]. Tests by Van Iseghem et al. with various nuclear waste glasses in the presence of Boom Clay [9] showed that in most cases, the formed layers were not protective. Glass coupons were treated to remove the alteration layer after 62 days, and then exposed again to the clay slurry. Protective alteration layers were observed only at 190°C for two glasses forming thick layers (SM527 and WG124), whereas for the glass with only a thin alteration layer (SON68), the layer was not protective. Tests at lower temperature (40°C and 90°C) did not reveal any protective effect from the alteration layers. Possibly, these layers were not yet dense enough after 62 days.

Whether the protective effect of a surface layer is due to its effect on silica diffusion is not clear. Grambow argues that the effects of a protective alteration layer can also be described by the inclusion of ion exchange reactions and water diffusion as parallel processes to matrix dissolution (following the first-order rate law) [10].

There are indications that for long contact times, the corrosion enhancing effect of clay is stopped, because it reaches a saturation, where it can no longer act as a pump. This will have a *direct effect* on the further dissolution of glass silica, assuming the first-order rate law is correct. *Indirectly*, the saturation of the solution with leached glass components will increase the retention of these components in the glass alteration layer, making this layer more protective. There is, however, still uncertainty about the importance of these two mechanisms. In the next sections, we will have a look at the most important problems involved. The first problem concerns the occurrence of very high silica concentrations in some tests in concentrated clay slurries; the second problem concerns the lack of knowledge about the impact of the environmental materials on the composition and properties of the glass surface layers. A third problem concerns the fate of the released glass constituents in the clay.

3. Anomalous Si concentration data

In some experiments at high clay concentrations, the silica concentration in solution (with or without glass) was higher than the silica concentration at saturation ($C^*_{\mathrm{Si,saturation}}$) for the concerned glass at lower clay concentrations or in absence of clay. This was the case for tests with SON68 in concentrated FoCa and Boom Clay mixtures, with concentrations after ultrafiltration of more than 300 mg silica per liter clay water at 90°C [11]. This is about 10 times higher than the concentration of silica in equilibrium with the glass surface ($C^{*}_{\mathrm{Si,saturation}}$), observed in tests at lower clay concentrations at similar pH (pH 7.5–8.5). Nevertheless, relatively high dissolution rates were observed. In the Boom Clay mixture e.g. the glass dissolution rate was about 0.1 g m^{-2} day^{-1} (this is 1/10th of the forward rate r_0). In an in situ test with glass SON68 in Boom Clay at 90°C, a constant dissolution rate of approximately the forward rate at pH 8 (this is 0.95 g m^{-2} day^{-1}) was observed for more than 7.5 years [12]. The exact silica concentration is not known for the latter tests, but for similar in situ tests at 80–90°C, silica concentrations were 20–34 mg/l at pH 6.3–8.3. This is approximately $C^{*}_{\mathrm{Si,saturation}}$, so we would expect a low glass dissolution rate. The nevertheless high rates seem to be in contradiction with both suggested corrosion decreasing mechanisms (saturation effect and protective layer effect).

Several hypotheses have been proposed to explain the high silica concentrations mentioned in [11]. The following hypotheses are most likely:

1. The observed silica concentrations would correspond to saturation with amorphous silica at pH <9°C and 90°C; this amorphous silica phase would be present in small amounts in the clay, and dissolve rapidly in the pore water. Such a poorly characterised phase has indeed been demonstrated for Boom Clay. This explanation is however in contradiction with the relatively high glass dissolution rates.
2. Complexation of dissolved silica by organic ligands; in this hypothesis, the concentration of H_4SiO_4 would be much lower than the total silica concentration.

The last hypothesis is consistent with the high dissolution rate. The available experimental evidence suggests, however, that the complexation of silica by humic acids is small [13,14]. So, the correctness of the hypothesis still has to be confirmed experimentally. If it turns out that the silica in solution is not complexed, but present mainly as H_4SiO_4, it should be concluded that the first-order rate law is not valid in the presence of aggressive clay media, unless we consider that $C^{*}_{\mathrm{Si,saturation}}$ is increased by the presence of clay.

