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Research paper

Na-montmorillonite dissolution rate determined by varying the Gibbs free energy of reaction in a dispersed system and its application to a coagulated system in 0.3 M NaOH solution at 70 °C

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ABSTRACT

Na-montmorillonite (Na$^+$Mt) dissolution in a 0.3 mol dm^{-3} NaOH solution has been investigated at a pH of 12 at 70 °C using a combination of flow-through and batch-type experiments to constrain a predictive geochemical model. The flow-through dissolution experiments were conducted in a dispersed system (initial water/solid ratio = 1000 cm^3 g^{-1}) with varying concentrations of Si and Al to derive a Na$^+$Mt dissolution rate as a non-linear function of the Gibbs free energy of reaction, $\Delta G_{r,\mathrm{mont}}$. This rate equation was used to simulate the batch-type Na$^+$Mt reaction experiments conducted in a coagulated system (initial water/solid ratio = 20 cm^3 g^{-1}) in order to examine the applicability of the $\Delta G_{r,\mathrm{mont}}$ rate equation to higher $\Delta G_{r,\mathrm{mont}}$ conditions and to understand the effect of secondary mineral precipitation on the dissolution rate.

The model simulation of the batch-type experiment adopting the empirical rate equations of Na$^+$Mt dissolution and secondary mineral analcime precipitation was able to reproduce the measured changes in the amount of dissolved Na$^+$Mt and concentrations of Si and Al in solution. The results showed that the empirical rate equation of Na$^+$Mt dissolution determined in the far from equilibrium dispersed system was applicable to the coagulated system over a higher $\Delta G_{r,\mathrm{mont}}$ range and that the concentrations of Si and Al in the batch experiment were controlled by the precipitation of analcime. This implies that the precipitation of secondary minerals will strongly influence the rate of Na$^+$Mt dissolution in the coagulated system. The effects of secondary mineral precipitation on the montmorillonite (Mt) dissolution rate will be, therefore, important in the high density, low water/solid system such as the intended bentonite buffer to be used as the primary barrier in a purpose built repository for the geological disposal of nuclear waste.

1. Introduction

Low level radioactive wastes contain poorly sorbing soluble nuclides such as iodine-129 and carbon-14, which effectively control the maximum dose from a purpose built repository for the geological disposal of nuclear waste. Many repository designs, therefore, envisage the use of a bentonite buffer as a hydraulic barrier to mitigate the release of such radionuclides by impeding groundwater flow. The function of the bentonite buffer as a hydraulic barrier is provided by Mt, which is a swelling clay mineral and forms the major component of bentonite. Cementitious mortar and concrete will almost certainly be used as construction materials to give the repository structural integrity. Cement pore-waters are, however, highly alkaline with a pH = 10–13.5 (Atkinson, 1985), which can permeate into the bentonite buffer, dissolve Mt and result in the loss of the hydraulic barrier. This chain of events emphasizes the importance of Mt dissolution rates under highly alkaline conditions in the context of the safety case for the geological disposal of low level radioactive wastes. Most research efforts have, therefore, focused on the determination of the dissolution rate of Mt, but have tended to use dispersed systems of relatively high water/solid ratios, *e.g.* 240–1000 cm^3 g^{-1} (*e.g.* Amram and Ganor, 2005; Bauer and Berger, 1998; Cama et al., 2000). The bentonite buffer, however, is a dense system of low water/solid ratio, in which the dissolution of minerals, the increase of solute concentrations and the precipitation of secondary minerals will likely take place more readily. This feature of the bentonite buffer necessitates a sound understanding of the relation between the dissolution kinetics of primary minerals, the variation in pore-water chemistry and the precipitation kinetics of secondary minerals. These relations, however, remain unclear not only in the dense system of the bentonite buffer, but also in the dispersed and coagulated systems typically investigated in laboratory experiments.

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Table 1
Thermodynamic data of primary and secondary minerals used in this study.

