Sorption of Cr(VI) on Mineral Assemblages of Goethite with Clays and Oxides

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Introduction

Anthropogenic activities have caused Cr(VI) contamination of many natural systems (Grossl et al., 1997). In aqueous solution Cr(VI) is highly mobile, however, adsorption of Cr(VI) anions to mineral surfaces impedes movement (Mesuere and Fish, 1992). Sorption behavior is dependent upon pH and the presence of competing ions (Richard and Bourg, 1991). Many studies have been conducted to observe the sorption behavior of Cr(VI) on single minerals and surface complexation models (SCMs) have been developed to describe these interactions but there is little information regarding the effects of mineral-mineral interactions on sorption.

Hypotheses

SCMs for single sorbate/sorbent systems need to account for mineral-mineral interactions to accurately predict sorbate behavior with multiple minerals.

Goals

- Measure Cr(VI) sorption on mineral assemblages of goethite, kaolinite, montmorillonite, γ-alumina, hydrous manganese oxide (HMO), & hydrous ferric oxide (HFO) (Table 1) as a function of pH, ionic strength & pCO_2.
- Compare predictions from existing SCMs with measured edges of mineral assemblages to assess mineral-mineral interactions.
- Use knowledge gained to create more accurate SCMs for mineral mixtures.

Table 1: Materials

Mineral	Purchased/ Synthesized	Recipe/ Manufacturer	Surface Area m^2/g	XRD
Goethite	Synthesized	Schwertmann & Cornell, 2000	~30	Figure 1
HMO	Synthesized	Stroes-Gascoyne et al., 1987	~400	Figure 2
HFO	Synthesized	Lund et al., 2008	~300	Figure 3
Montmorillonite (SWy-2)	Natural purchased	Clay Minerals Society	~32	Not shown
Kaolinite (KGa-1b)	Natural purchased	Clay Minerals Society	~13.6	Not shown
γ-Alumina (γ-Al_2O_3)	Synthesized purchased	Inframat Advanced	~233	Not shown

