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Effect of Zn^{2+} and Cu^{2+}-bearing salts on the dissolution of silicate glasses

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Zn^{2+}-bearing salts have been used for a long time to protect the glass surface against corrosion of glassware in dishwashers[1], or of flat glass during transport and storage[2]. However, the mechanisms by which Zn^{2+} ions diminish the extent of glass corrosion are not well known. In parallel to the study of the effects of Zn(II) salts on the kinetics and morphology of glass alteration in *atmospheric* conditions[3], we investigated the effects of these salts on the glass alteration in *immersion* conditions, by measuring the glass dissolution kinetics in solutions bearing increasing concentrations of salts. In this text, the results for a mixed (Na,K) glass, of which composition is 71.3 SiO_2, 0.8 Al_2O_3, 0.8 MgO, 5.0 CaO, 11.0 Na_2O, 11.0 K_2O (wt%), are described and discussed. All the studied alkali, alkaline-earth-silicate glasses behaved the same way in these dissolution experiments, although their dissolution rate was different.

The experiments were conducted at 80°C and free pH, with an S/V ratio (S, exposed surface of glass, and V, volume of the solution) of about 0.5 cm^{-1}, according to the procedure described in (Tournié *et al.*, 2013). ICP-AES[4] was used for solution analysis. Two observations can be first reported: (i) Whatever the nature of the counter-ion of the zinc salt in solution (chloride, $ZnCl_2$, nitrate, $Zn(NO_3)_2$, or citrate, $Zn_3(C_6H_5O_7)_2$), the results were the same. These counter-ions thus played no role in the dissolution experiments. (ii) The effects of the Zn(II) salts were apparent from a concentration of 10^{-3} M. This concentration is slightly above the solubility of Zn^{2+} ions with respect to $Zn(OH)_2$ at 80°C and pH =6.5 ($1.8.10^{-4}$ M). The normalized mass losses[5], NL, in Na and in Si are shown as a function of time in figures 1a and 1b, for the experiments in pure water and in water with 10^{-3} M $ZnCl_2$. In pure water, the dissolution of the glass is incongruent. The release rate of alkalis is almost 10 times higher than that of Si and Ca (K and Ca NL are not shown). In water

[1] See the text of Karlheinz Hahn in this book
[2] See the text of Sophie Papin et al., in this book
[3] See the text of Fanny Alloteau et al., in this book
[4] Inductively-Coupled Plasma – Atomic Emission Spectroscopy
[5] The normalized mass loss in element *i* is calculated by : $NL_i = \frac{c_i \times V}{m \times x_i \times \Sigma}$, where c_i is the concentration of element i in solution ($g.L^{-1}$), V is the volume of solution, m and Σ are the mass and specific surface of the glass powder exposed to the solution and x_i is the weight fraction of element *i* in the glass.

bearing 10^{-3} M $ZnCl_2$ salt, the release rate of alkalis was unchanged (figure 1a), while no release of Si and Ca could be detected for the first 20 days of the experiment (figure 1b). During this 20 days period, the Zn^{2+} concentration decreased in the solution (figure 1b), and the pH was constant around 7 (figure 1a). The leaching of alkalis corresponds to a pH increase well observed in the pure water experiment (up to pH 10.5, not shown). The leaching rate was the same in the experiment with $ZnCl_2$ solution, but the pH stayed neutral because the formation of hydroxide anions was immediately followed by the precipitation of the Zn^{2+} ions, forming zinc hydroxide. This direct relationship is demonstrated in figure 2: the total amount of cations in the solution was constant, the loss in Zn^{2+} compensating exactly the release in alkalis. After 20 days, when all Zn^{2+} ions have precipitated, the pH started to increase (figure 1a) and Si started to dissolve (figure 1b).

The nature of the Zn(II) hydroxide precipitates is unclear. At the end of the experiments, only hemimorphite of composition $Zn_4Si_2O_7(OH)_2.H_2O$, was observed in the altered glass powder (figure 3). Hemimorphite is a deeply insoluble hydroxysilicate phase: in equilibrium with this phase, the Si solubility is $3.2.10^{-9}$ M at 80°C and pH 7 (according to the solubility constant given in (Mc Phail *et al.*, 2006)). The observation of hemimorphite raised two questions: (a) Was Si entirely immobilized in hemimorphite during these first 20 days? (b) Was the existence of such an insoluble phase, responsible for the Zn(II) precipitation and the related buffering power of the $ZnCl_2$ solution? By assuming that all Zn^{2+} ions eventually formed hemimorphite, we calculated that only one third of the Si, that had not been released compared with the pure water experiment, had been fixed in hemimorphite crystals. The two other thirds had not been dissolved, probably thanks to the neutral pH that had stabilized the silicate network with respect to dissolved silica. To answer question (b), the same experiments were carried out with $CuCl_2$ bearing solutions. According to available thermodynamic data[6], Cu^{2+} ions and Zn^{2+} ions have the same solubilities (with respect to their hydroxides), but Cu^{2+} ions do not form insoluble hydroxysilicates analogous to hemimorphite. Indeed, the dissolution behaviors were the same with $CuCl_2$ and with $ZnCl_2$ (not shown). Only a brown precipitate bearing Cu and no Si (according to SEM-EDX) was observed and attributed to amorphous $Cu(OH)_2$. Thus, the existence of hemimorphite has no link with the dissolution behavior, which is rather explained by the supersaturation of the solution with respect to the metal hydroxide. In the $ZnCl_2$ experiment, it is possible that $Zn(OH)_2$ precipitated first and transformed into hemimorphite after some induction time.

