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Uptake of CO_2 and precipitation of $CaCO_3$ in alkaline solutions - Mechanisms and Rates

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The uptake of CO_2 in calcium ion bearing alkaline solutions and the subsequent precipitation of calcium carbonate is valid for many natural and man-made environments, e.g. causing the formation of travertine and drainage sinter, respectively (Clark et al., 1992; Dietzel et al., 1991). More recently such a CO_2 uptake is debated as an option for CO_2 sequestration by using alkaline residue materials, which contain e.g. CaO, in aqueous suspensions (Back et al., 2011). However significant gaps of knowledge exist with respect to combined CO_2 absorption uptake and $CaCO_3$ formation behavior in alkaline solution.

In the present study CO_2 uptake and $CaCO_3$ precipitation mechanisms and rates were experimentally studied by diffusion of CO_2 through a polyethylene membrane (0.2 mm thickness) from an inner to an outer solution containing carbonic acid (pH = 7.5) and $CaCl_2$ (10 mM), respectively (25°C). The pH of the outer solution was kept constant during two analogous sets of experiments at 8.3, 9.0, 10.0, 11.0, and 11.5 by adding 0.5 M NaOH solution. At a critical Ion Activity Product (IAP) $CaCO_3$ is formed in the outer solution. The NaOH titration curve and measured Ca^{2+} concentrations reflect CO_2 uptake rate and the precipitation rate of $CaCO_3$. By using automated pH stat. technique it is possible to detect $CaCO_3$ nucleation at a resolution down to ≈ 1 ‰ of Ca^{2+} bound in $CaCO_3$ for a pH between 8.3 and 10.

XRD and (micro)Raman pattern as well as SEM imaging clearly reveal the formation of calcite and vaterite at pH 8.3 and 9, whereas at pH 10, 11, and 11.5 calcite, aragonite and vaterite are formed. The experimental results show that at elevated pH of the outer solution the uptake rate of CO_2 (equal to carbonate accumulation rate: CAR) is significant higher and less time for nucleation and ongoing formation of $CaCO_3$, t_{fc}, is required compared to lower pH conditions (e.g. pH 8.3 and 10 result in CAR = 3.9 10^{-5} and 5.1 10^{-5} mM s^{-1} and t_{fc}= 7.9 and 1.1 h, respectively). Surprisingly at the given total experimental time of $\approx$ 20 h the amount of precipitated $CaCO_3$ was similar for all 10 experiments. This can be explained by significantly higher $CaCO_3$precipitation rates (R) at low versus high pH (e.g. pH 8.3 and 10 result in R = 1.3 10^{-7} and 4.2 10^{-8} mM s^{-1}, respectively) if once a critical IAP is reached (e.g. IAP $\approx 10^{-7.4}$ and $10^{-6.8}$ at pH 8.3 and 10.0, respectively). Subsequent to this first precipitation step (duration of about 2 to 3 hours), the $CaCO_3$precipitation rate is lowered down to a nearly constant precipitation rate for all experiments. The obtained relationships are discussed in the scope of using alkaline residue materials for CO_2 sequestration.

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