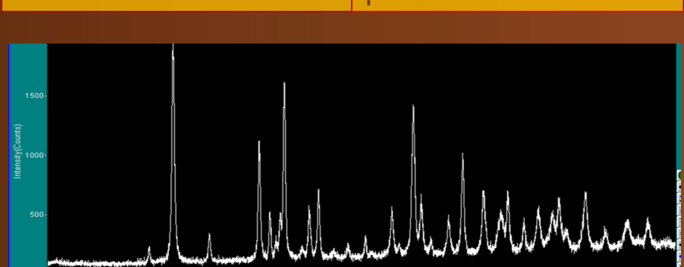


Figure 1: XRD pattern of goethite 2θ Cu-Kα

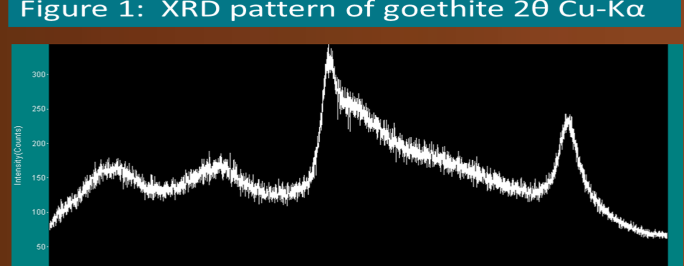


Figure 2: XRD pattern of HMO 2θ Cu-Kα

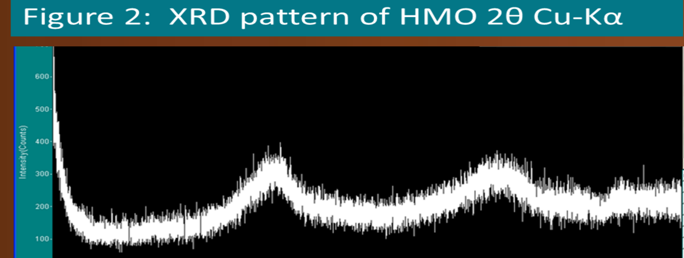


Figure 3: XRD pattern of HFO 2θ Cu-Kα

Experimental Method

- Ultrapure water, 10^{-5} M Cr(VI) & background electrolyte mixed in a 1 L flask ; 60 mL control removed; Solids are then added to the solution in prescribed amount and batch slurry is allowed to equilibrate for 1 hr
- pH is then lowered to ~3.5 and 60 mL of slurry removed; batch slurry is then titrated upward and at each ~0.5 pH increment, a 60 mL aliquot is removed and placed on a rotating shaker
- After 24 hr, 48 hr, 1 wk & 2 wk of mixing ~15 mL of slurry is removed from each aliquot, slurry pH rechecked, centrifuged and filtered, then tested for Cr(VI) using UV/VIS spectrophotometry and total Cr analyzed by ICP-OES

Results and Discussion

- Binary mix experiments conducted with equal mineral surface areas (total surface area 2x title values)
- 0.01 M $NaNO_3$, 10^{-5} M Cr(VI) either at 0% pCO_2 or in atmospheric conditions
- Pure goethite edges shown for comparison (Figure 4)