One could also argue that the apparent contradiction between silica saturation and relatively high glass dissolution rates is temporary, because some time of surface restructuration is necessary before saturation effects become fully effective in controlling long-term release of soluble glass constituents [10]. In the case of the long experiments described in this paragraph, this explanation is, however, unlikely.

4. The impact of clay on the characteristics of the glass alteration layers

The physico-chemical characteristics of the alteration layer (for SON68, this is a gel-like material for low temperature and relatively short term), and the impact of the environmental materials on these characteristics, are not sufficiently known [7]. Following the mentioned hypotheses, the environmental materials could have a negative impact on the protective properties of the alteration layer, because of the extraction of protective elements. An increase of the clay/glass surface area ratio is known to increase the corrosion rate of e.g. the SON68 glass in Boom Clay or FoCa clay (see next section). It was however not demonstrated that the lower dissolution rate in the diluted clay slurry was due to a protective effect of the alteration layer. On the other hand, tests with SON68 in Boom Clay with relatively low clay/glass surface area ratios have shown a gradual decrease of the dissolution rate, over a constant intermediate dissolution rate, to a very low long-term dissolution rate after about 4 years. The low long-term dissolution rate was ascribed to the protective effect of the gel layer, which was found to be stable after 4.5 years [3].

Some high alumina glasses form thin alteration layers from which only the more soluble elements are leached, even in concentrated clay. Silica and alumina dissolve congruently at the interface between this layer and the solution, and show no depletion in the alteration layer. This is e.g. the case for glass SAN60 [12]. Such dense alteration layers are more likely to have protective properties. In the case of SAN60, diffusion through this layer is probably rate determining.

In the assumption that the alteration layer formed in a clay environment can be protective, it is not clear which part of the glass layer is protective: it could be the main depletion zone (characterised by the depletion of network modifiers and decrease of network formers; for SON68, this is called a gel; for the high-alumina glasses, this layer is thin or not existing), the gradient layer (with steep concentration gradients), or the diffusion layer (the most inner layer, next to the pristine glass).

5. Mechanisms of sorption onto clay

If the sorption of glass constituents on the clay is site specific, it is likely that saturation of the clay will occur. If, however, the released glass components are removed by growth of pre-existing or secondary phases, saturation of the clay is less likely, and the process can continue until exhaustion of one of the system components [1]. In principle, both mechanisms may occur, depending on the concentration of the glass components in the groundwater. This is illustrated by Fig. 1. Initially the solution concentration of e.g. silica increases with time, by dissolution from the glass surface. At this stage, sorption is linear, with a specific distribution coefficient K_d between solution and solid ($K_d = C_s/C_l$, where C_s is the concentration of the sorbed species on the solid, and

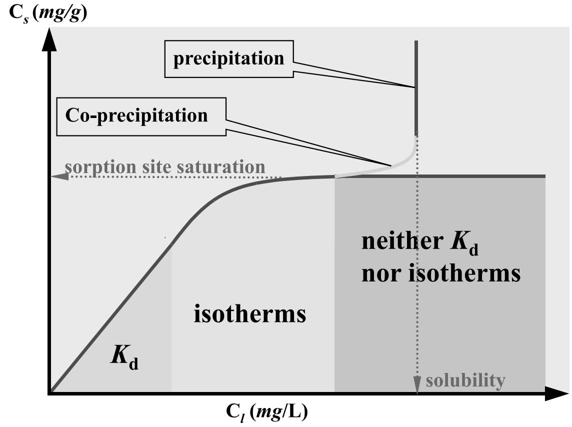

Fig. 1. General evolution of the concentration of species sorbed on the solid phase (C_s) as a function of the concentration of species dissolved in the liquid phase (C_l) (based on [15]).

C_l is the concentration of the sorbed species in the liquid). At further reaction progress, the total amount of released silica will approach the amount of available sorption sites, and the sorption curve will level off, following a specific isotherm. At still further reaction progress, all sorption sites will be occupied, and precipitation of silica-containing phases will occur. In the rest of the text, we will use the general term 'silica immobilisation', when we do not want to make the distinction between sorption and precipitation.

