

Short-term corrosion of HLW glass in aqueous solutions enriched with various metal cations

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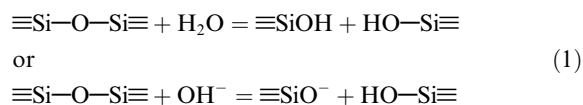
Abstract

Static short-term corrosion tests were performed with the simulated HLW glass GP WAK1 at 80 °C and constant pH in deionized water, in water enriched with a single element (Si, Al, Nd and Mg) and enriched with two elements (Si + Al, Si + Nd, Si + Mg). The objective of the experiments was to study the effect of Si and other dissolved species on the initial high and on the low final rate under Si-saturated conditions. In pure water and Si-enriched water the release rates of B (Li) are nearly identical despite the different Si concentration in the solution. Close to saturation, the dissolution rates decrease sharply due to condensation reactions of the silanol groups forming a highly protective surface layer. In solutions enriched with Al or Nd, the initial B release rate is similar to pure water, but the release of Si is much lower. Therefore, Si saturation and the low final rate are attained after longer times. In the solutions enriched with Si and an additional element, the initial high B release rate drops down already after few hours to the low final rate as saturation conditions are attained much earlier. In all solutions studied, the dissolution rate slows down after Si saturation to the same low constant rate depending on the solution pH. The impact of the results on the corrosion mechanism and long-term behaviour of HLW glasses is discussed.

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1. Introduction

Contact of borosilicate nuclear waste glass by aqueous solutions results in the diffusion of water into the glass surface and ion exchange with the highly mobile modifier ions. A reaction zone is created within which a hydration and H₃O⁺/alkali inter-diffusion profile form. The diffusion controlled ion exchange slows down rapidly and the dissolution of the glass by hydrolysis of the silicate network becomes the dominant phenomenon:



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The reverse reactions are referred to as condensation reactions. In a closed system the solution becomes saturated with respect to H₄SiO₄ within a few days at temperatures of 80 °C and high S/V ratios. Below pH 9 the Si saturation concentration is independent of the pH. When silica approaches its solubility limits, condensation reactions of the silanol groups take place forming a largely amorphous alteration layer (gel layer). Subsequently, the initial high dissolution rate slows down by several orders of magnitude.

Under static conditions the dissolution of glass in water is congruent for soluble elements like Li, B, Ca, etc. In the corrosion experiments described below, the release of Si has been found lower by about a factor of 2–3 from the beginning of corrosion than that calculated based on the release of B or Li. The release of less soluble elements, e.g. Al, Fe, RE (rare earths), was even lower at pH values above 4. Grambow [1,2] has developed a dissolution/precipitation model (reaction path model) for glass corrosion, where it is assumed that the

glass dissolves by a first order dissolution rate law ($R = R_0(1 - a_{\text{Si}}/a_{\text{Si}}^*)$) with R = dissolution rate, R_0 = forward corrosion rate far from Si saturation, $a_{\text{Si}} = \text{H}_4\text{SiO}_4$ activity, and $a_{\text{Si}}^* = \text{H}_4\text{SiO}_4$ activity at saturation). The activity of H_4SiO_4 in the solution is the key parameter which is assumed to limit the dissolution rate. From the first order law, it is expected that the glass dissolution rate linearly decreases with rising silica activity. Many corrosion experiments [3–5] have shown, however, that the corrosion rate decreases by several orders of magnitude from the initial rate, but does not attain zero even under silica-saturated conditions. Recently, Grambow and Müller [6] have anew discussed in detail the role of the first order rate law and of surface layers in glass dissolution. Vernaz et al. [7] could show, that there is no one-to-one relation between the H_4SiO_4 activity and the dissolution kinetics. Further, if a pristine glass specimen is placed in a ‘saturated’ leachate, the glass is altered at its initial high rate like in pure water [7,8]. These results are interpreted that the ‘saturation’ concentration (C^*) is not an intrinsic glass (or gel) solubility limit related to the glass composition. The steady-state silica concentration is the result of the quantity of glass that has to be dissolved to form a protective gel layer. C^* is not interpreted as a glass solubility limit, instead it is a dynamic equilibrium arising when the alteration virtually ceases due to the formation of a protective gel layer. The evolution of the protective gel is explained by an increase of the re-condensed silica fraction with the dissolved silica concentration in solution. With increasing re-condensed silica in the gel, its density increases and the porosity diminishes. The hydrolysed silica diffusion coefficient also diminishes and finally, the gel evolved into a barrier against alteration. Silica attains a dynamic equilibrium between the hydrolysed and re-condensed silica fraction. C^* was found to be highly dependent on the glass surface area to solution volume (S/V) ratio [8]. This S/V -dependence supports the hypothesis that C^* is not a true solubility limit or thermodynamic equilibrium concentration. However, many results of leaching experiments performed at INE with the HLW glass GP WAK1 in water and brines [4,9] and even with the glass R7T7 contradict clearly an increase of C^* with the S/V ratio. Therefore, some results are also presented in this paper which demonstrate that C^* is independent of the S/V ratio for a given glass composition. The consequences on the glass alteration mechanism are discussed.

