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

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Anthropogenic activities have caused toxic Cr(VI) contamination of many natural systems. Cr(VI) travels readily in aqueous solution but can be impeded by sorption by reactions with Fe-bearing solids. Subsurfaces are not homogeneous, yet most surface complexation models (SCM) are developed for simple, single substrate systems, and do not account for mineral-mineral interactions. The goal of this study is to measure sorption of Cr(VI) on mineral assemblages of goethite, kaolinite, montmorillonite, γ-alumina, hydrous manganese oxide (HMO), and hydrous ferric oxide (HFO) as a function of pH and $pCO_2$, and to compare measurements to predictions from SCMs developed for single solid systems.

Goethite was synthesized by heating a mixture of KOH and $Fe(NO_3)_3 \cdot 9$ H2O at 70°C for 60 hours [1]; montmorillonite (SWy-2) and kaolinite (KGa-1b) were obtained from the Clay Minerals Society; γ-alumina ($\gamma$-$Al_2O_3$) was purchased from Inframat Advanced Materials; HMO was synthesized by alkametric titration [2] and 2-line HFO was synthesized according to [1]. Synthesized solids were confirmed by XRD and surface area measurements of all solids were completed using 11-point $N_2$BET analysis.

Adsorption edges were measured over a pH of 3.5 to 10, in open atmosphere or under 0% $pCO_2$. Binary mixtures of solids were used based on equal surface area (~5 g/L total solid) with $10^{-5}$ M Cr(VI) and 0.01 M $NaNO_3$. Batch slurries of Cr(VI), $NaNO_3$, and solids were equilibrated for ~1 hr at circumneutral pH. The pH was then lowered to 3.5 by addition of $HNO_3$, and then titrated upward with removal of ~60 mL aliquots of slurry at each ~0.5 pH increment. After 24 hr, 48 hr, 1 week and 2 weeks of mixing, ~15 mL of slurry was removed from each aliquot and the pH rechecked. Each slurry sample was centrifuged, the supernatant syringe-filtered (0.45 μm) and tested for Cr(VI) using the diphenylcarbazide method.

In all systems containing goethite sorption is near 100% below pH ~6. The sorption edge spans from 6-9 pH with <10% Cr(VI) sorbed at pH >9. The pH at which 50% of Cr(VI) is sorbed is ~6.8 for goethite-montmorillonite and increases to ~7.1 for goethite-kaolinite and ~7.7 for goethite-γ-alumina. Edges for the goethite-clay mixtures appear to be dominated by sorption on goethite, whereas mixtures of goethite and γ-alumina result in edges that are intermediate between those obtained for the pure end-member solids; this will also be assessed using component additivity surface complexation modeling.

Adsorption is rapid for goethite-montmorillonite, goethite-γ-alumina and goethite-kaolinite combinations with little change in sorption with increasing aging from 24 hrs to 2 weeks. All systems exhibit little variation in sorption under atmospheric compared to 0% $pCO_2$ conditions.

[1] Schwertmann & Cornell (1991) *Iron Oxides in the Laboratory,* Wiley-VCH, 604 pp.

[2] Stroes-Gascoyne, Kramer & Snodgrass (1987) Applied Geochemistry 2, 217-226.

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# Noble gas and C stable isotopes quash fears over $CO_2$ storage leaks at Weyburn

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In January 2011 it was extensively reported that the Kerr family had been forced to move from their property located above the Weyburn-Midale Monitoring and Storage Project in Saskatchewan, Canada. A geochemical consultant from Petro-Find GeoChem Ltd., who was hired on behalf of the Kerr's, reported measurements of $\delta^{13}C$ ($CO_2$) isotope values in soil gases rich in $CO_2$ which were similar to those of the $CO_2$ injected into the deep oil reservoir. The Petroleum Technology Research Centre (PTRC), who are responsible for the environmental monitoring of the Weyburn $CO_2$-EOR and storage operation, published a detailed response correctly stating that Petrofind had not taken the similar baseline $\delta^{13}C$ ($CO_2$) isotope measurements conducted prior to the injection into account. Also as $\delta^{13}C$ ($CO_2$) is not a unique tracer, there were several other natural sources that could account for the measured values. Whilst this response went some way to addressing the public perception fears raised by the alleged $CO_2$ leakage claims, it was clear that more research was required to re-establish confidence in the safety and security of $CO_2$ stored at Weyburn. This was imperative for both the project itself and the future of $CO_2$ storage. IPAC-$CO_2$ undertook a detailed independent incident response protocol focused on the near surface soil gases, the noble gas composition of the shallow groundwaters and a hydrogeological analysis.

Noble gases are extremely powerful tracers of source and the subsurface processes that act on $CO_2$. They have recently proved to be effective at tracing the migration of natural mantle derived deep $CO_2$ up a fault above the St. Johns Dome-Springerville $CO_2$ reservoir in Arizona [1]. A clear component of the helium fingerprint observed in the gaseous $CO_2$ contained in the deep reservoir could be traced in waters from both the groundwater wells and the springs emerging at the surface above the reservoir.

Here we use similar methodology to investigate the alleged leakage and we report noble gas and carbon stable isotope measurements from four groundwater wells surrounding the Kerr quarter, near Goodwater in Saskatchewan. We compare these to the noble gas and carbon isotope composition measured from fluids sampled from a production well and $CO_2$ and water from enhanced oil recovery injection wells associated with the Weyburn-Midale oil field, located near to the Kerr quarter. To determine if migration of dissolved $CO_2$ from the Weyburn oil field is responsible for the alleged $CO_2$ anomaly, we compare the noble gas and carbon stable isotope tracers in the water and $CO_2$ injected into the oil field, and the fluids produced from the field, with those measured in the groundwater well waters.

We find no evidence in any of the noble gas data that there is any presence of deep crustal derived noble gases within the groundwaters surrounding the Kerr quarter. The absence of crustal derived noble gases derived from depth means that there is no evidence of the migration of $CO_2$ from the Weyburn oil field into the groundwater on the Kerr quarter or surrounding area.

[1] Gilfillan et al., (2011) *IJGCC*, **Volume 5**, Issue 6, p 1507-1516