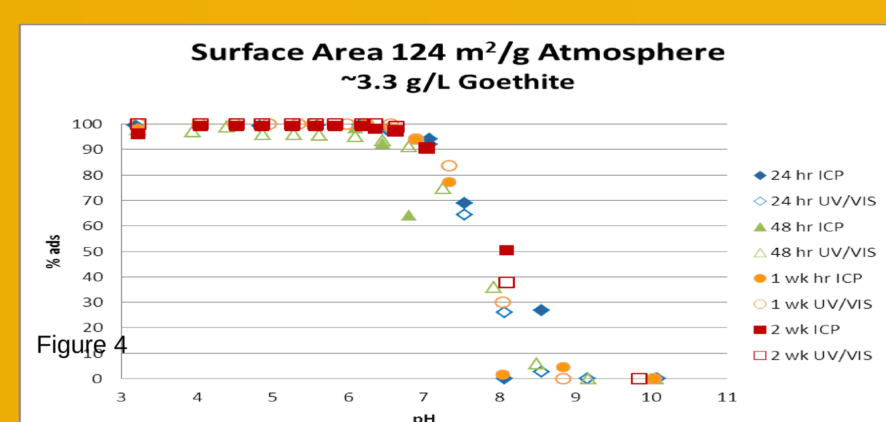
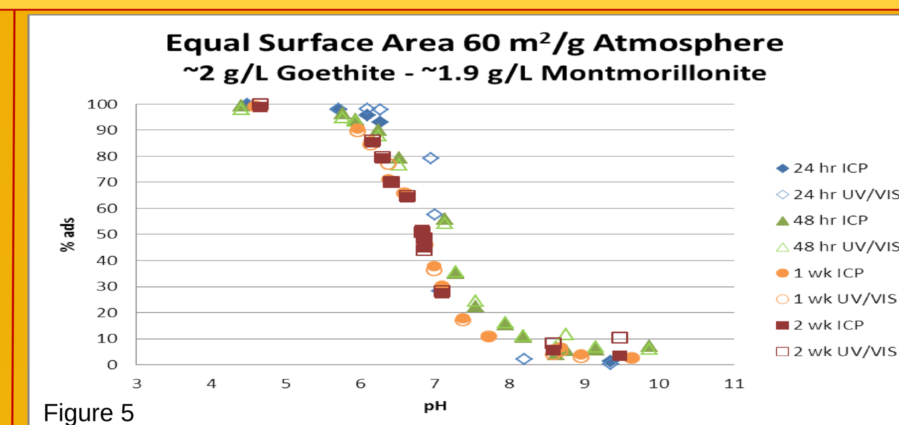
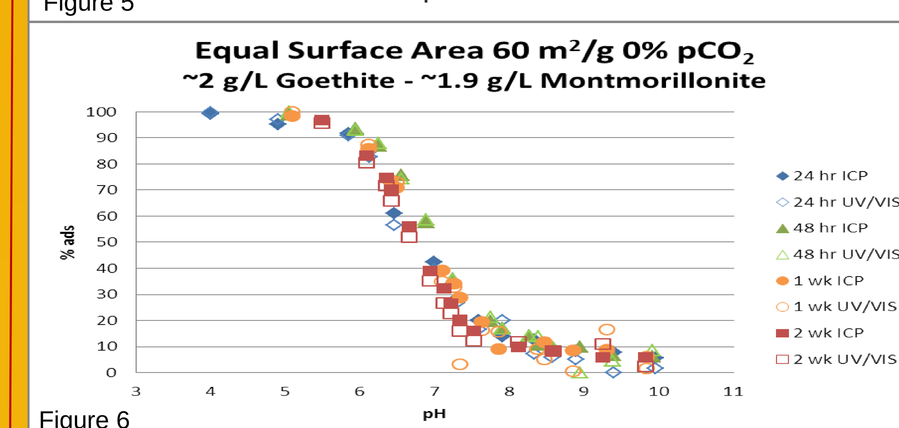
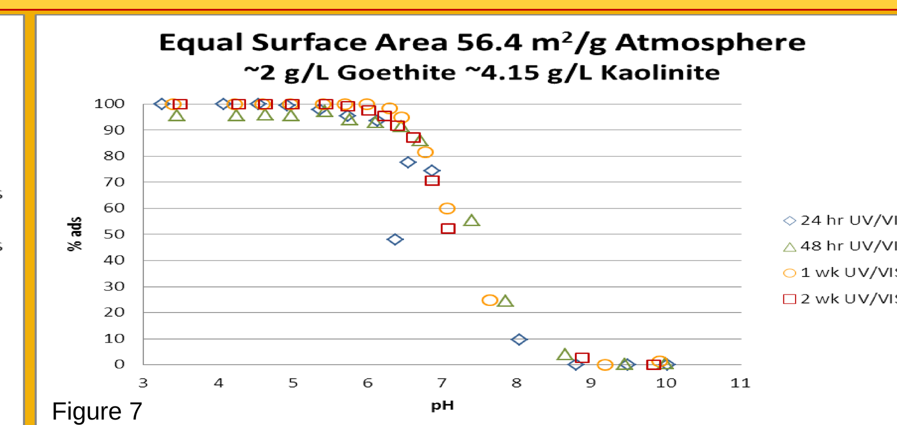
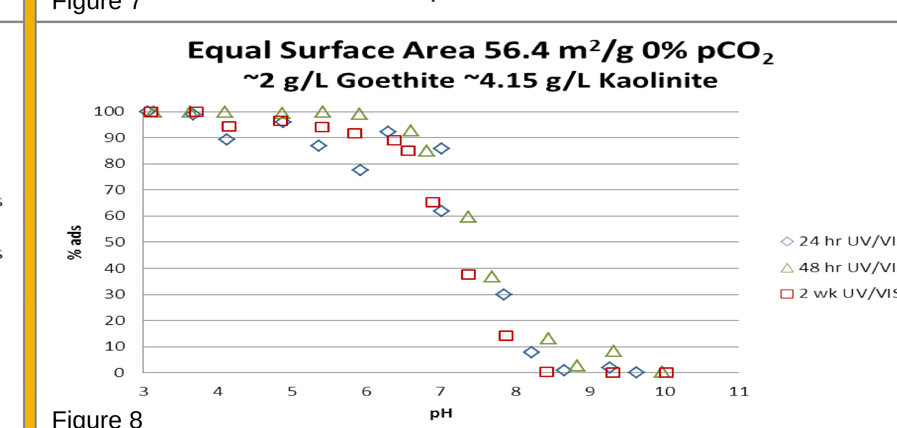


Figure 4: Adsorption of Cr(VI) on goethite as a function of time. ~100% sorbed at pH <6; <10% sorbed at pH >9. pH_{50}: ~7.5