Mineral	Reaction	Log *K* (25 °C)	Log *K* (70 °C)
Na^+Mt	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O = 0.33Na^+ + 0.33Mg^{2+} + 1.67Al^{3+} + 4H_4SiO_4$	2.30	−0.34
Analcime	$NaAlSi_2O_6 \cdot H_2O + 4H^+ + H_2O = Na^+ + Al^{3+} + 2H_4SiO_4$	6.91	4.72
Quartz	$SiO_2 + 2H_2O = H_4SiO_4$	−4.03	−3.39
Calcite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$	−8.47	−8.90
Analcime-like (Si_R = 0.6)[a]	$Na_2Al_2Si_3O_{10} \cdot 2H_2O + 8H^+ = 2Na^+ + 2Al^{3+} + 3H_4SiO_4$	17.54	13.58
Sepiolite	$Mg_2Si_3H_7O_{11.5} + 4H^+ + 0.5H_2O = 2\ Mg^{2+} + 3H_4SiO_4$	15.01	12.93
Gibbsite	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	7.78	5.42
Brucite	$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$	16.30	13.77

[a] Hypothetical analcime-like solid with a Si/(Al + Si) molar ratio, Si_R = 0.6. All data taken from JNC TDB 990900c1.tdb (Arthur et al., 1999), except for the analcime-like solid (Si_R = 0.6) estimated in this study.

Furthermore, these relations have stood in the way of establishing the sole effect of the solute concentration such as Si (Cama et al., 2000) on the dissolution rate of Mt under high alkaline conditions by conventional methods of detecting changes in the solute concentration during dissolution in dispersed systems.

The current study investigated the Na^+Mt dissolution rate under high alkaline conditions using a flow-through dissolution experiment in a dispersed system with varying concentrations of Al and Si at a pH of 12 at 70 °C. An empirical rate equation of Na^+Mt dissolution was then derived considering the dependency on the Gibbs free energy of reaction, $\Delta G_{r,\mathrm{mont}}$. A batch type Na^+Mt reaction experiment was also conducted in a Na–Si–Al system at pH of 12 at 70 °C in order to examine the applicability of the empirical rate equation to a coagulated system and to understand the effect of secondary mineral precipitation on the dissolution rate of Na^+Mt. This approach somewhat simplifies the highly alkaline disturbance expected in a real repository system where primary mineral dissolution and secondary mineral precipitation are sensitive to both the chemistry of the cement pore-waters and the prevailing geochemical conditions (see Gaucher and Blanc, 2006).

2. Methods

2.1. Characterization of Na^+Mt

Purified Na^+Mt (Kunipia-F®) and Na^+Mt (Kunipia-P®) from Kunimine Industry Co. were used in the current study. Kunipia-F® contained 98 mass% Na^+Mt, with the remainder consisting of calcite, quartz and other soluble impurities. Its structural formula is $(Na_{0.431}, K_{0.002}, Ca_{0.002})\ (Al_{1.560}, Mg_{0.305}, Fe_{0.099}, Ti_{0.007})\ (Si_{3.949}, Al_{0.051})\ O_{10}(OH)_2$. Kunipia-P® obtained by hydraulic elutriation of Kunipia-F® was almost 100% Na^+Mt.

Table 2
Input and output solution pH and Si and Al concentrations from selected flow-through dissolution experiments. Also shown are the calculated change in Si/Al concentration ratio, ΔSi/ΔAl, the Gibbs free energy of reaction for Na^+Mt dissolution, $\Delta G_{r,\mathrm{mont}}$, and the dissolution rate, *r*, of Na^+Mt (see footnotes).

