Supporting Information on

Sorption Speciation of Nickel(II) onto Ca-Montmorillonite: Batch, EXAFS Techniques and Modeling

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Figure Captions

Fig. SI-1 Acid-base titrations of Ca-montmorillonite (5.0 g/L) as a function of pH in 0.001, 0.01 and 0.1 mol/L Ca(NO$_3$)$_2$ at T = 20 $^{\circ}$C (A) and at three different temperatures in 0.001 mol/L Ca(NO$_3$)$_2$ (B). The lines are calculated using FITEQL 3.2.

Fig. SI-2 Sorption edges of Ni(II) at different ionic strengths. m/V = 0.5 g/L, $C_{Ni(II)initial}$ = 10 mg/L, T = 20 $^{\circ}$C and I = 0.001, 0.01 and 0.1 mol/L Ca(NO$_3$)$_2$.

Fig. SI-3 XANES spectra of the reference and sorption samples at different pH (A) and temperature (B).

Fig. SI-4 Raw k^3-weighted $\chi(k)$ spectra of experimental samples (A) and their corresponding pseudo radial distribution functions (RDFs) (B) at three different temperatures. m/V = 0.5 g/L, $C_{Ni(II)initial}$ = 10 mg/L, pH = 7.5, T = 20, 40 and 60 $^{\circ}$C, I = 0.001 mol/L.

Acid-base Titration of Ca-montmorillonite. Potentiometric titration of Ca-montmorillonite suspensions (5.0 g/L) were performed over a wide range of pH (3.2-10.6) to measure proton sorption/desorption as a function of pH and ionic strength (0.1, 0.01, and 0.001 mol/L $Ca(NO_3)_2$) at 20 $^{\circ}$C with a Mettler-Toledo DL 50 Automatic Titrator. Before the titration, the suspensions were titrated up to pH ~3 quickly with 1 mol/L HNO_3 and purged with argon gas for about 1 h. Then the titration was carried out from pH ~3 to pH ~10.5 by using 0.0911 mol/L NaOH.
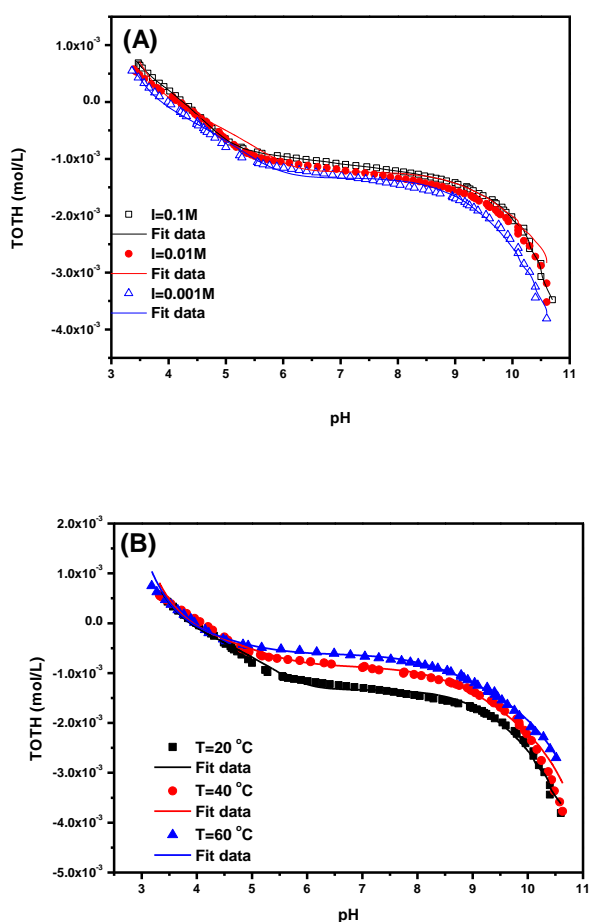

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Table SI-1 Surface site concentration and intrinsic surface complexation constants of Ca-

montmorillonite calculated by FITEQL 3.2. C_{Solid} = 5.0 g/L, BET= 64.4 m^2/g, N_{X2Ca} = 110

mmol/100g, $T = 20\ ^oC$.

