

Direct observation of zeolite nucleation from compacted bentonite under hyperalkaline condition

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Since dissolution issue of smectite arose on engineered barrier system using bentonite (absorbent clay from shale consisting mostly of smectite) for radioactive waste repository for past several decades, smectite studies are focusing on (1) dissolution kinetics [1, 2], (2) hydraulic property of smectite in various states (gel to compacted [3]) and (3) alterations into the other clay and zeolites [4]. Former two issues are closely related to undersaturation of pore water and reactive surface area of smectite grains as a function of density. As the result, the pore water produced from locally dissolved smectite can gain the supersaturation with respect to potential secondary phases. The third one, the alteration, can finally lead the total thermodynamic system to the next equilibrium state consisting of secondary phases.

For understanding the alteration, we had carried out direct observation on pure montmorillonite and bentonite composed of montmorillonite, quartz and albite with or without minor amount of zeolite additive under Na, K and Ca hydroxide solution at 70 °C (pH 12.1) [2]. Two methods were used: (1) interferometric measurement of montmorillonite dissolution [2, 5]; (2) direct optical observation of new precipitations. The former gave the rate as a function of density, the latter provided information about nucleation. Sooner or later, the pore water likely attained to local equilibrium, as long as solution flow is limited by compaction.

Differed from previous result, dissolution of pure montmorillonite in the rates varied from 1E-9 (density < 0.01) to 1E-13 mol/m²/s (density > 1.2) [2] did not always derive precipitation of secondary phases. However, the system, bentonite was not the case. Bentonite especially with minor amount of zeolite caused prominent nucleation of secondary zeolite after a long induction period (weeks) after solution-flow was shut-off.

This alteration behavior could be interpreted with heterogeneous nucleation model. Interfacial free energy, $\gamma_{S/L}$ between secondary phases and alkaline solution was evaluated by wetting angle measurements. There are two end-members such as low and high silica zeolite, those are analcime (ANA: NaAlSi₂O₆; Si/Al = 2.0) and clinoptilolite (CLP: (NaKCa)₃Al₃Si₁₅O₃₆; Si/Al = 5.0). Their $\gamma_{S/L}$ were measured to be and 50.54 and 71.31 mJ/m², respectively. Chemical equilibrium calculation predicts that CLP is the most stable phase in this reaction system. Microanalyses, however, identified the product as phillipsite (PHI: (NaKCa)₄Al₄Si₁₂O₃₂; Si/Al = 3.0) as intermediate composition between CLP and ANA or laumontite (LAU: CaAl₂Si₄O₁₂; Si/Al = 2.0). When PHI was seeded to the bentonite system, secondary zeolite was PHI. Also, the observed induction periods (InI) mostly correlate with supersaturations (1/S²). However, the I sometimes became longer than that by CLP seeding. Seed crystal with higher $g_{S/L}$ such like CLP has lower solubility and likely promotes PHI nucleation more than CLP itself. Fast PHI nucleation by CLP-seeding was an unusual. Direct observation could give us an interesting information. During the early observation in the presence of CLP seed recognized two-step process in which spherical objects were growing in ten times faster rate (5.6E-3 nm/s) than the later phase evolving to faceted (5.1E-2 nm/s). This may have contributed to shortening the induction. Such an amorphous phase is often observed especially at room temperature reaction.

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[1] Cama et al. (2000) *GCA*, 64, 2701-2717; [2] Satoh et al. (2013) *Clay Min.*, 48, 285-294; [3] Terada et al. (2018) *Mat. Res. Exp.*, 6, 035514; [4] Dunkel and Putnis (2014) *Eur. J. Min.*, 26, 61-69; [5] Ueta et al. (2016) *J. Nuc. Sci, Tech.*, 53, 184-191.

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