5.1. Evidence for silica sorption on Boom Clay and FoCa clay

Tests with ^{32}Si in compact Boom Clay at 25°C, in the absence of glass, and in conditions of silica saturation, suggest that silica is indeed sorbed by Boom Clay [6]. The exact sorption mechanism and the sorption kinetics were not identified. Two hypothetical mechanisms were mentioned for conditions close to silica saturation: first, dissolved silica could be sorbed by the gibbsite layers, accessible on the basal plane of kaolinite (1:1) and on the frayed edges of (2:1) clay minerals (illite and smectite); second, positively charged complexes between aluminum and silicate, such as protoimogolite ($SiO_2Al_2(OH)_4$-$(H_2O)_6^{2+}$) could be formed in solution [16–19], and could be sorbed onto the negatively charged clay minerals. The total sorption capacity of Boom Clay for silica is not well known (see Section 5.3). Tests with FoCa clay suggested a sorption process with a capacity of about 3 mg Si per gram of clay [7].

Modelling exercises often describe the sorption of silica by the distribution coefficient K_d. For instance, the dissolution of SON68 at 90°C in relatively concentrated clay mixtures (1540 g FoCa clay or Boom Clay clay per liter water) has been simulated with such a model [11]. These tests, performed at 90°C, yielded similar values for the silica migration parameters as the ^{32}Si experiments in compact Boom Clay at 25°C [6]. A range 0.002–0.05 $m^3\ kg^{-1}$ was defined for the sorption of Si on Boom Clay and FoCa clay. It should be clear, however, that the description of Si sorption by a K_d is only valid for experiments where the amount of released silica is small compared with the number of sorption sites.

5.2. Evidence for silica precipitation in Boom Clay

At clay saturation, the silica that is further released by the waste glass can in principle be removed by growth of pre-existing or secondary phases, with possible recrystallisation into new clays [12,20–22]. Geochemical modelling for glass SON68 suggested that growth of pre-existing phases is more likely than the formation of new secondary phases in Boom Clay [23]. It is however very difficult to distinguish experimentally sorption or incorporation in pre-existing minerals, from new precipitated phases. Although secondary phases are often found at high temperature, they have been observed in Boom Clay at $\leqslant$ 90°C only in few experiments [12,24]. The reason for this may be that in these tests, the amount of silica that is leached within a few years testing is too low. As a result, the sorption capacity of the clay may not be reached, or the formed secondary phases may be too small. It is however expected that secondary phases will finally form, even at relatively low temperature [25]. Calculations of total immobilised silica on the Boom Clay suggest that this is indeed the case (see Section 5.3).

5.3. Calculation of immobilised silica in Boom Clay and FoCa clay

As explained before, the term 'immobilisation' is used here as a general term for sorption and/or precipitation. The sorption capacity for silica has never been determined explicitly in Boom Clay. For specific glass leach tests, one can, however, calculate the total amount of silica that is immobilised by the clay, based on the mass losses of the glass samples. This has been done for a series of leach tests at 90°C, performed at SCK·CEN, i.e. tests in mixtures of 10, 500 and 2000 g of (wet) Boom Clay per liter clay water, and tests of 1000 g of (dry) FoCa Clay per liter clay water, for $SA/V = 100\ m^{-1}$. For the calculations, we assumed that 75% of the silica was retained in the gel in the case of the mixture of 10 g clay per liter clay water. For the more concentrated clay mixtures, congruent dissolution was assumed. These assumptions were based on SIMS profiles measured at 90°C in the mixtures of 10 and 500 g Boom Clay per liter clay water. The tests have been performed with various nuclear waste glasses, including the SON68 glass. They were reported in [9] and [11].