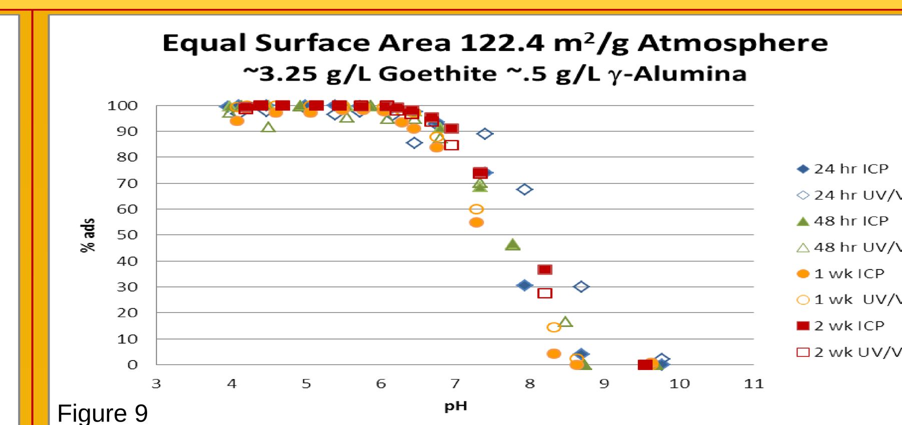


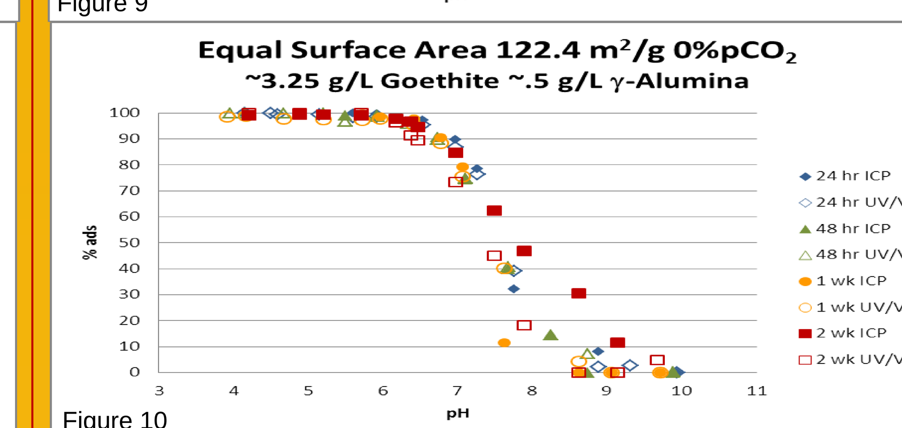




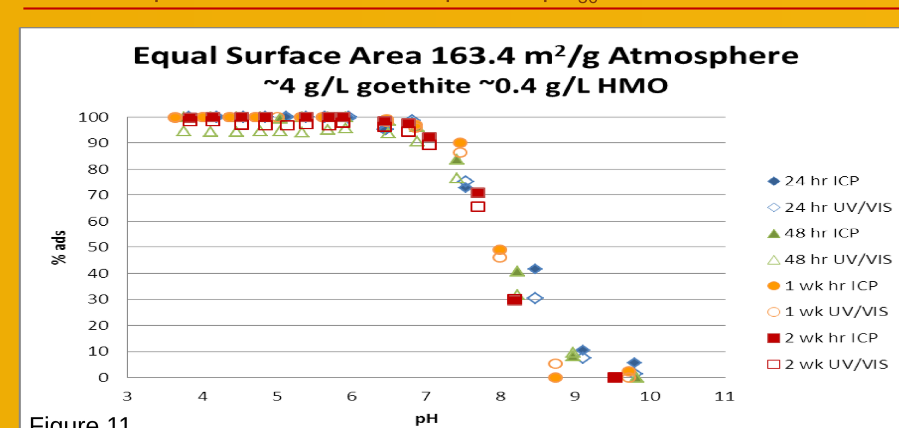


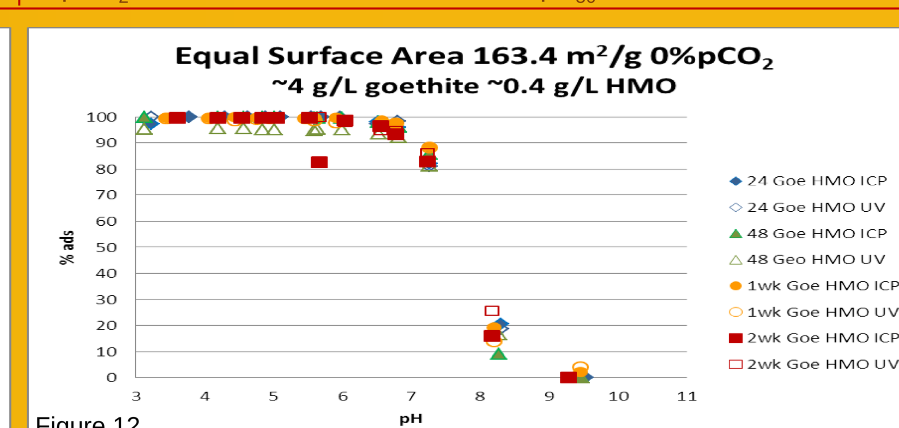
Figures 5-8: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as function of time & pCO_2. Little variation observed from 0 to atms pCO_2 or with times from 24 hr to 2 wk. pH_{50} for montmorillonite mixtures: ~6.8 & for kaolinite mixtures: ~7.1



