Modelling Cu, Zn, Cd and Pb Adsorption by Iron Oxyhydroxides in SO$_4$-rich Systems Simulating Acid Mine Drainage.

Peter Swedlund

February 2004

THE UNIVERSITY OF AUCKLAND
NEW ZEALAND

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy.

For the cygnets and the swan.

"Such great happiness I never dreamed of,

When I was but the ugly duckling."

(Anderson, 1844)

ABSTRACT

Acid mine drainage (AMD) typically involves waters with low pH (pH 2-4) and high concentrations of Fe, SO_4 and potentially toxic trace metals. Adsorption onto iron oxyhydroxides is the dominant mechanism controlling the transport and toxicity of trace metals in water bodies impacted by AMD. The purpose of this study was to apply the Diffuse Layer Model (DLM) to describe the adsorption of trace metals by iron oxyhydroxides from these systems, using synthetic iron oxyhydroxide minerals, ferrihydrite, pure acicular goethite, SO_4-rich goethite prepared from $FeSO_4$ oxidation and a synthetic schwertmannite.

The ferrihydrite adsorption of the trace metals Cu, Zn, Cd and Co from single sorbate systems was accurately described using the DLM with two surface site types (type-1 and type-2) having site densities of 0.005 and 0.2 mol (mol Fe)$^{-1}$ respectively. The ferrihydrite adsorption of SO_4 from single sorbate systems was accurately described using the DLM with adsorption on the type-2 sites. However, the enhanced adsorption of Cu, Zn, Cd and Co in the presence of SO_4 was not predicted using adsorption constants derived from single sorbate systems. By including a neutral ternary complex with stoichiometry $\equiv Fe_{(2)}OHMeSO_4$ (where $\equiv Fe_{(2)}OH$ is a type-2 surface site and Me is the trace metal) the effect of SO_4 on metal adsorption was accurately described for the range of Me, Fe and SO_4 concentrations studied. The adsorption of Cu and Zn onto schwertmannite at total metal to iron ratios (Me_T:Fe) up to 8×10^{-3} was almost identical to that predicted for ferrihydrite in the presence of 0.01 mol kg^{-1} SO_4. To model the ferrihydrite adsorption of Pb from single sorbate systems a third higher affinity site (type-0) with a site density of 0.00035 mol (mol Fe)$^{-1}$ was required. The effect of SO_4 on Pb adsorption could only be modelled by including a neutral ternary complex on both the type 1 and type 2 sites in the case of Pb.

Metal adsorption onto a pure acicular goethite could be accurately described by the DLM with two surface site types. The type 2 site density that provided the best fit to the goethite adsorption data was 0.027 mol (mol Fe)$^{-1}$ corresponding to 2.3 nm^{-2}. The type-1 site density that provided the best fit to goethite adsorption of Cu, Pb and Cd was 0.00028 mol (mol Fe)$^{-1}$ corresponding to 0.024 nm^{-2}. For Zn adsorption on goethite the type-1 site density was significantly larger at 0.0015 mol (mol Fe)$^{-1}$ corresponding to 0.13 nm^{-2}. In all cases studied the presence of SO_4 caused an increase in the extent of metal adsorption by goethite. This increased adsorption of metals in the presence of SO_4 was accurately predicted by including ternary complex formation at both the high and low affinity adsorption sites.

For both ferrihydrite and goethite the values of adsorption constants for ternary complex formation ($logK_{xMe}^{TC}$) were related to the adsorption constant for metal adsorption in the absence of SO_4 ($logK_{xMe}^{INT}$). This was evident from a plot of $logK_{xMe}^{TC}$ as a function of $logK_{xMe}^{INT}$ for all metals, which showed a linear relationship with slope of 0.69 and intercept of 8.03. This relationship suggests that the enhancement of metal adsorption on both oxyhydroxides due to SO_4 occurs by the same process.

When comparing Cu, Zn and Cd adsorption onto ferrihydrite and acicular goethite the effect of the larger goethite adsorption constants are approximately compensated for by the lower goethite site densities. Therefore the Cu, Cd and Zn adsorption isotherms on ferrihydrite and acicular goethite are fairly similar at low adsorption densities. In the case of Pb, the site densities and adsorption constants are both larger on ferrihydrite and there is a large difference between the ferrihydrite and acicular goethite adsorption isotherms.

Sulfate-rich goethite had considerably higher site densities, per mol of oxide, than the pure acicular goethite. Adsorption onto the sulfate-rich goethite could be modelled reasonably accurately using the parameters developed to model adsorption onto the pure acicular goethite but with a higher surface area and a higher ratio of type-1 to type 2 sites. In general, therefore, the parameters developed for pure goethite are apparently similar to those for the sulfate-rich goethite, but are not directly transferable. The difficulty in measuring the surface area of the highly aggregated sulfate-rich goethite makes comparisons between the two goethites more difficult.

