

Impact of ISA and chloride on the retention of $^{14}\text{CO}_3^{2-}$ by cement and calcite

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^{14}C is produced from stable parent isotopes (^{13}C , ^{14}N , ^{17}O) present in different components of nuclear reactors. Steel components containing ^{14}C are disposed in repositories for short-lived low and intermediate level wastes (L/ILW-SL). ^{14}C can potentially be released as small organic molecules or in the inorganic form as $^{14}\text{CO}_3^{2-}$. Retention mechanisms proposed for the uptake of $^{14}\text{CO}_3^{2-}$ in cement-based repositories for L/ILW-SL include adsorption onto positively surfaces of C-S-H phases or isotopic exchange carbonate phases (e.g. CaCO_3 , AFm- CO_3) present in hydrated cement [1]. Calcite is considered as the final degradation stage of cement, occurring once C-S-H phases are dissolved. Isosaccharinic acid (ISA) is a polyhydroxycarboxylic acid forming upon degradation of cellulose in alkaline conditions. ISA is known to form stable complexes with Ca, which may affect the retention of $^{14}\text{CO}_3^{2-}$ by C-S-H phases and calcite. High concentrations of stable chloride (up to $\approx 4\text{--}5\text{ M}$) are described for specific waste streams containing evaporator concentrates. This study focuses on the uptake of $^{14}\text{CO}_3^{2-}$ by cement and calcite in the absence and presence of ISA and chloride.

Hydrated cement paste (CEM I) and calcite were characterized by XRD, TGA and SEM-EDX, before and after the sorption experiments. Batch sorption experiments with hydrated cement paste were conducted at $\text{pH} \approx 13.6$ under Ar atmosphere. Sorption experiments with calcite were performed under air at $\text{pH} \approx 8.3$. A systematic variation of key parameters was implemented: (i) solid-to-liquid ratios ($1\text{--}50\text{ g}\cdot\text{L}^{-1}$), (ii) initial concentrations of $^{14}\text{CO}_3^{2-}$ ($8.9\cdot 10^{-11}\text{--}8.6\cdot 10^{-9}\text{ M}$), (iii) equilibration time (2–140 days), (iv) ISA concentrations ($1\cdot 10^{-5}\text{--}0.2\text{ M}$), and (v) chloride concentrations ($1.0\cdot 10^{-4}\text{--}2.0\text{ M}$). Phase separation was achieved by ultrafiltration or ultracentrifugation. The concentration of ^{14}C was quantified by liquid scintillation counting.

The uptake of $^{14}\text{CO}_3^{2-}$ by cement is fast and moderately strong, with $R_d \approx 10^3\text{ L}\cdot\text{kg}^{-1}$ and a minor uptake increase has been observed for an equilibration time up to 60 days ($t_{\text{eq}} = 60\text{ days}$). Sorption experiments reflect a strong dependency of the uptake on the initial concentration of $^{14}\text{CO}_3^{2-}$, which is attributed to isotopic exchange processes. Chloride has a negligible impact on the uptake of $^{14}\text{CO}_3^{2-}$. A decrease of about one order of magnitude of R_d in logarithmic units related to ISA is observed only at $[\text{ISA}] > 10^{-2}\text{ M}$. In the case of calcite, the overall uptake strongly depends on the equilibration time. At short equilibration times, $^{14}\text{CO}_3^{2-}$ is mainly adsorbed on the surface of calcite particles ($R_d \approx 10^2\text{ L}\cdot\text{kg}^{-1}$). A systematic increase of the uptake is observed with time ($R_d \approx 10^3\text{ L}\cdot\text{kg}^{-1}$), caused by the recrystallization of calcite and isotopic exchange processes. Chloride and ISA have a negligible impact on the retention of $^{14}\text{CO}_3^{2-}$ under the investigated boundary conditions.

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References: 1. M. Ochs, D. Mallants, L. Wang (2016), Springer, 301pp.