THE EFFECT OF ANIONS ON THE ADSORPTION OF COPPER AND ZINC ONTO GOETHITE

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INTRODUCTION

The adsorption of metals onto mineral surfaces (i.e., goethite) is an important process that can influence the mobility of metals in the regolith. This process has implications and potential impacts in areas such as mineral exploration geochemistry, minerals processing, groundwater contamination (including heavy metal remediation from soils and solution), acid mine drainage and acid sulfate soils.

The mobility of metals is controlled by groundwater conditions (i.e., groundwater flow, pH, salinity) as well as dissolution/precipitation and adsorption properties of minerals. Adsorption is likely to be an important process occurring in the regolith (Cairns *et al.* 2001), but the number of studies focussing adsorption in natural systems is limited. While the adsorption of metals onto minerals from experiments is well documented (e.g., Yates 1975, Kooner 1993), these were often conducted in inert electrolyte solutions such as KNO_3, $NaNO_3$ or $NaClO_4$ to discourage the formation of aqueous metal complexes and surface complexes at the mineral surface. While these studies provide valuable data for understanding adsorption reactions, they do not reflect natural groundwater conditions. Efforts to understand the effect of anions commonly present in groundwater on the adsorption of metals onto mineral surfaces have been made but results from different studies conflict (e.g., Barrow *et al.* 1982, Balistrieri & Murray 1982, Crisenti & Sverjensky 1999) and there is uncertainty of the effect various anions have on metal adsorption.

This paper presents experimental data examining the effect of anions (Cl^- and SO_4^{2-}) on the adsorption of oxidised copper and zinc onto synthetic goethite. It aims to answer the question of whether anions enhance or suppress metal adsorption and to illustrate how this knowledge may be applied to natural systems.

METHODS

Adsorption experiments were conducted as a series of between 11 and 12 individual experiments. Goethite (0.075 g) was added to a 125 mL glass reaction vessel with 80 mL of 10 ppm Cu^{II} or Zn in 0.1-5.0 molal NaCl or 1×10^{-3}-1.0 molal Na_2SO_4 solutions. The pH was adjusted accordingly using either 0.1 M HNO_3 or 0.1 NaOH. pH was measured using a Thermo Orion 290A+ pH Meter and ROSS Sure Flow electrode. The reaction vessel was sealed with a Dreschel head and placed in a water bath at 25 ± 0.1°C to maintain constant temperature. Nitrogen gas was passed through each reaction vessel to provide an inert atmosphere and to minimise the effect of dissolved CO_2 adsorption onto goethite. The goethite solution was left for 16 hours to ensure that the equilibrium between goethite and the dissolved metal was achieved. At the end of the experiment, 30 mL of solution was withdrawn from the reaction vessel and filtered with a 0.45 μm syringe filter before being analysed for copper or zinc using Inductively Coupled Plasma-Atomic Emission Sprectrometry (ICP-AES).

EXPERIMENTAL RESULTS

The adsorption of copper and zinc in the range of Na_2SO_4 solutions studied increases with increasing pH, which is typical for the adsorption of metals onto goethite (Dzombak & Morel 1990). A given degree of adsorption occurs at more alkaline pH for zinc than copper, which is consistent with previous adsorption studies of these metals (e.g., Balistrieri & Murray 1982, Kooner 1993) (Figure 1).

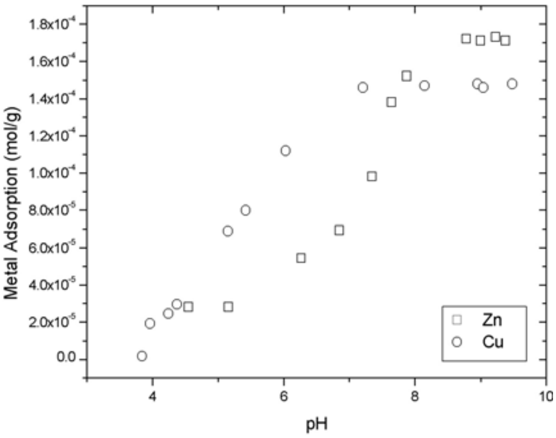

Figure 1: Concentration of adsorbed Cu^{II} and Zn onto goethite in 0.01 molal Na_2SO_4. Experimental conditions are total metal concentration of 10 ppm, 0.98 g/L goethite, 1 atmosphere at 25°C.