In the tests with the mixture of 500 g of Boom Clay per liter clay water, the glass dissolution rate shows a clear decrease with time up to about 1000 days. This is illustrated for glass SON68 in Fig. 2. A decrease of the dissolution rate to values smaller than 0.1 g m^{-2} day^{-1} occurs when 3–7 mg of silica is immobilised per gram of clay. Depending on the glass, this happens after 180–540 days. The immobilisation of silica later increases to 5–10 mg/g clay, depending on the glass type. In the more diluted clay medium (10 g Boom Clay per liter clay water), the decrease of the dissolution rate to values lower than 0.1 g m^{-2} day^{-1} occurs already between 28 and 80 days, when about 2 mg of silica should be immobilised per gram of clay.

The fact that the dissolution rate shows a clear decrease in both clay media when 2–7 mg of silica is immobilised per gram of clay, can indicate that the sorption capacity for silica in Boom Clay is in this range. In principle, the number of sorption sites will depend on the sorption mechanism. The total cation exchange capacity (CEC) for Boom Clay is in the range 20–30 meq/100 g, this would be 5.6–8.4 mg Si per gram of clay [26]. If silica is sorbed through the formation of positively charged complexes, the total CEC may be a good approximation for the number of sorption sites for silica. This value fits with the sorption capacity suggested by the leach tests in the concentrated clay medium (about 7 mg/g), but is higher than the sorption capacity calculated for the diluted clay medium (about 2 mg/g). If silica is sorbed by surface complexation of a negatively charged or neutral species, only 10–20% of the CEC should be active sorption sites [27], this is 2–6 meq/100 g, so 0.6–1.7 mg silica per gram of clay. In that case, saturation of the clay would occur already within 3–27 days (diluted clay medium) or within 27 days (concentrated clay medium), so the decrease of the glass dissolution rate would occur later than the saturation of the clay, especially in the concentrated clay medium.

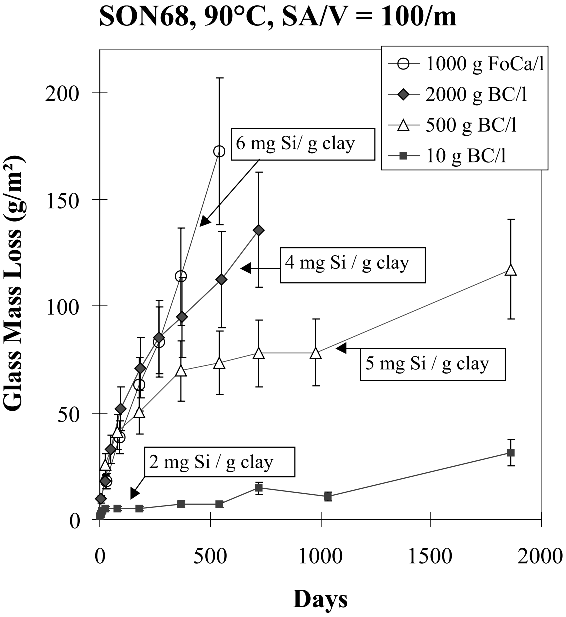

Fig. 2. Mass losses for glass SON68 for tests at 90°C in mixtures of respectively 1000 g FoCa clay, and 2000, 500, and 10 g of Boom Clay (BC) per liter clay water (SA/V = 100 m^{-1}) with indication of the estimated amount of immobilised silica per gram clay. The 95% confidence interval on the mass losses is estimated at 20%. Data from [9,11].

In some cases, the dissolution rate increases after 1000 days. A slight increase is observed for SON68 in the mixture of 500 g Boom Clay per liter clay water (the mass loss after 1860 days corresponds to a silica immobilisation of 7 mg/g clay) and for the mixture of 10 g Boom Clay per liter clay water (immobilisation of about 30 mg Si per gram of clay after 1860 days, assuming 75 % retention in the gel). The corrosion resumption was more obvious for the high alumina glass SM527, where it lead to the (calculated) immobilisation of at least 22 mg of silica per gram of clay after 1860 days in the mixture of 500 g of Boom Clay per liter clay water. The corresponding dissolution rate was 0.9 g m^{-2} day^{-1}. In the mixture of 10 g Boom Clay per liter clay water, the amount of immobilised silica was still much larger after 1860 days, when the glass coupons were almost completely disintegrated (see Fig. 3). Such corrosion resumption may be caused by the precipitation of silica, after the saturation of the sorption sites on the clay, especially in the case of the high alumina glasses, which can form zeolites as secondary phases [28]. The data suggest that a similar mechanism cannot be excluded in the case of glass SON68.

