CARBONATE FORMATION AT ALKALINE CONDITIONS

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Calcium Carbonate ($CaCO_3$) can be induced by CO_2 uptake in Ca^{2+} ion bearing alkaline solutions as it is valid for many natural and man-made environments, e.g. formation of travertine and scaling (CLARK et al., 1992 and DIETZEL et al., 1992). However, significant gaps of knowledge exist with respect to reaction kinetics (CO_2 uptake and $CaCO_3$ precipitation) in alkaline solutions as well as in respect to distinct $CaCO_3$ polymorph formation.

In the present study CO_2 uptake and $CaCO_3$ precipitation were experimentally studied by diffusion of CO_2 through a polyethylene membrane from an inner into an outer solution containing 10 mM of $CaCl_2$ (25 °C). The pH was kept constant during two analogous sets of experiments at 8.30, 9.00, 10.00 11.00 or 11.50 by titration using diluted NaOH solution.

By exceeding an IAP (Ion Activity Product) threshold $CaCO_3$ is formed in the outer solution. (Micro)Raman and XRD pattern indicate the $CaCO_3$ polymorphs calcite, vaterite and aragonite. Calcite and vaterite were precipitated at all pH values, whereas aragonite was only present at pH $\geq$ 11.00. The evolution of the NaOH titration curve and Ca^{2+} concentration reflects parameters like the CO_2 uptake rate ($\propto$ ACAR: aqueous CO_3^{2-} accumulation rate; NIEDERMAYR et al., 2013) and the overall precipitation rate of $CaCO_3$ (R_{CaCO3}). At elevated pH of the outer solution the ACAR is significantly higher and less time for nucleation of $CaCO_3$, t_{fc}, is required compared to lower pH conditions (e.g. pH 8.30 and 10.00 result in ACAR = 9.2 ±0.1 and 121 ±0.6 $\mu M\ h^{-1}\ l^{-1}$ and t_{fc} = 8.3 ±0.3 and 1.6 ±0.5 h, respectively). At pH $\geq$ 11.00 the $CaCO_3$ nucleation and precipitation begins instantaneously after starting the experiment. Interestingly, at the given total experimental time of 20 h the relative Ca^{2+} concentration decrease (equivalent to the amount of precipitated $CaCO_3$) was similar (22 ±4 mol% in respect to initial Ca^{2+} concentrations) for all experiments. This can be explained by the significantly higher R_{CaCO3} values subsequent to nucleation at low versus high pH (e.g. pH 8.30 and 10.00 with R_{CaCO3} = 645 ±64 and 178 ±15 $\mu M\ h^{-1}\ l^{-1}$, respectively) which correlates with a general decrease of the surface concentration of $>CaHCO_3^0$ at the $CaCO_3$ surfaces (e.g. RUIZ-AGUDO et al., 2011 for calcite). Thus, the combined effect of the aqueous carbonate accumulation rate and the precipitation rate of $CaCO_3$ controls the quantity of $CaCO_3$ precipitation in alkaline environments.

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