Retention of $^{14}CO_3^{2-}$ by hydrated cement and calcite: impact of ISA and chloride

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KEYWORDS: Sorption, cement, calcite, $^{14}CO_3^{2-}$, ISA, recrystallization

Introduction

^{14}C is present in different components of nuclear reactors due to the activation of stable parent isotopes, and are partially disposed of in repositories for low and intermediate level and short-lived waste (L/ILW). In the waste, ^{14}C can be found in the form of small organic molecules or as $^{14}CO_3^{2-}$. Retention mechanisms proposed for the uptake of $^{14}CO_3^{2-}$ in cement-based repositories include adsorption onto C-S-H phases or isotopic exchange with inactive carbonate phases present in cement [1]. Calcite itself is considered as the remaining material after the complete degradation of cement (degradation stage IV). Isosaccharinic acid (ISA) is a polyhydroxycarboxylic acid forming upon degradation of cellulose in alkaline conditions. ISA is known to influence the surface properties of cement (e.g. surface charge) and to form stable complexes with Ca. Both processes may affect the retention of $^{14}CO_3^{2-}$ by cement and calcite. High concentrations of stable chloride (up to ≈ 4–5 M) are described for specific waste streams containing evaporator concentrates. This study focuses on the uptake of $^{14}CO_3^{2-}$ by cement and calcite in the absence and presence of ISA and chloride, aiming at the quantification description and mechanistic understanding of the retention processes.

Experimental

Hydrated cement paste (CEM I) and calcite were characterized by XRD, TGA, BET and SEM-EDX before and after the sorption experiments. Batch sorption experiments with hydrated cement paste were conducted at pH ≈ 13.6 under Ar atmosphere. Sorption experiments with calcite were performed under air at pH ≈ 8.3. A systematic variation of key parameters was implemented: (i) solid-to-liquid ratios (1–50 $g \cdot L^{-1}$), (ii) initial concentrations of $^{14}CO_3^{2-}$ ($8.9 \cdot 10^{-11}$–$8.6 \cdot 10^{-9}$ M), (iii) equilibration time (2–365 days), (iv) ISA concentration ($1.0 \cdot 10^{-5}$–0.2 M), and (v) chloride concentration (1.0 10^{-4}–2.0 M). Phase separation was achieved by ultrafiltration or ultracentrifugation. The concentration of ^{14}C was quantified by liquid scintillation counting.

Results and discussion

The uptake of $^{14}CO_3^{2-}$ by cement is fast and moderate, with $R_d \approx 10^3$ $L \cdot kg^{-1}$ quantified at $t \leq 60$ days. A slight increase in the uptake is observed at long contact times, t = 365 days. Chloride and ISA have a minor impact on the uptake of $^{14}CO_3^{2-}$ by cement. The decrease in R_d observed at S/L = 1 $g \cdot dm^{-3}$ and [ISA] > 10^{-2} M is attributed to the formation of stable Ca-OH-ISA complexes and consequent dissolution of cement phases. For calcite, a low-to-moderate uptake of $^{14}CO_3^{2-}$ ($R_d \approx 10^2$ $L \cdot kg^{-1}$) is observed at short contact times, with a systematic increase of the uptake taking place with time ($R_d \approx 10^3$ $L \cdot kg^{-1}$ at t = 60 days). These observations are explained by adsorption followed by incorporation / isotopic exchange triggered by the recrystallization of calcite. The latter process was successfully described with the homogeneous recrystallization model reported previously by Heberling et al. [2]. As for cement systems, chloride and ISA have a minor impact on the retention of $^{14}CO_3^{2-}$ by calcite. This work provides a sound basis for the quantitative description and mechanistic understanding of $^{14}CO_3^{2}$ retention in L/ILW repositories, accounting also for the impact of ISA and high chloride concentrations.

Acknowledgments: *This work is funded by ONDRAF/NIRAS.*

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