Results of dynamic leach tests described by Vernaz et al. [10] revealed that other species than Si control the dissolution kinetics of HLW glasses. The results demonstrate the kinetically limiting character of Al, but do not indicate whether it is the only element besides Si involved in controlling the rate. Other dissolved glass constituents like Zr, Al, Fe, RE, Mg and Ca and elements released from minerals existent in potential salt, clay or granite repositories and in backfill materials

could also have an influence on the saturation effect. To reveal more clearly the effect of other dissolved species on the dissolution of HLW glasses, static short-term corrosion tests with the glass GP WAK1 were performed in water enriched with Si, Al, Nd and Mg under constant pH conditions.

2. Experimental

The static dissolution experiments with the simulated HLW glass GP WAK1 (the composition of this glass, quite similar to the well-known French glass R7T7, is given in [11]) were performed at 80 °C in deionized water and in water enriched each with a single element, Si (80 mg/l), Al (25 mg/l), Nd (100 mg/l) and Mg (100 mg/l) as well as in water enriched with two elements, Si + Al, Si + Nd and Si + Mg (each element had the same concentration as before). The various elements were added in form of chlorides and Na_2SiO_3 . The prepared solutions at pH 4.5 and 8.5 were stored several hours before glass powder was added. Small amounts of precipitates were observed in the solutions containing Si and an additional element. The Si concentrations in these solutions lowered up to about 75 g/L, those of Al to 20 mg/l, Nd to 95 mg/l, whereas the Mg concentration remained near 100 mg/l. To adjust an S/V ratio of 1000 m^{-1} , 2.5 g glass powder of the grain size 200–280 μm were exposed to 50 ml water. During the short-term tests of each 30 days, the pH value in the solutions was controlled at 4.5–5 and in a second series at 8.5–9 by addition of HCl acid. The pH of the solution was measured with a pH electrode (Ross system). The experiments were performed under ambient air conditions. Temperature was controlled to ± 1 °C using a water bath. The release of Li, B, Si and the concentrations of the various elements added to the solutions were monitored by analyses of the leach solution after 1, 5 and 9 h and after 1, 2, 7, 14 and 30 days by ICP-AES analyses.

3. Results and discussion

3.1. Effect of S/V ratio on silica saturation

To demonstrate that the Si saturation concentration is independent of the S/V ratio, Fig. 1 shows the concentration of Si in dependence on the product $t \cdot S/V$ at constant pH values between 2 and 10 from additional leach tests with the glass GP WAK1 at 80 °C in pure water over 30 and 100 days. The S/V ratios used were 10 and 1000 m^{-1} . The Si concentration at pH 2 up to 8 are approximately constant between 100 and 160 mg/l over the total range of $t \cdot S/V$. Therefore, the saturation concentration of Si is independent of the S/V ratio. At pH 9, C^* is not yet attained at the lowest $t \cdot S/V$ value of

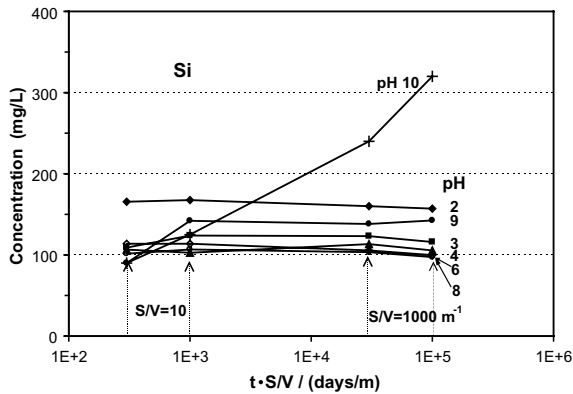


Fig. 1. Concentration of Si as a function of the product $t \cdot S/V$ at various pH values in water at 80 °C.