| Ionic strength	Site	Density (mol/g)	Reaction	logK
0.001mol/L				
	$\equiv AlOH$	3.11×10^{-4}	$\equiv AlOH + H^+ \Leftrightarrow \equiv AlOH_2^+$	4.40
			$\equiv AlOH \Leftrightarrow \equiv AlO^- + H^+$	-4.83
	$\equiv SiOH$	2.43×10^{-4}	$\equiv SiOH \Leftrightarrow \equiv SiO^- + H^+$	-4.92
			$\equiv X_2Ca + 2H^+ \Leftrightarrow \equiv 2XH + Ca^{2+}$	2.46
	WSOS/DF			15.12
0.01mol/L				
	$\equiv AlOH$	2.96×10^{-4}	$\equiv AlOH + H^+ \Leftrightarrow \equiv AlOH_2^+$	3.21
			$\equiv AlOH \Leftrightarrow \equiv AlO^- + H^+$	-5.86
	$\equiv SiOH$	2.36×10^{-4}	$\equiv SiOH \Leftrightarrow \equiv SiO^- + H^+$	-1.99
			$\equiv X_2Ca + 2H^+ \Leftrightarrow \equiv 2XH + Ca^{2+}$	4.98
	WSOS/DF			19.09
0.1mol/L				
	$\equiv AlOH$	3.56×10^{-4}	$\equiv AlOH + H^+ \Leftrightarrow \equiv AlOH_2^+$	2.66
			$\equiv AlOH \Leftrightarrow \equiv AlO^- + H^+$	-7.02
	$\equiv SiOH$	2.19×10^{-4}	$\equiv SiOH \Leftrightarrow \equiv SiO^- + H^+$	-1.98
			$\equiv X_2Ca + 2H^+ \Leftrightarrow \equiv 2XH + Ca^{2+}$	4.88
	WSOS/DF			16.63
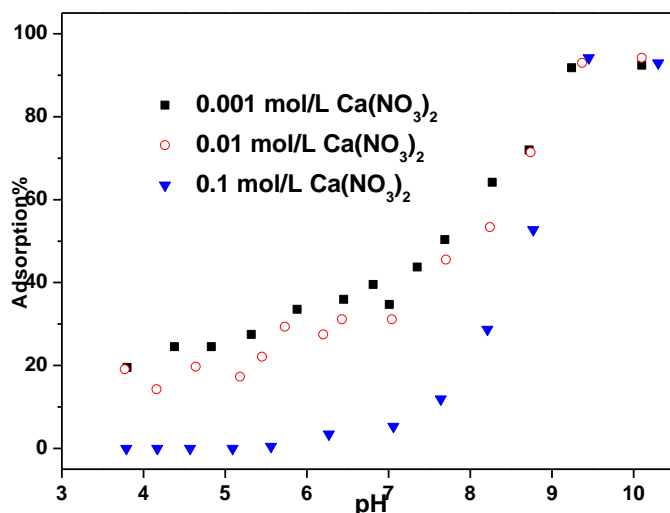
Fig. SI-2 Sorption edges of Ni(II) at different ionic strengths. m/V = 0.5 g/L, $C_{Ni(II)initial}$ = 10 mg/L, T = 20 ^{o}C and I = 0.001, 0.01 and 0.1 mol/L Ca(NO$_3$)$_2$.

From the ionic strength dependence, one can deduce that cation exchange is the main mechanism for Ni(II) sorption on Ca-montmorillonite at pH < 7, which is also supported by the very slow increase of Ni(II) sorption at this pH range. This is consistent with increased sorption on the permanent charge sites with decreasing Ca^{2+} concentration. The ionic strength-dependent sorption suggests that Ni^{2+} exchange reaction on permanent charge sites is the predominant sorption process at the lowest Na$^+$ concentration. The results of Ni(II) sorption are similar to that found and described previously for Cu(II) sorption as a function of pH and Na$^+$ concentrations.[1] It was reported that an increase in Na$^+$ concentration results in a displacement of metal ions from the interlayer sites and a shift in metal ions sorption from the interlayer to the edge sites.

Sample Preparation for EXAFS Analysis. Ni(II) sorption samples were prepared by adding Ni^{2+} (in the form of Ni(NO$_3$)$_2$ solution) to freshly prepared Ca-montmorillonite suspensions. The initial Ni(II) concentration (10 mg/L) and the reaction pH were chosen to achieve high Ni(II) loading on Ca-montmorillonite while avoiding that the bulk solutions were undersaturated with respect to crystalline Ni(OH)$_2$(s).[2,3] The samples were shaken end-over-end for 2 weeks. Samples

for EXAFS measurements were prepared from the residual wet pastes obtained after centrifugation

of the suspensions. Samples preparation and equilibration steps were carried out in a glove box