No discernable change to the copper adsorption curve occurred when the Na_2SO_4 concentration increased, suggesting that the concentration of SO_4^{2-} has little effect on the adsorption of copper onto goethite. However, the adsorption curve for zinc moved towards more alkaline pH when the Na_2SO_4 was greater than 0.1 molal (Figure 2), indicating that SO_4^{2-} suppressed

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zinc adsorption by approximately 50%.

In NaCl solutions, zinc adsorption is more complex. Adsorption increased with increasing pH over the entire pH range studied, as observed in Na_2SO_4 solutions; however, it also increased by 60% with increasing NaCl concentrations between 0.1 molal and 1.0. However this trend reversed at still higher salinities and in solutions with 4 molal NaCl, zinc adsorption decreased by approximately 70% (Figure 3).

Copper adsorption in NaCl solutions shows a similar behaviour to the zinc, although the adsorption curve for copper was again more complex (Figure 4). Copper adsorption was enhanced at pH < 5 over the entire NaCl range studied, forming a distinctive “knee” in the adsorption curve. Adsorption was increased by 20-30 times at 2 molal NaCl, before decreasing again at NaCl concentrations between 2 and 5 molal.

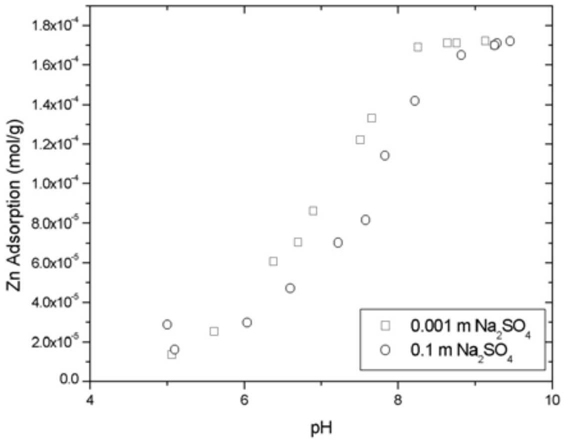

Figure 2: Adsorption of Zn onto goethite in 0.001 and 0.1 molal Na_2SO_4. Zn adsorption is suppressed as the Na_2SO_4 concentration increases. Experimental conditions are total Zn concentration of 10 ppm, 0.98 g/L goethite, 1 atmosphere at 25°C.

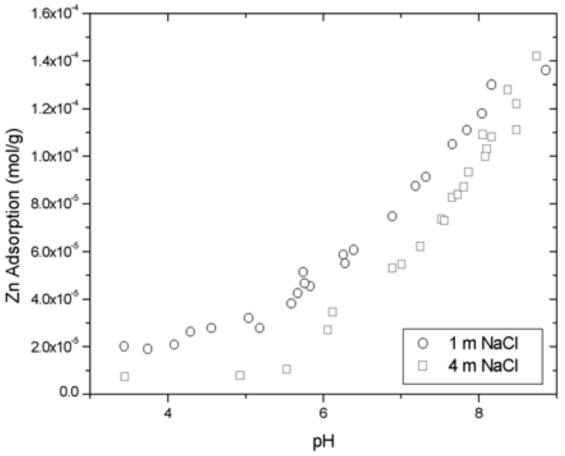

Figure 3: Adsorption of Zn onto goethite in 1 and 4 molal NaCl. Adsorption is reaches a maximum at 1 molal NaCl, and decreases in NaCl concentrations >1 molal. Experimental conditions are total Zn concentration of 10 ppm, 0.98 g/L goethite, 1 atmosphere at 25°C.

GEOCHEMICAL MODELLING

Geochemical modelling is a tool that can be used to help understand the reactions that occur in experiments. A model represents the total adsorbed and dissolved metal as the sums of several distinct chemical complexes on the surface and in the bulk liquid, whose relative activities are linked through thermodynamic equilibria. The fitted thermodynamic properties for these species can be used to interpolate between experimental conditions, or even extrapolate beyond the conditions of experiments. In addition, modelling is a validation tool that can test the reliability of experimental data provided there is a sufficient range of experimental conditions available.