300 days m^{-1} (30 days at $S/V = 10 m^{-1}$), but after 1000 days m^{-1} , the silica saturation is attained as well and the concentration remains constant. Up to pH 9, the dissolved species is unionized orthosilicic acid [12]. At pH 10, it appears that the Si concentration may depend on the S/V ratio. However, the strong increase of the Si concentration at the highest $t \cdot S/V$ value of 10^5 days m^{-1} is related to the hydrolysis of the dissolved orthosilicic acid. The glass dissolution rate at pH 10 was not high enough to attain the high solubility limit of Si at the lower S/V ratio as well as after 30 days at the higher S/V ratio under these conditions. The independence of C^* from the S/V ratio was confirmed as well by results of long-term corrosion tests with the simulated HLW glass R7T7 in brines at S/V ratios of 10 up to 21 000 m^{-1} and temperatures from 110 to 190 °C performed at INE. At S/V ratios of 2100 and 21 000 m^{-1} the silica concentrations were even lower than at the lowest S/V ratio of 10 m^{-1} . The lower Si concentration may be explained by the higher amount of dissolved glass constituents which favour the formation of secondary silicate phases. A steady-state between glass hydration and secondary phase formation could be established which controls the silica concentration [3].

3.2. Results from the short-term tests in pure water and in silica-enriched water

The time-dependent release of B and Si at 80 °C during corrosion of glass GP WAK1 in pure and in Si-enriched water (80 mg/l Si) at pH 4.5 shows Fig. 2. One of the benefits of using B is that B is never contained in secondary phases. In both solutions the release of B is nearly identical up to 24 h despite the different silica concentration in the solutions. After 24 h the B release in pure water proceeds with the same high rate. Contrary to pure water, the release rate of B in the Si-enriched solution diminishes sharply and then remains constant.

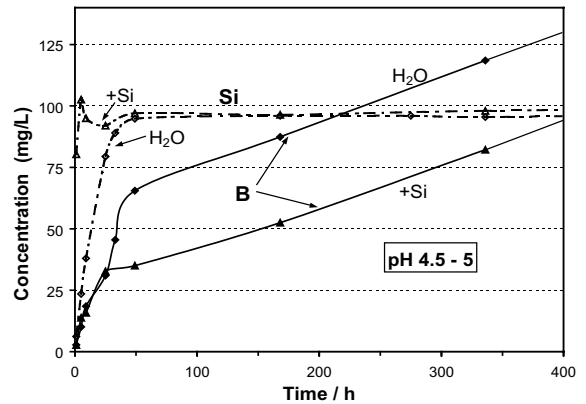


Fig. 2. Evolution of the concentration of B and Si during dissolution of glass GP WAK1 in pure and Si-enriched water at 80 °C and constant pH.

In pure water the low constant rate is attained not until 50 h. As shown by the run of the Si concentrations, Si has attained in both solutions a constant ‘saturation’ concentration of about 100 mg/l when the reaction rates drop down. The observed B release in the two solutions implies that the dissolution rate is independent of the Si concentration in the solution during the early stage of glass corrosion. The initial high rate proceeds as long as the Si saturation concentration has not been attained. Near saturation, the dissolution rate drops down due to condensation reactions of the silanol groups in the gel, which make the gel layer more dense and protective against B and alkali leaching [13]. Studies of the gel layer on glass samples leached in water at various pH conditions with X-ray photoelectron spectroscopy (XPS) were conducted by Schild et al. [14]. The development of the protective layer at the glass/solution interface forms a diffusion barrier that limits exchange phenomena. Subsequently, the glass dissolves with low constant rate up to about 30 days. A similar release behaviour of B and Si was found at pH 8.5.

