1.8.25

Geochemical modelling of SON68 and SM539 glass dissolution and gel formation at different temperatures using a solid solution model

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One of the waste forms resulting from the Belgian programme for nuclear energy is vitrified high level waste as SON68 or SM539 glass. Aspects of the safety analysis of waste disposal in a Boom Clay layer are the stability of the glass in the clay environment, the interaction between glass-interstitial clay water-Boom Clay and the estimation of the long term dissolution rate. Understanding the incongruent release of glass constituents and the possible formation of secondary gel or crystalline phases is indispensable.

The objective of this study is to describe the composition of the leachant in contact with inactive glass by modelling the precipitation of a gel phase as an ideal solid solution in equilibrium with the leachant. The waste glass is assumed to dissolve completely and congruently. To address the observed incongruent release of elements in the leachant, equilibrium with a secondary ideal solid solution representing the gel phase is assumed which consists of end-members in oxide, hydroxide or metasilicate form such as SiO_2, Al_2O_3, $Fe(OH)_3$ and $CaSiO_3$ for SON68 or SiO_2, Al_2O_3, $Fe(OH)_3$, $CaSiO_3$, $MgSiO_3$ and Na_2SiO_3 for SM539.

Dissolution of the two glasses in two test media, distilled water and synthetic clay water, and three temperatures (40, 90, and 150°C) gave data for short- (leachant strongly under saturated) or longer- (leachant saturated with glass) term processes, glass surface area and leachant volume ratios ranging from 10 m^{-1} to 10000 m^{-1}.

At 90°C, model calculations using standard thermodynamic data results in acceptable predictions of solution composition, especially for distilled water. However, extrapolation of the ideal solid solution at 90°C to the other two temperatures results in a less accurate description. The solubility K of the end members in the solid solution is optimized using the available data for each temperature. Plotting as Log(K) – $1/T$ (K) gives a straight line allowing estimation of the temperature dependence for the end members. In this way, one model can describe the composition of the leachant and the secondary gel formation during dissolution at the three temperatures. Extrapolation of the model for the distilled water system to the synthetic clay water system is currently underway.

This study shows that geochemical modelling (congruent glass dissolution and precipitation of a secondary ideal solid solution in equilibrium with the leachant) allows a macroscopic and simplified description of the actual microscopic processes and mechanisms for a range of temperatures and/or reaction progresses.

1.8.26

Study of heavy metal uptake by natural and modified zeolites from Mongolia

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Sewage sludge is widely used as a fertilizer, but there is often a major problem with high concentrations of heavy metals contained within it. The heavy metals are mobile and have the potential to enter the food chain. Many zeolites have already been shown to immobilize heavy metals. This paper examines the potential for such uses from new characterisations of Mongolian clinoptilolites.

Three different samples of Mongolian natural zeolites (clinoptilolites) have been investigated for their uptake characteristics of several different cations from aqueous solution. Cation exchange capacities (CEC) were also determined. The methodology was radiochemical, using the tracer ^{22}Na (isotope dilution analysis). The ^{22}Na released into solution due to ion exchange with metal solutes was analysed by liquid scintillation counting. One of the zeolites (CLIN2) was selected for further study using homoionic (ammonium, sodium, potassium, caesium, calcium, magnesium, strontium, barium) and acid modified (chlorohydric, nitric and sulphuric) forms.

Good selectivities (K_D) were recorded for all three clinoptilolites. Sequences are as follows: CLIN1 Cd>Cu>Pb>Cs>Zn>Sr; CLIN2 Pb>Cd>Cs>Zn>Cu>Sr; CLIN3 Pb>Cd>Cs>Cu>Zn>Sr. For the homoionic forms, optimal sorption was found for the cations listed in Table 1.

Table 1.

Homoionic form	CLIN1	CLIN2	CLIN3
NH4	Cd	Pb	Cs
Na	Pb	Pb	Pb
K	Cs	Cd=Cs	Pb
Cs	Pb=Cs	Cs	Cs
Ca	Cd	Cd=Cs	Cd
Mg	Cd	Pb	Pb
Sr	Cd	Zn	Pb
Ba	Cs	Zn	Cd

Acid treatment of CLIN2 significantly increased both the specific surface area and the microporosity. It also increased the KD for Pb from 510 to 569 (HCl modified) and the KD for Cd from 504 to 564 (HNO3 modified).

Contrasting performances of the clinoptilolites are attributed to mineralogical variations (e.g. composition, CEC) related to their geological formation.