We present geochemical modelling data for the copper adsorption onto goethite in 2 molal NaCl (Figure 5) and zinc adsorption in 1 molal NaCl (Figure 6). Describing the formation of surface complexes is similar to the formation reactions used to express aqueous complexes. For example, the formation reaction for the $SOCu^+$ copper surface complex can be described by the reaction:

$$SOH + Cu^{2+} = SOCu^+ + H^+ \qquad (1)$$

“S” in Equation 1 is a cation at an adsorption site on the mineral surface.

The enhanced zinc adsorption in 1 molal NaCl in acid conditions (pH < 5.5) is predicted to be caused by the formation of $SOHZnCl_2$ surface complex; however, when the pH increases above 5.5, the predominant surface species changes to $SOHZn^{2+}$.

The enhanced adsorption of copper in NaCl solutions is also caused by changes to the surface complexes as a function of pH. The model indicates that formation of copper chloride surface complexes is responsible for the enhanced copper adsorption in NaCl solutions at pH values < 5. The “knee” that occurs at pH < 5 is predicted to be caused by changes of predominant copper chloride species from $SOHCuCl^\circ$ to $SOCu^+$ at approximately pH 5.7.

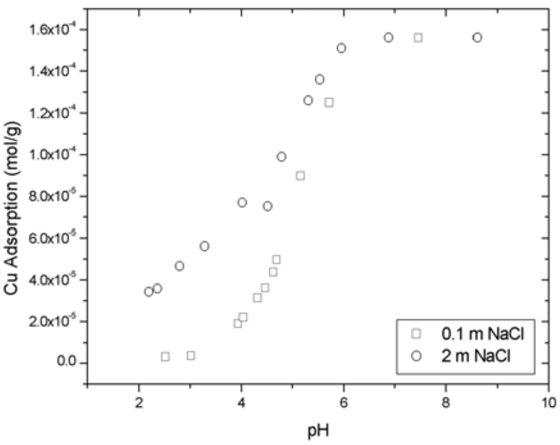

Figure 4: Adsorption of Cu^{II} onto goethite in 0.1 and 2 molal NaCl. Adsorption is enhanced in NaCl concentrations greater than 0.1 molal, reaching a maximum at 2 molal NaCl. Total Cu^{II} concentration 10 ppm, 0.98 g/L goethite, 1 atmosphere at 25°C.

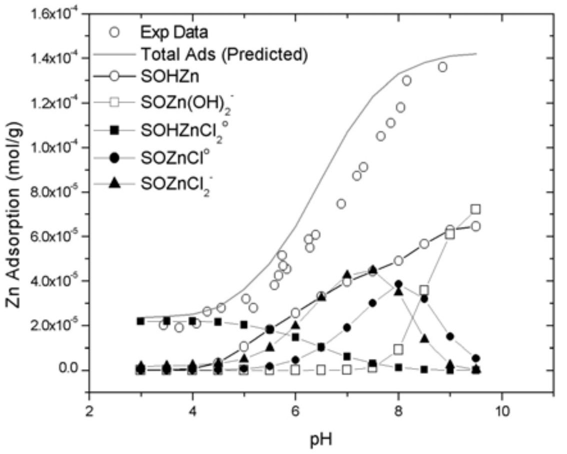

Figure 5: Geochemical modelling results of Cu^{II} adsorption in 2 molal NaCl showing the distribution of copper-chloride surface complexes on goethite. Model parameters are total Cu^{II} concentration of 10 ppm, 0.98 g/L goethite, 2 molal NaCl, total goethite surface area of 36.05 m^2/g, adsorption site density of 16.4 sites/nm^2.

APPLICATIONS TO NATURAL ENVIRONMENTS

We apply the thermodynamic properties for the formation of copper surface complexes to the Lake Tyrrell district in Victoria, Australia. Salinities in the Lake Tyrrell area range between near sea-water to halite saturation, corresponding to NaCl concentrations of approximately 0.02 to 5.6 molal, while the pH of groundwater ranges between approximately 2.5 and 4.5 (Long *et al.* 1992, Lyons *et al.* 1992).