Experiment #	Reaction time (days)	Flow rate (ml min^{-1})	Ionic strength (M)	Input		Output			ΔSi/ΔAl	$\Delta G_{r,\mathrm{mont}}$[b] (kJ mol^{-1})	r_{esa}[d] (mol m^{-2} s^{-1})
				Si (mM)	Al (mM)	pH (25 °C)	Si[a] (mM)	Al[a] (mM)			
H18-Al0.1	14	0.2	0.30	0	0.1	13.41	0.004	0.099	−3.78	−147.0	-1.97×10^{-10}
H18-Al0.5	14	0.2	0.30	0	0.5	13.41	0.039	0.45	−0.75	−115.0	-8.18×10^{-11}
H18-Al1	14	0.2	0.31	0	1	13.41	0.45	0.81	−2.44	−84.1	-6.03×10^{-11}
H18-Si0.05	12	0.2	0.30	0.047	0	13.36	0.17	0.043	2.75	−110.0	-9.93×10^{-11}
H18-Si0.1	12	0.2	0.30	0.087	0	13.37	0.20	0.038	2.95	−108.0	-8.78×10^{-11}
H18-Si0.25	12	0.2	0.30	0.24	0	13.38	0.34	0.035	2.76	−103.0	[c]
H18-Si0.5	12	0.2	0.30	0.47	0	13.39	0.57	0.045	2.36	−95.6	[c]
H18-Si1	14	0.2	0.30	1	0	NR	0.92	0.030	−2.68	−92.1	-1.62×10^{-10}
H18-Si5	14	0.2	0.31	5	0	NR	4.96	0.029	−1.45	−72.8	[c]
H18-Si10	14	0.2	0.31	10	0	NR	10.10	0.022	2.46	−65.7	[c]
H19-Al0.1Si0.01	14	0.2	0.30	0.011	0.12	13.28	0.071	0.16	1.40	−113.0	-9.49×10^{-11}
H19-Al5	14	0.2	0.36	0	5.45	13.26	0.055	5.76	0.18	−97.5	[c]
H19-Al10Si0.01	14	0.2	0.41	0.011	10.6	13.29	0.082	10.70	0.96	−88.4	[c]
H20-Bl	20	0.2	0.30	0	0	13.38	0.030	0.007	4.31	−138.0	-1.19×10^{-10}
H20-Al7	20	0.19	0.38	0	7.19	13.33	0.061	7.29	0.62	−94.6	-1.06×10^{-10}
H20-Al15	20	0.22	0.46	0	15.60	13.30	0.049	15.60	−0.79	−90.8	[c]
H20-Si0.2	20	0.2	0.30	0.18	0	13.33	0.22	0.020	1.96	−110.0	-1.40×10^{-10}
H20-Si1	20	0.11	0.30	1.02	0	13.33	1.12	0.031	3.24	−89.7	-9.79×10^{-11}
H20-Si2	20	0.19	0.30	2.02	0	13.31	2.16	0.041	3.52	−80.7	-1.04×10^{-10}
H21-Bl	40	0.009	0.31	0	0	13.43	0.88	0.435	2.06	−79.9	-5.83×10^{-11}
H21-Si2	40	0.008	0.31	1.99	0	13.45	2.98	0.49	2.03	−65.1	-6.92×10^{-11}
H21-Al1	40	0.008	0.32	0	1.12	13.46	0.94	1.54	2.21	−72.6	-6.10×10^{-11}
H21-Al5	40	0.009	0.36	0	5.37	13.42	0.83	5.87	1.67	−66.4	-8.21×10^{-11}

[a] Output concentrations were taken at the end of the times shown.
[b] Brucite equilibrium was assumed and compatible with the experimental concentrations of $Mg < 4.11$ μmol dm^{-3}. Charge balanced with the concentration of Na (0.3 mol dm^{-3}).
[c] No significant difference in volume changes.
[d] The dissolution rate of Na^+Mt per unit edge surface area, r_{esa} (mol m^{-2} s^{-1}), as given by $r_{esa} = dA_{basal}hV/(A_{edge\,=\,2\,days}Time_{>2\,days})$, where dA_{basal} is the change in the averaged basal surface area per particle (m^2), *h* the height of dehydrated particle (m), *V* the number of moles per unit volume (mol m^{-3}), $A_{edge\,=\,2\,days}$ the averaged edge surface area per particle at 2 days of reaction time (m^2), and $Time_{>2\,days}$ is the time in excess of 2 days (s).