Borosilicate glass alteration driven by magnesium carbonates

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Multi solid interactions: experiment and modeling

Geochemical modeling of glass and silicate mineral alteration is a major challenge for understanding natural processes in the earth sciences (e.g. chemical compositions of natural waters and oceans...). In confined media, solids reactivity quickly controls solution compositions. The alteration of a simplified synthetic glass, representative of the French reference nuclear glass in the presence of a simple Mg-bearing phase is a key step towards the understanding of the interactions between nuclear glass and nearfield materials in geological repository. Indeed, magnesium in solution is one of the elements known to potentially enhance glass alteration. In a first study, hydromagnesite was chosen as the simplest and as the most reactive Mg bearing carbonate.

Experiments were performed in closed system at 90°C and characterized by SEM, XRD and TofSIMS. They revealed that glass alteration is enhanced in presence of hydromagnesite at 90°C.

Geochemical modeling was performed using the GRAAL model [1] implemented within the CHESS/HYTEC reactive transport code. The model was efficient enough for quantifying the amount of present solids, the pH and the elements concentration with time whatever the glass/hydromagnesite ratio.

Future experimental and modeling work will concern more representative solids, like dolomite and smectites.

[1] P. Frugier *et al*., (2009) *Journal of Nuclear Materials* **392** 552-567.

Carbonation of forsterite and serpentine: Modeling the optimum conditions in terms of pH and temperature

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Carbonation of forsterite into magnesite and quartz following the reaction:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

has been assumed in a plethora of studies. However the consumption of metals by the formation of secondary phases has been overlooked.

In this study we intent to shed some light and define the conditions of successful carbonation experiments and industrial CO_2 mineralization projects in terms of pH and temperature. In order to minimize the precipitation of secondary phases we have mapped out the thermodynamic stability of magnesite relative to mineral phases like antigorite and brucite from 25 to 200°C, a pH ranging from 4 to 8 and 10 bars of CO_2 and performed both closed system batch simulations and kinetic simulation of the carbonation of forsterite and serpentine using the kinetics expressions and data available in the literature.

The results illustrate several important constrains on the formation of magnesite or serpentine. A key role in the reaction process is played by the temperature, due to the lowering reaction rates below 100°C where both magnesite and quartz fail to precipitate;whereas at temperatures greater than 200°C the overall forsterite to magnesite reaction is thermodynamically unstable. Furthermore, the pH effect cannot be ignored, as at pH below 4 the magnesite is extremely soluble and will not precipitate whereas at pH above 9 brucite is becoming the dominant precipitating phase, thus it is unlikely that carbonation will occur.