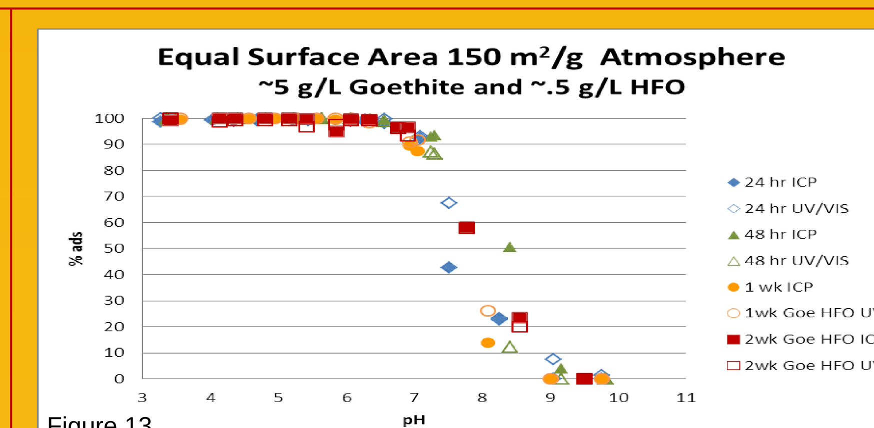


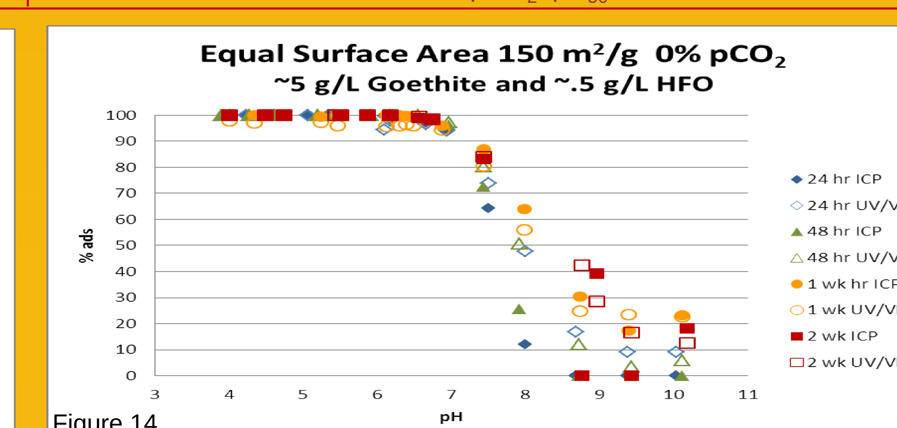
Figures 9,10: Adsorption of Cr(VI) on goethite-γ-alumina mixture. Little variation observed from 0 to atms pCO_2. pH_{50} at ~7.7





Figures 11,12: Adsorption of Cr(VI) on mix of goethite-HMO as function of time & pCO_2. Little variation observed from 0 to atms pCO_2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution. pH_{50}: ~7.8 pH