under N_2 atmosphere ($CO_2 < 5$ ppm, and $O_2 < 5$ ppm).
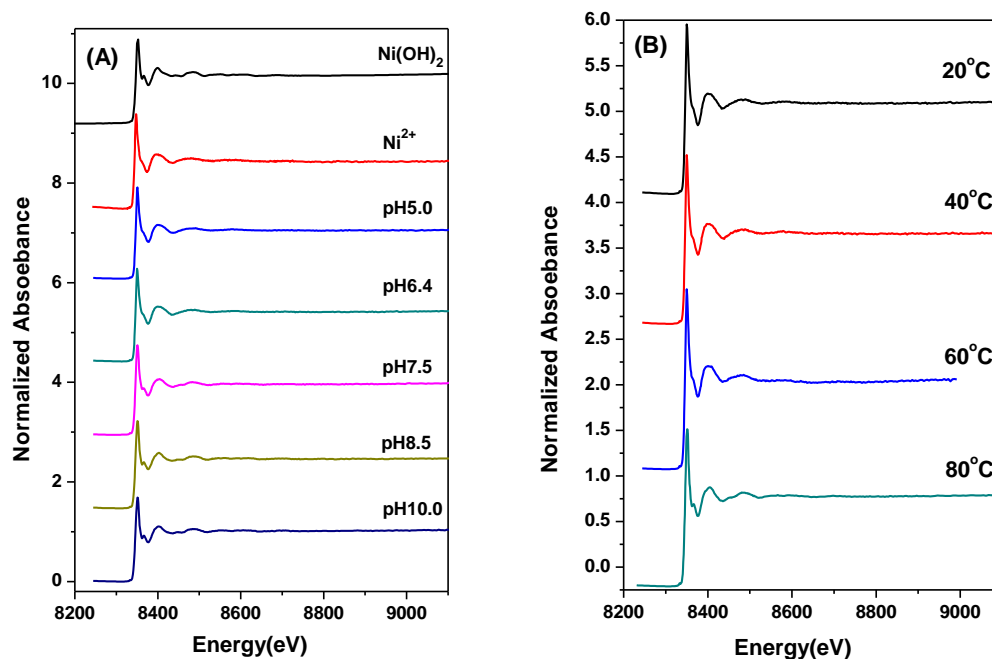

Fig. SI-3 XANES spectra of the reference and sorption samples at different pH (A) and temperature
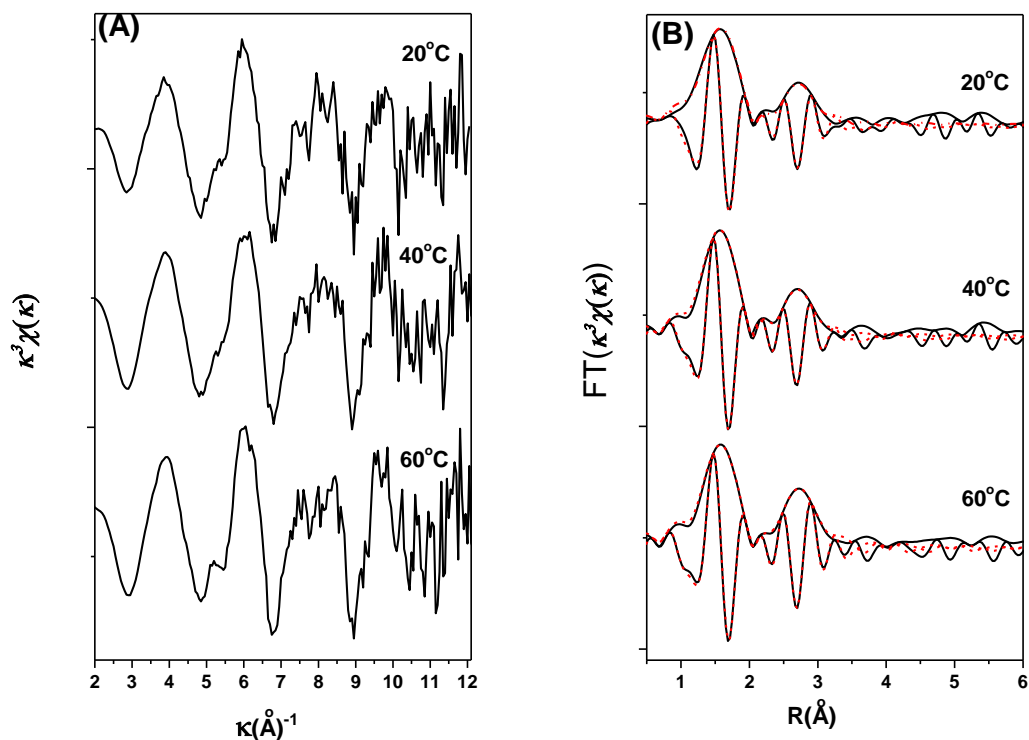
(B).

Fig. SI-4 Raw k^3-weighted $\chi(k)$ spectra of experimental samples (A) and their corresponding pseudo radial distribution functions (RDFs) (B) at three different temperatures. m/V = 0.5 g/L, $C_{\text{Ni(II)initial}}$ = 10 mg/L, pH = 7.5, T = 20, 40 and 60 $^\circ$C, I = 0.001 mol/L.

Literature Cited

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