For the tests at 90°C at higher Boom Clay concentration (2000 g of wet clay per liter clay water, SA/V = 100 m^{-1}), about 4 mg of silica was immobilised per gram of clay after 2 years (Fig. 2). This corresponds to a relatively high dissolution rate of approximately 0.1 g m^{-2} day^{-1} for glass SON68 between 1 and 2 years, which suggests that the sorption sites on the clay are not yet saturated in these conditions. In tests in the same medium with glasses SON68 and SM539 at SA/V = 2500 m^{-1}, the normalised boron release after 2 years corresponds to respectively 8–11 mg Si immobilised per gram clay, assuming congruent dissolution. The high Si immobilisation suggests that even in this concentrated clay medium, precipitation of leached silica can have occurred. The corrosion rate was very low in this case, though. In the medium with 2000 g of Boom Clay per liter clay water at 90°C, the silica concentrations were very high (see Section 3). It is not certain that the silica sorption processes that take place at low temperature, are the same in these conditions, where the clay shows a net release of silica with time.

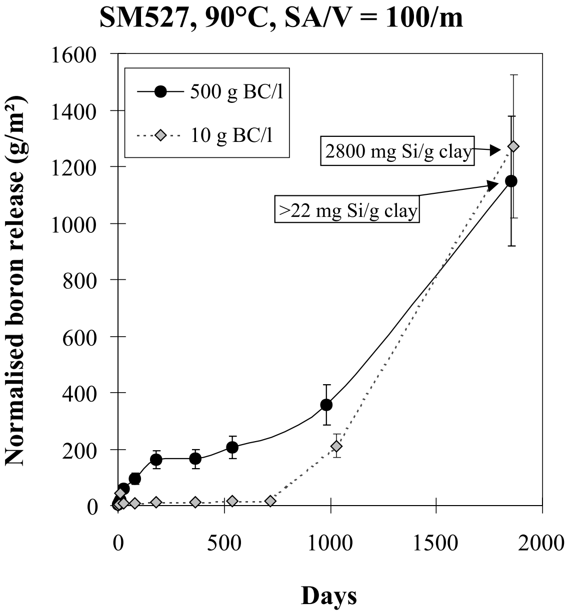

Fig. 3. Normalised boron release for the aluminoborosilicate glass SM527 for tests at 90°C in mixtures of respectively 10 and 500 g of Boom Clay (BC) per liter clay water ($SA/V = 100\ m^{-1}$), with indication of the estimated amount of immobilised silica per gram clay. The 95% confidence interval on the normalised boron release is estimated at 20%. Data from [9].

For the tests at 90°C with 1000 g FoCa clay per liter clay water at 100 m^{-1}, 6–7 mg silica was immobilised per gram clay after 540 days for glasses SON68 and SM539, assuming congruent dissolution. Although the clay saturation limit of 3 g, mentioned in literature [7], was exceeded (or at least approached, if silica retention in the alteration layer was important), the dissolution rate continues at the high rate of 0.3–0.5 g m^{-2} day^{-1} (Fig. 2). Saturation of the sorption sites apparently did not decrease the dissolution rate. This suggests again that in this case, precipitation of leached silica occurs, especially for the SM539 glass, where congruent dissolution is more likely, but possibly also for SON68.

5.4. Impact of precipitation on the glass dissolution rate

On a geological timescale, the sorption sites on the clay in the immediate surroundings of the glass will be saturated. The silica that is further released by the waste glass can diffuse to the clay at larger distance (and get absorbed), and/or it can be removed by growth of preexisting or secondary phases. Whether diffusion or precipitation is dominant, will depend on the precipitation kinetics of the growing phases (for parallel processes, the fastest one is rate determining). If the precipitation is fast enough, diffusion of silica through the clay can be excluded as rate determining process for glass corrosion on the long term, because the silica will precipitate before it can diffuse. If the precipitation is slow (i.e. oversaturation), silica will diffuse easier to the clay at larger distance. On geological timescales, silica precipitation (kinetics) may, however, set again the lower boundary for the dissolution rate. If a protective layer is formed, the overall dissolution rate should then be low anyway.