Figures 13, 14: Adsorption of Cr(VI) on mix of goethite-HFO as function of time & pCO_2. Little variation observed from 0 to atms pCO_2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution. pH_{50}: ~8 pH

Surface Complexation Modeling

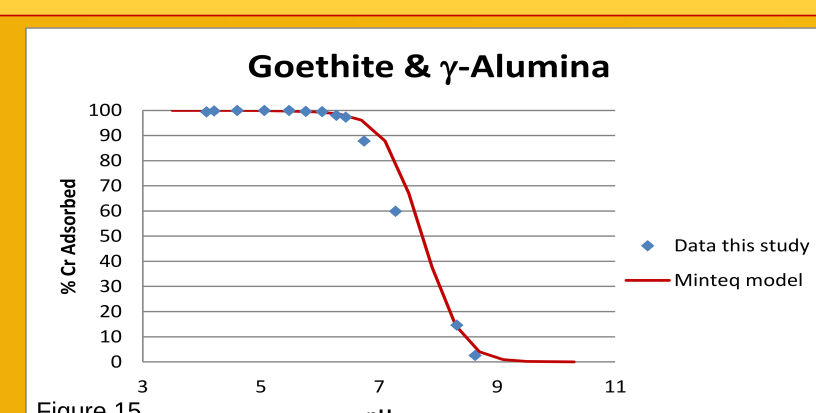


Figure 15: Sorption data from this study (blue), and Minteq model prediction using goethite optimized DLM (Mathur and Dzombak, 2006) and γ-alumina DLM (Reich and Koretsky, 2011); all parameters in Table 2.

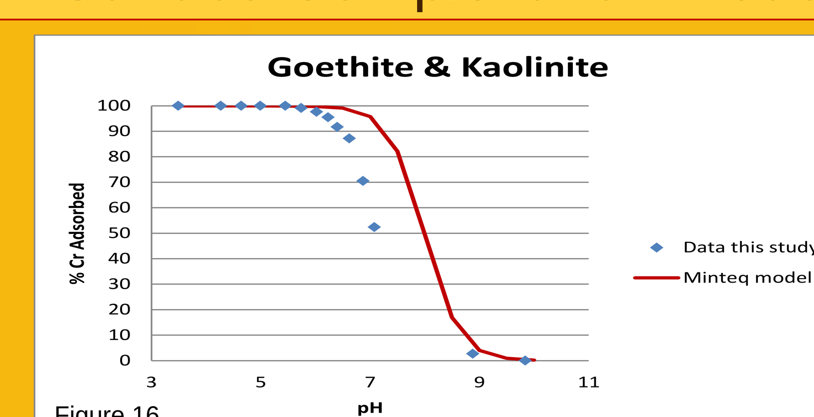


Figure 16: Sorption data from this study (blue), and Minteq model prediction using goethite optimized DLM (Mathur and Dzombak, 2006) and kaolinite DLM (Schaller, et al., 2009); all parameters in Table 2.

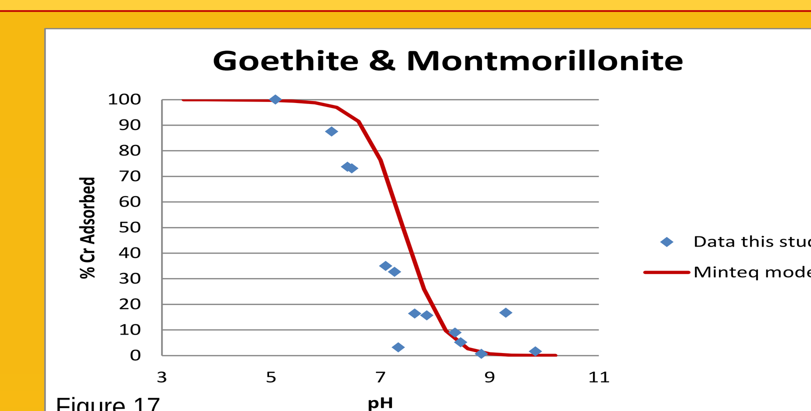


Figure 17: Sorption data from this study (blue), and Minteq model prediction using goethite optimized DLM (Mathur and Dzombak, 2006) and modified kaolinite DLM (Schaller, et al., 2009); all parameters in Table 2.