The adsorption of Cu, Zn and Cd onto the SO_4-rich goethite exceeds that of ferrihydrite because the higher adsorption constants of goethite are combined with the considerably higher site densities of the SO_4-rich goethite compared to the acicular goethite. In contrast the higher site densities of the SO_4-rich goethite does not completely compensate for the low $logK^{INT}$ values of Pb adsorption on goethite. Therefore SO_4-rich goethite adsorption of Pb is lower than that of ferrihydrite.

When applied to literature data from AMD oxides the parameters derived in this thesis have significantly improved the ability of the DLM to predict trace metal adsorption in AMD systems, compared to using ferrihydrite as a proxy for all iron oxyhydroxides and adsorption data derived only from single sorbate systems.

Acknowledgements

There are many people who have contributed to this work. Firstly I must express my great gratitude to my primary supervisor, J.G. Webster, for her unstinting support and enthusiasm. Jenny is one of the rare people with insight into the somewhat parallel almost impenetrable complexities of both environmental systems and bureaucracies. This has made her an excellent supervisor. G.M. Miskelly was an invaluable 2IC, always happy to be accosted with numerous and diverse questions and was highly skilled at finding my deliberate mistakes. And lastly Jim Metson. Thanks for showing me some of the trickier tricks of trade, could be useful one day. However, next time you look a prospective student in the eye and declare your "great interest in the project" you should, in all fairness, explain that this "great interest" is purely pecuniary.

This brings me to those people who have helped me survive. Christina Clapp suffered my interminable ranting for nigh on three years. I'll take your secret to the grave; well no one I tell believes it anyway. Geoff Waterhouse and I had to consume chemical substances to alleviate the symptoms and spent many a happy hour discussing creative solutions to the problem. Damien, Baek, Chen and Nicole were all "brothers in arms" and Friday afternoons at OGH were very enjoyable times. Glenn Boyes, Vincent Lane, Paul Butler, Noel Renner, Peter Buchanan, Jeff Boyle, Shane Crump, Catherine Hobbis, "Briney" James, Prof. O'Connor, Assoc. Prof. Wright, Ritchie Simms and may others helped in various capacities along the way. Thanks.

Finally the family. Dad assisted every Saturday night with the always-appreciated Chinese takeaways and beer and refrained from the vengeful refrain "Are you there yet? Are you there yet?". Jane is to me as the periodic table is to chemistry, bringing understanding and structure to an otherwise dizzyingly incomprehensible confusion. Our children, Hannah and Ruskin, bring the dizzyingly incomprehensible confusion without which life would be dull. The elusive perfect balance. I am, in my opinion, the luckiest man in the world.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

List of Abbreviations

σ	Surface charge ($C\ m^{-2}$)
Ψ	Surface potential (V)
γ_x	Activity coefficient for species x
A^{2-}	Divalent anion
AAS	Atomic adsorption spectroscopy
AMD	Acid mine drainage
ARD	Acid rock drainage
ATR-IR	Attenuated total reflectance infrared spectroscopy
DLM	Diffuse layer model
EDL	Electric double layer theory
$\equiv Fe_{(x)}OH$	A type x surface hydroxyl group
GFAAS	Graphite furnace atomic adsorption spectroscopy
IC	Ion chromatography
ICPMS	Inductively coupled mass spectrometry
LFER	Linear free energy relationship
$logK_{A1}^{INT}$	First acidity constant of a surface hydroxyl group
$logK_{A2}^{INT}$	Second acidity constant of a surface hydroxyl group
$logK_{xMe}^{TC}$	Log of the formation constant for $\equiv Fe_{(x)}OHMeSO_4$
$logK_{xMe}^{INT}$	Log of the formation constant for $\equiv Fe_{(x)}OMe^+$
Me	A divalent trace metal
Me_{ads}	Adsorbed metal
Me_{aq}	Dissolved metal
Me_T	Total metal concentration i.e. dissolved plus adsorbed
N_s	Total site density
N_{sx}	Site density of type x sites
PPZC	Pristine point of zero charge
SEM	Scanning electron microscopy
s_T	Estimated error in total component concentration
s_X	Estimated error in species concentration
TLM	Triple layer model
TOTH	Total proton concentration
WSOS/DF	Weighted sum of squares divided by the degrees of freedom
XRD	X-ray diffraction
Y_X	The difference between the calculated and measured value of x