Beryllium solubility, hydrolysis and sorption in cementitious systems

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Beryllium is a chemotoxic element expected in radioactive waste due to its use in nuclear reactor as reflector or moderator. The amphoteric character of Be(II) is reported in the literature, involving the predominance of anionic hydrolysis species under alkaline conditions. This work aims at developing comprehensive thermodynamic models for the solubility and hydrolysis of Be(II), and to quantitatively evaluate the uptake of Be(II) by cementitious materials.
All experiments were performed in Ar-gloveboxes at $t = (22 \pm 2)$ °C. Undersaturation solubility experiments were conducted with commercial BeO(cr) and freshly prepared $Be(OH)_2$(am). Samples were equilibrated in dilute to concentrated NaCl, KCl and $CaCl_2$ with $5 \leq pH_m \leq 14.5$. Sorption experiments were performed with ordinary Portland cement, low pH cement and C-S-H phases with Ca:Si = 0.6, 1.0 and 1.6. Batch sorption samples were prepared with 10^{-6} M $\leq$ $[Be(II)]_0 \leq 10^{-2.5}$ M and S/L ratios of 0.2–50 $g \cdot L^{-1}$. Total concentration of Be(II) in the aqueous phase was quantified by ICP–MS. Selected solid phases in solubility/sorption experiments were characterized by a multi-method approach.
XRD indicates that $Be(OH)_2$(am) converted into β-$Be(OH)_2$(cr) in the course of the solubility experiments. Solubility data confirm the amphoteric character of Be(II) with a solubility minimum at $pH_m \approx 9$ ($[Be(II)] \approx 10^{-7}$ M). Above this pH_m, solubility increases with slopes of +1 and +2, corresponding to the formation of $Be(OH)_3^-$ and $Be(OH)_4^{2-}$. Thermodynamic and activity models are derived for the system Be^{2+}–Na^+–K^+–Ca^{2+}–H^+–Cl^-–OH^-–H_2O(l) based on these data. Sorption experiments show a relatively strong uptake of Be(II) by all investigated cementitious materials ($\log_{10} R_d \approx 3.5$–$5.5$). Slow sorption kinetics suggest that additional processes beyond surface complexation might be involved in the uptake of Be(II). These results represent the first experimental evidence on the sorption of Be(II) by cementitious materials, and provide a valuable input for the safety assessment of repositories for the disposal of radioactive waste.

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