Therefore, a possible explanation for the beneficial effect of Zn(II) salts on glass aqueous alteration relies on the buffering power of supersaturated Zn(II) solutions in contact with the glass (the glass surface probably plays a nucleating role in the Zn(II) hydroxide precipitation, as demonstrated in (Spark *et al.*, 1995) for amorphous silica surface). In such a solution, alkalis are released "normally", but the pH is maintained neutral thanks to Zn(II) precipitation. Consequently, the silicate network of the glass is protected: the glass is leached, but it does not appear "corroded". It is possible that part of the protection may also be due to the passivation of the glass surface by Zn(II) chemisorption, as demonstrated for the atmospheric alteration conditions. This passivation would vanish when hemimorphite forms. Further studies are necessary to address this question.

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[6] Database (log K values at 20°C) provided by the Hydra and Medusa softwares, by Ignasi Puigdomenech, Department of Chemistry, Kungliga Tekniska Högskolan, Stockholm, Sweden (2013).

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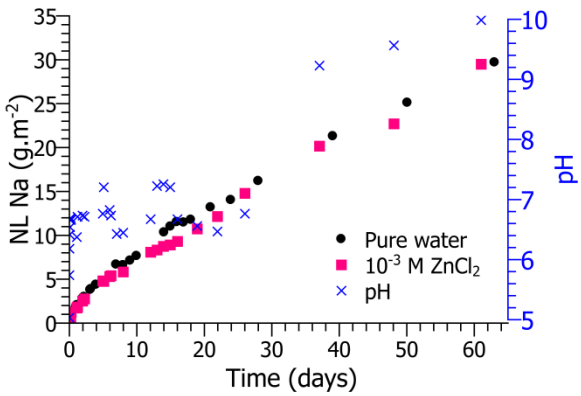

Fig. 1a: Na normalized leached fraction of glass powder as a function of time, in pure water (black dots) and in $ZnCl_2$ solution (pink squares). The pH of the $ZnCl_2$ solution during the experiment is depicted on the right axis (blue crosses).

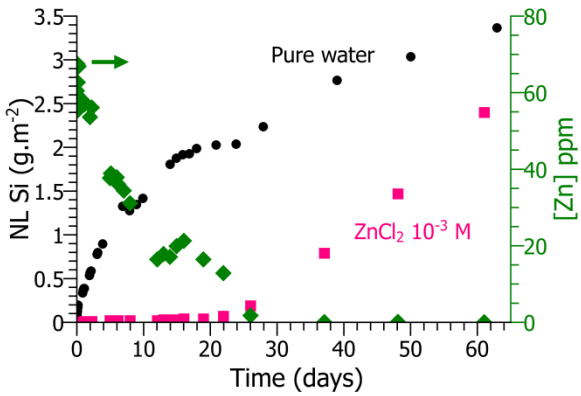

Fig. 1b: Si normalized leached fraction of glass powder as a function of time, in pure water (black dots) and in $ZnCl_2$ solution (pink squares). The Zn^{2+} concentration of the $ZnCl_2$ solution during the experiment is depicted on the right axis (green diamonds).

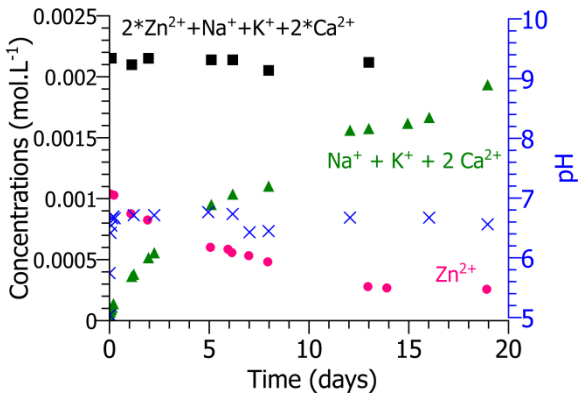

Fig. 2: Ionic concentrations in the $ZnCl_2$ solution during the dissolution experiment. The alkali and alkaline-earth concentration increases with time due to glass leaching (green dots). The Zn^{2+} concentration decreases with time because of subsequent zinc hydroxide precipitation (pink dots). The total cationic concentration stays constant for electroneutrality reasons (black squares).

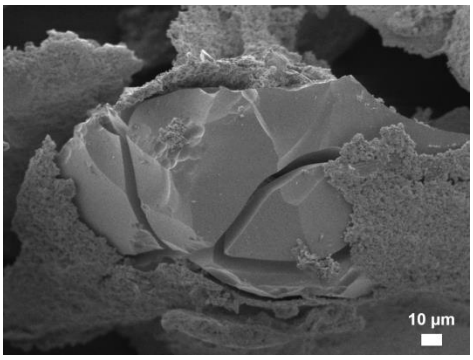

Fig. 3: SEM image (secondary electrons) of the altered glass powder after the dissolution experiment in the $ZnCl_2$ solution. The surface of the glass grain is covered by hemimorphite precipitated crystals ($Zn_4Si_2O_7(OH)_2.H_2O$).