3.3. Short-term tests in Al-enriched water

Fig. 3 shows the release curves of B and Si in Al-enriched water at pH 4.5–5 and, for comparison, in pure water as well. In the Al-enriched water, the B concentration follows quite closely to the release in pure water up to 50 h. Subsequently, in the Al-enriched water the B concentration continues to increase with a high rate, in contrast to pure water where the leach rate decreases as Si has attained saturation concentration. After about 170 h, the B leach rate in the Al-enriched solution attains the same low constant rate like in pure water as shown by the parallel run of the B concentrations.

The different runs of the corrosion in the two solutions can be explained by the different course of silica

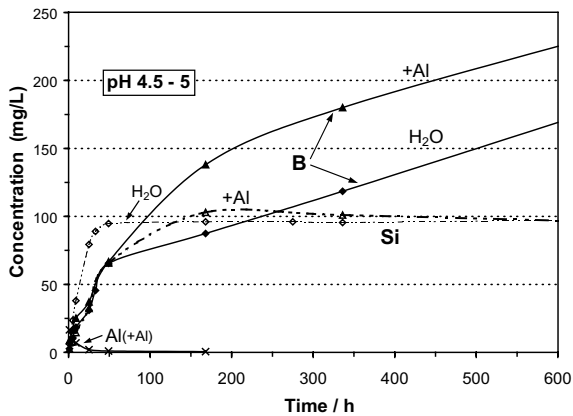


Fig. 3. Evolution of the concentration of B and Si during dissolution of glass GP WAK1 in pure and Al-enriched water at 80 °C and constant pH.

concentration and, above all, the specific time of silica saturation. In Al-enriched water the increase of the Si concentration with time is much slower than in pure water but the B release is rather similar in both solutions up to 24 h. As the initial high release rate nearly persists until Si saturation is attained (after about 170 h compared to 50 h in pure water), the amount of B (or glass) dissolved in Al-enriched water is clearly higher than in pure water. The slower Si release in the Al-enriched solution may be caused by sorption of Al ions in the gel layer. The Al concentration in this solution (also shown in the diagram) decreases strongly within short time.

3.4. Short-term tests in Nd + Si-enriched water

Fig. 4 shows the release of B and Si in the solution enriched with Nd and Si compared to pure water. The initial high B release rate drops down already after 9 h in the enriched solution to a similar low rate like in pure water at Si saturation. The Si concentration of initially about 75 mg/l decreases due to precipitation of Nd-silicates, presumably, as the solution becomes over-saturated with respect to such silicate phases in the early stage of glass corrosion. Afterwards, the Si concentration remains nearly constant over several days and then approximates slowly the saturation concentration found in pure water. Even if the Si concentrations in this solution are far below the saturation concentration in pure water over longer times, a low B dissolution rate is attained already after 9 h. Obviously, by precipitation or sorption of Nd-silicate phases, a dense and protective surface layer has formed within short time. It can be concluded that the interim low Si concentration also represents a 'saturation' concentration with respect to a Nd-silicate layer on the glass surface. After the Nd concentration has diminished to a low constant value

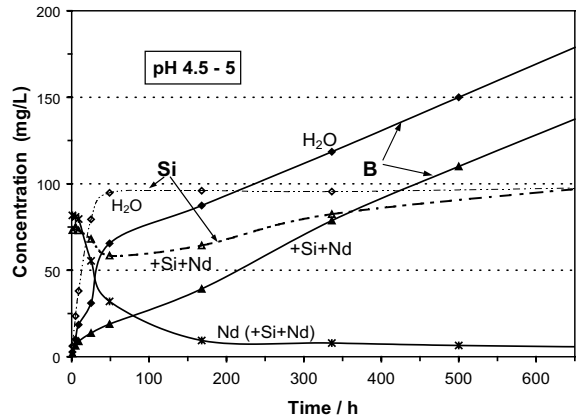


Fig. 4. Evolution of the concentration of B and Si during dissolution of glass GP WAK1 in pure and Nd + Si-enriched water at 80 °C and constant pH.

after 170 h, Si approximates slowly the saturation concentration found in pure water.