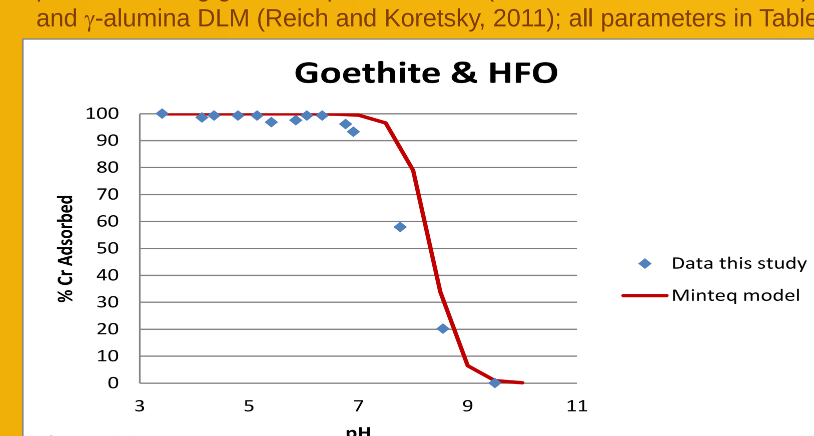


Figure 19: Sorption data from this study (blue), and Minteq model prediction using goethite optimized DLM (Mathur and Dzombak, 2006) and HFO DLM (Dzombak and Morel, 1990); all parameters in Table 2.

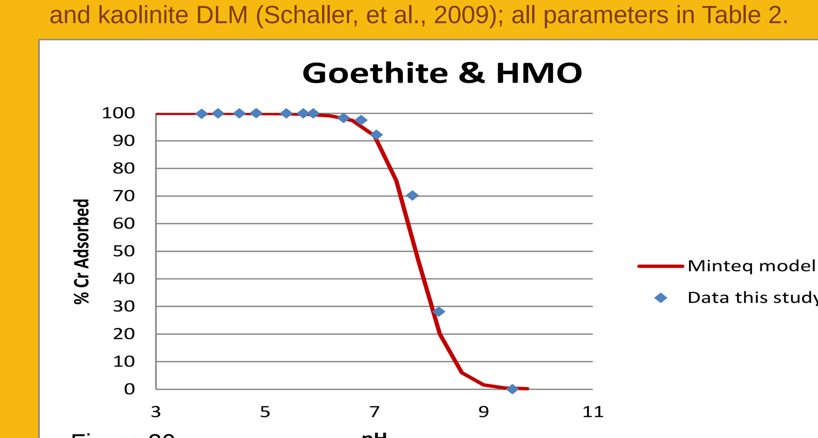


Figure 20: Sorption data from this study (blue), and Minteq model prediction using goethite optimized DLM (Mathur and Dzombak, 2006) and HMO optimized DLM (Tonkin, et al., 2004); all parameters in Table 2.