Secondary phase formation can, however, not only prevent the decrease of the glass dissolution rate, it can also cause an increase of this rate. This has been observed for aluminoborosilicate glasses in pure solutions [3,29,30], but there are indications that it can also occur in clay media (see results for SM527 in Section 5.3). It seems logical that such corrosion increase will take place, if the precipitation occurs before the glass has had the chance to form a protective alteration layer. The results for glass SM527 in Fig. 3, with low intermediate dissolution rates (0.01 g m^{-2} day^{-1} in the diluted clay medium) and a very high rate after more than 1000 days, suggest however that it can also cause the destruction of a possibly protective alteration layer, especially for high-alumina glasses (these glasses tend to form thin surface layers of typically 0.1–0.2 μm, which may nevertheless be protective). There is less evidence for such evolution in the case of glass SON68, but there are some indications that it is possible also for glasses with relatively low alumina content (see Fig. 2 for SON68 and a corrosion increase observed for glass SM513 in situ [12]). The formation of a protective layer can therefore not guarantee that the dissolution rate remains low for larger reaction progress. It is not clear whether the increase of the glass dissolution rate in the case of secondary phase formation is due to the effect on the silica concentration in solution, following the first-order rate law. If the precipitation kinetics are slow, it could also be the precipitation *rate* that determines the overall dissolution rate.

5.5. Influence of elements, other than silica

Apart from silica, other glass components can be sorbed by the clay, or precipitate. This will have consequences for the glass dissolution rate, especially when elements are concerned that can make the alteration layer protective, such as alumina or calcium. In natural Boom Clay, these elements are assumed to be controlled by the presence of kaolinite and calcite, respectively. Geochemical calculations suggest that these phases will also determine the Al and Ca concentration in the presence of glass SON68 [23]. The alumina concentration in the glass alteration layers is in general close to the pristine glass concentration for tests in Boom Clay. In other words, alumina is released only at the interface between alteration layer and leachate. The enrichment of

FoCa clay with leached Al causes the transformation of the various clay fractions towards clays with a higher Al content [21]. This was not yet observed experimentally for Boom Clay.

6. Conclusions

Boom Clay and FoCa clay initially delay the onset of glass 'saturation'. Many tests show however a gradual decrease of the dissolution rate, to sometimes very low long-term rates. This decrease is linked to the saturation of the interstitial solution and the clay with mainly silica. The silica saturation concentration $C^*_{\mathrm{Si,saturation}}$ seems to increase by the presence of clay. The low long-term rates are further explained by the formation of a protective alteration layer that limits silica diffusion, or, alternatively, by ion exchange or water diffusion. For some experiments, the dissolution rate remains high, in spite of likely clay saturation. In this case, precipitation probably occurs, after saturation of the sorption sites on the clay. The continuous transfer of glass constituents to these phases can in principle make the formation of a protective alteration layer impossible, but this has not been demonstrated explicitly. For high alumina glasses, destruction of a possibly protective layer even seems to occur. In these cases, the precipitation of elements such as Al and Si probably determines the long-term dissolution rate, which can be high.

For future research, some questions should be looked at in more detail. How can we explain the often high glass dissolution rates in clay slurries with high silica concentrations? Is the low long-term dissolution rate due to diffusion of silica or of water through a protective alteration layer? Can a protective alteration layer be formed in concentrated clay media at very high clay/glass surface ratios, as expected in situ? Do package components exist that can be added to have a beneficial effect on a protective alteration layer? Is it possible that a protective layer is destroyed by its transformation in more stable precipitates? In this regard, the fate of the released glass components, and their sorption and precipitation kinetics should be investigated further.

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