We calculated the concentration of adsorbed copper between 0.1 and 5 molal NaCl at pH 2.5, 3 and 4; with 3 ppm dissolved copper and 40 g/L goethite. The results are shown in Figure 7. The highest predicted concentration of adsorbed copper was 44 ppm at 1 molal NaCl at pH 4. As the NaCl concentration increased, the concentration of adsorbed copper was predicted to decrease due to the formation of $CuCl_2(aq)$ and $CuCl_3^-$ aqueous complexes. Therefore, copper adsorbed in a moderately saline environment may be remobilised if the groundwater conditions change to become either fresh or more saline. However, dissolved copper may be trapped on the surface of goethite if, for example, fresh water becomes more saline, or highly saline waters are diluted or there is mixing of hypersaline and fresh water.

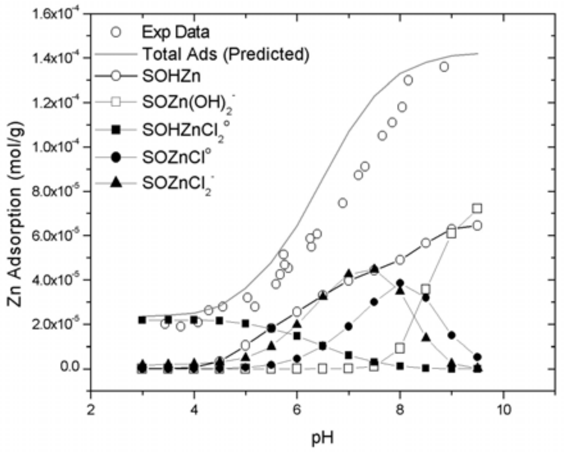

Figure 6: Geochemical modelling results of Zn adsorption in 1 molal NaCl showing the distribution of zinc and zinc-chloride surface complexes on goethite. Model parameters are total Zn concentration of 10 ppm, 0.98 g/L goethite, 1 molal NaCl, total goethite surface area of 36.05 m^2/g, adsorption site density of 16.4 sites/nm^2.

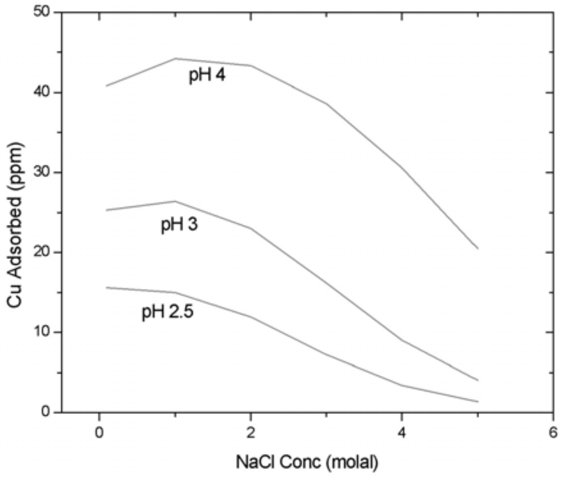

Figure 7: Predicted concentrations of copper in goethite rich sediments at Lake Tyrrell. Model parameters are 3 ppm dissolved Cu^{II}, 40 g/L goethite, pH 2.5, 3 and 4, goethite surface area of 36.05 m^2/g and adsorption site density of 16.4 sites/nm^2.

CONCLUSION

The results presented show that anions affect the adsorption of copper and zinc onto goethite. NaCl has a greater influence on copper and zinc adsorption onto goethite than Na_2SO_4. The largest increase in adsorption occurred with Cu^{II} adsorption onto goethite in 2 molal NaCl, where adsorption was enhanced by 20-30 times in acidic pH (< 5). The largest increase in Zn adsorption was in the 1 molal NaCl experiment where a 60% increase in adsorption was noted.

In contrast to experiments with NaCl, zinc adsorption was suppressed by up to 50% when the concentration of Na_2SO_4 was greater than 0.1 molal. No change to the adsorption of copper in Na_2SO_4 was observed, suggesting that the concentration of SO_4^{2-} has little effect on Cu^{II} adsorption.

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