Table 2: Model Parameters

Model Parameters	Dzombak and Morel HFO DLM	This Study HFO DLM	Mathur and Dzombak Goethite DLM	This Study Goethite DLM	Reich and Koretsky γ-alumina DLM	This Study γ-alumina DLM	**Modified from Schaller, et al. Kaolinite DLM	**Modified from Schaller, et al. Montmorillonite DLM
Surface Area (m^2/g)	600	300.5	60	30.6	233	233	13.6	32
Solid Concentration (g/L)	0.05	0.5	0.84	2-5	5	0.5	2	1.9
Site Density ($sites/nm^2$) site 1	2.25581	2.25581	2	2	5.9873	5.9873	0.425	3.7
Site Density ($sites/nm^2$) site 2	0.05639	0.05639	-	-	-	-	0.05984	0.425
Cr(VI) Concentration (M)	$10^{-7.55}$	10^{-5}	$10^{-6.3}$	10^{-5}	10^{-5}	10^{-5}	-	-
$NaNO_3$ Concentration (M)	0.1	0.01	0.1	0.01	0.01	0.01	0.01	0.01
Surface Complexation Reactions	**Log K**	**Log K**	**Log K**	**Log K**	**Log K**	**Log K**	**Log K**	**Log K**
$SOH + H^+ = SOH_2^+$ (site 1)	7.29	7.29	6.93 +/- 0.07	6.93	7.3	7.3	2.1	2.1
$SOH + H^+ = SOH_2^+$ (site 2)	7.29	7.29	-	-	-	-	-	-
$SO^- + H^+ = SOH^+$ (site 1)	-8.93	-8.93	-9.65 +/- 0.05	-9.65	-8.6	-8.6	-8.1	-8.1
$SO^- + H^+ = SOH^+$ (site 2)	-8.93	-8.93	-	-	-	-	-	-
$SCO_3^- + H_2O = SOH + CO_3^{-2} + H^+$ (site 1)	12.78	12.78	-	-	-	-	-	-
$SCO_3^- + H_2O = SOH + CO_3^{-2} + H^+$ (site 2)	12.78	12.78	-	-	-	-	-	-
$SCO_3H + H_2O = SOH + CO_3^{-2} + 2H^+$ (site 1)	20.37	20.37	-	-	-	-	-	-
$SCO_3H + H_2O = SOH + CO_3^{-2} + 2H^+$ (site 2)	20.37	20.37	-	-	-	-	-	-
$(SOH_2)_2CO_3 = 2SOH + CO_3^{-2} + 2H^+$ (site 1)	-	-	-	-	24.3	24.3	-	-
$SCrO_4^- + H_2O = SOH + CrO_4^{-2} + H^+$ (site 1)	10.85	10.85	11.17 +/- 0.19	*	-	-	9.73365[a]	-
$SCrO_4^- + H_2O = SOH + CrO_4^{-2} + H^+$ (site 2)	10.85	10.85	-	-	-	-	-	-
$SHCrO_4 + H_2O = SOH + CrO_4^{-2} + 2H^+$ (site 1)	-	-	17.11 +/- 0.47	17.83923[a]	-	-	-	12.0387[a]
$SHCrO_4 + H_2O = SOH + CrO_4^{-2} + 2H^+$ (site 2)	-	-	-	-	-	-	-	-
$SOHCrO_4^{-2} = SOH + CrO_4^{-2}$ (site 1)	3.9	3.9	4.05 +/- 0.21	2.90158[a]	-	-	4.22405[a]	3.27294[a]
$SOHCrO_4^{-2} = SOH + CrO_4^{-2}$ (site 2)	3.9	3.9	-	-	-	-	-	-
$SOH_2CrO_4^- = SOH + CrO_4^{-2} + H^+$ (site 1)	-	-	-	-	10.3	10.3	-	-

* This species was determined to have little effect on the model and was eliminated after optimization in FITEQL 4.0. Log K values [a] were optimized in FITEQL 4.0 to accomidate a wider variety of solid concentrations, ionic strengths and sorbent concentrations. **Protonation and deprotonation reactions from Schaller, et al. 2009, Cd+2 adsorption on kaolinite. Cr(VI) adsorption species [a] optimzied in FITEQL 4.0.

Conclusions

- Binary systems containing goethite have sorption near 100% below pH ~6
- Goethite-clay mixtures appear to be dominated by goethite, whereas mixtures of goethite with γ-alumina, HFO, or HMO edges are intermediate based on prior data
- SCMs for kaolinite and montmorillonite mixtures shift the sorption edge indicating the models require further calibration or that mineral-mineral interactions are effecting sorption behavior

Future Work

- Compare SCM predictions for mixtures with HMO, kaolinite and montmorillonite to experimental data & verify model calibrations
- Complete edge experiments on mixtures of all minerals based on equal surface area at atmosphere, 0% pCO_2 and 5% pCO_2 with 0.1 M $NaNO_3$ and 0.01 M $NaNO_3$ and compare with SCM predictions.

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Acknowledgements

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