3.5. Results from the short-term tests in the other enriched solutions

In the Mg- and Nd-enriched solutions, the B release rates are rather similar and slightly lower, respectively, than in pure water. In both solutions, the release rates of Si are clearly lower like in the Al-enriched solution (Fig. 3). Consequently, Si saturation is attained after longer times in the two solutions, and the amounts of glass dissolved at Si saturation are higher than in pure water. In the solutions enriched with Al + Si, the run of the B and Si concentrations is comparable to their run in the Nd + Si enriched solution (Fig. 4). The B concentration runs clearly below the concentration in pure water and the initial Si concentration of about 75 mg/l decreases due to precipitation/sorption of Al-silicate phases which form as well a protective surface layer. In the Mg + Si-enriched solution, the run of the B and Si concentration is rather similar to the solution enriched only with Si (Fig. 2). Precipitation of Mg-silicates could not be detected. Therefore, the Si concentration of initially 80 mg/l increases strongly by glass dissolution and attains the saturation concentration within short time. The glass dissolution rates in all solutions studied at pH 4.5 were nearly identical after Si saturation and remained constant up to about 30 days. At pH 8.5 the dissolution rates were constant as well after Si saturation but clearly lower than at pH 4.5.

3.6. Effect of pH and longer reaction times on the corrosion rate

Further corrosion tests over longer times (up to 100 days) at various constant pH values between 2 and 10

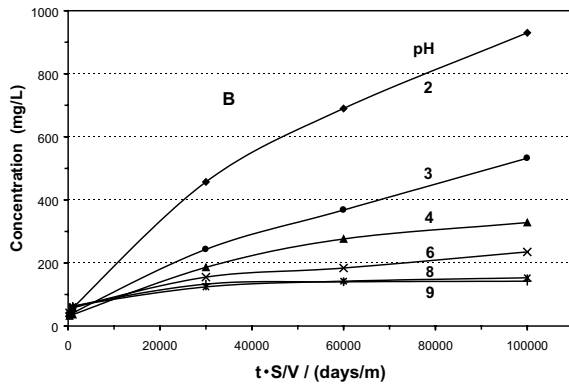


Fig. 5. Evolution of the concentration of B as a function of $t \cdot S/V$ during dissolution of glass GP WAK1 at pH values between 2 and 9.

revealed that the glass dissolution rate declines after 30 days as shown by the B release in Fig. 5. The release curves also show that the dissolution rates diminish with increasing pH value in the solution. The decrease of the dissolution rate with rising pH is explained by Grambow and Müller [6] by a diffusion mechanism of water into the glass network and assuming decreasing diffusion coefficients with increasing pH. Mathematical modelling of glass corrosion by Lemmens et al. [13] also confirmed that high pH values lead to lower diffusion coefficients for Si and for other elements as well. The decrease of the diffusion coefficients may be caused also by variation of the elemental composition of the gel in dependence of pH as less soluble elements, and at high pH even Mg and Ca are increasingly retained. The decrease of the initial constant dissolution rate after 30 days (Fig. 5) can be explained: (1) the gel layer may become more dense and stable by proceeding ageing, (2) the gel layer thickness increases with reaction time, and (3) the concentrations of elements released from the glass, like RE, U and alkaline earths, increase in the leachate. These cations may intrude into the gel layer network and are sorbed onto ionizable functional groups of the gel forming a dense, less porous surface layer [15].

4. Impact of the results on glass alteration mechanisms

The alteration kinetics of HLW glasses in aqueous solutions is initially controlled by ion-exchange between network modifiers and protons in the solution and hydrolysis and dissolution of the silicate network. The initial high glass dissolution rate, which depends mainly on the glass composition, temperature and pH, persists until the Si concentration approximates the saturation concentration C^* . Obviously, the alteration layer formed during this 'under-saturated' period is highly porous and has no protective properties [8]. The Si concentration

