In situ measurement of dissolution and growth velocities of Ca(OH)$_2$ for CO$_2$ trapping

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In these latter days, CO$_2$ capture and storage (CCS) has attracted considerable attention as a greenhouse gas mitigation option against global warming problems. CCS is a technique to confine captured CO$_2$ to underground or sea for a long time. One of the trapping strategies is a mineralization of CO$_2$, into calcite (CaCO$_3$) for instance. Since calcite is a stable polymorph of calcium carbonate on the earth, it is expected to trap CO$_2$ during a long term. To produce calcite, it has been investigated as a convincing reaction that calcium hydroxide (Ca(OH)$_2$) crystal reacts with liquid containing CO$_3^{2-}$ (Lacker et al., 1995). However we do not know how long the transformation takes for Ca(OH)$_2$ crystal to calcite because there is no date of the growth and dissolution velocities of Ca(OH)$_2$ crystal. The purpose of this study is to solve the growth and dissolution mechanism of Ca(OH)$_2$ crystal by 'in situ measurement of these velocities of it'.

We adopted Phase-Shift Interferometer (PSI) for the measure of normal growth and dissolution rates of Ca(OH)$_2$. Since PSI has extremely high spatial resolution as a few nm in vertical direction, it can detect ultra-slow normal velocity of crystal surface ($<10^{-5}$ nm/s). We put a Ca(OH)$_2$ crystal in a solution which is adjusted from -0.46 to 0.29 in supersaturation by mixing 4 liquids (0.25 M CaCl$_2$, 0.50 M NaOH, 2.0 M NaCl solution and pure water which is completely degassed), and then measured the normal growth or dissolution rate of (001) face of the Ca(OH)$_2$ crystal.

We expect that the growth pattern was multi-nucleation in supersaturation $>0$ by normal growth rate depending on supersaturation because the normal growth rate rises sharply at a specific supersaturation. We obtained that step edge energy of two dimensional nucleus formed in multi-nucleation condition was 1.093$\times$10$^{-11}$ J/m by fitting into a theoretical formula for the first time. The value was smaller than that of calcite on (10-14) obtained from the previous work (Teng et al., 2000). The result is probably one of the reason that Ca(OH)$_2$ crystal grows by multi-nucleation in the range of the low supersaturation.

In addition, on the basis of the result of Ca(OH)$_2$ normal growth and dissolution rate, toward CO$_2$ mineral trapping we could predict how Ca(OH)$_2$ crystal behaved during dissolution in Ca(OH)$_2$-calcite crystals system on the condition that calcium ion concentrations (supersaturation) were [Ca$^{2+}$] $>10^{-2}$, $10^{-4.5} < [\text{Ca}^{2+}] < 10^{-2}$ and [Ca$^{2+}$] $<10^{-4.5}$ M and that hydroxide and carbonate ion concentration and temperature were constant.

We inferred that the behavior of Ca(OH)$_2$-calcite crystals when they co-exist in the solution and found that calcite can grow sooner or later even if the solution is initially undersaturated for calcite. From these results, we concluded that the behavior of Ca(OH)$_2$ crystal could be predicted in the various supersaturation systems understood the normal growth and dissolution rates as a function of supersaturation and CO$_2$ mineral trapping is enough to enable using Ca(OH)$_2$ crystal, which is an important candidate material for CO$_2$-storage in the future.

Keywords: calcium hydroxide, calcium carbonate, mineral trapping, multi-nucleation