has no effect on the dissolution rate in the *static* corrosion tests until silica saturation as expected from the first order rate law. This finding is in clear contrast to results of *dynamic* leach tests reported in literature [16], which show a strong effect of the silicic acid activity on the B release rate already at low Si concentrations. If silica attains saturation (about 100 mg/l Si at 80 °C in pure water below $\text{pH} \leq 9$), the dissolution rate drops down by several orders of magnitude due to condensation reactions of the silanol groups in the alteration layer and/or precipitation and sorption of hydrolysed species. A dense, highly protective silicate-rich layer develops on the glass surface forming a diffusion barrier that limits the diffusion of water into the gel [6]. C^* was found independent of the S/V ratio and, therefore, represents a thermodynamic equilibrium concentration. After saturation the glass dissolves with a low constant rate, depending on the pH value. Enriched metal ions in the solutions, like Mg, Al or RE, have no or only a minor impact on the B (or Li) release, but the dissolution rate of Si is clearly lower in these solutions than in pure water. Therefore, silica saturation is attained after much longer times. As the initial high B release rate proceeds until Si attains saturation, the B concentrations are clearly higher in the solutions enriched with metal cations. The slower Si dissolution can be explained by sorption of the added metal ions onto the gel layer of the glass.

In solutions enriched with Si and additional metal ions, precipitation of metal silicates can take place and the initial Si and metal concentrations decrease. Even if the Si concentration in such solutions is far below the saturation concentration C^* in pure water, a low constant dissolution rate is attained. It can be concluded that the lower Si concentration after precipitation also represents a saturation concentration with respect to a glass surface layer developed by precipitation or sorption of Me-silicate phases. After the concentration of the metal ions has strongly diminished with proceeding time (e.g. by sorption), the Si concentration approximates slowly the saturation concentration C^* found in pure water. In all solutions studied, the dissolution rate drops down at Si saturation to the same low constant rate depending on the solution pH. With rising pH value, the diffusion coefficient of water into the glass surface decreases [6] and correspondingly the constant dissolution rate. By ageing of the gel and retention of less soluble elements, the barrier effect of the gel layer increases and the initial constant release rate begins slowly to diminish with proceeding time.

5. Summary and conclusions

If HLW glasses come in contact with aqueous solutions under static conditions, the initial high dissolution

rate is nearly independent of the Si concentration in the solution. From that moment Si attains the saturation concentration, the dissolution rate slows down and then remains constant up to about 30 days under the described conditions. In Si-enriched solutions, Si saturation is attained much earlier and, therefore, the amount of B (or glass) dissolved is lower than in pure water. The decrease of the dissolution rate at silica saturation can be explained by condensation reactions of the silanol groups in the alteration layer forming a dense, highly protective gel on the glass surface. The silica saturation concentration C^* represents an intrinsic glass (or gel) solubility limit related to the glass composition. Metal ions in the solution (RE, Al or Mg) are sorbed on the alteration layer of the glass and lower mainly the dissolution rate of the silica network. Si saturation is attained after much longer times and the amount of glass dissolved is higher than in pure water. If additional metal ions are enriched in the solutions besides Si, metal silicate phases can precipitate or are sorbed onto the gel layer and the Si concentration decreases to values far below C^* found in pure water. Despite the apparently ‘under-saturated’ conditions, the B release rate remains in the range of the low final rate. It can be concluded that lower Si concentrations also represent a saturation concentration with respect to a protective surface layer formed by precipitated/sorbed metal silicates. Therefore, precipitation of metal silicates during glass corrosion must not lead compulsory to under-saturated conditions in the solution consuming the SiO_2 (am) in the system and to an acceleration of the dissolution rate, as reported in literature, e.g. [17]. However, if the Si concentration may be reduced by sorption of Si onto the clay minerals in a clay repository or by the growth of existent or newly formed siliceous minerals (e.g. smectite clay, analcime) in or outside the gel layer, the solution may become under-saturated and the glass dissolution rate increases.

The protective gel layer may not be stable over longer times and may detach from the glass surface. Then, unaltered, pristine glass would be exposed to a rather concentrated, silica-saturated solution. From the presented results and from results of Vernaz et al. [7], who replaced leached glass samples after a certain period by pristine glass samples, it is expected that the glass dissolves initially with the same high rate like in pure water. However, after short time (some hours), when the gel layer has attained a certain thickness, condensation reactions of the silanol groups take place under the saturated conditions and a protective gel layer develops

again. The release of B after gel layer detachment is expected to be quite similar to the release found in the Si + Nd-enriched solution (Fig. 4). As long as the aqueous solutions in a repository are silica saturated and the dissolved species is unionized H_4SiO_4 (below $\text{pH} \leq 9$), the glass dissolution rate remains low and can reduce even to zero after long reaction times, as shown by numerous long-term glass corrosion experiments.

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