Stability and surface structure of adsorbed REE complexes onto schwertmannite

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Introduction & Objectives

Background

Rare Earth Elements (REE) and Yttrium (REY) are raw materials critical for the development of modern technological industries. REY contents in aqueous environments affected by oxidative weathering of pyrite (i.e. acid mine drainage (AMD)) are several orders of magnitude above those of natural waters. The high REY concentration makes AMD a suitable target as a secondary source of these raw materials.

Schwertmannite ($Fe_8O_8(OH)_6SO_4$) is a poorly crystalline Fe(III) oxyhydroxysulfate that commonly occurs in AMD. It has been proved to be a sink for oxyanions (i.e. arsenates and chromates) and aqueous REY sulfate complexes due to its high surface area.

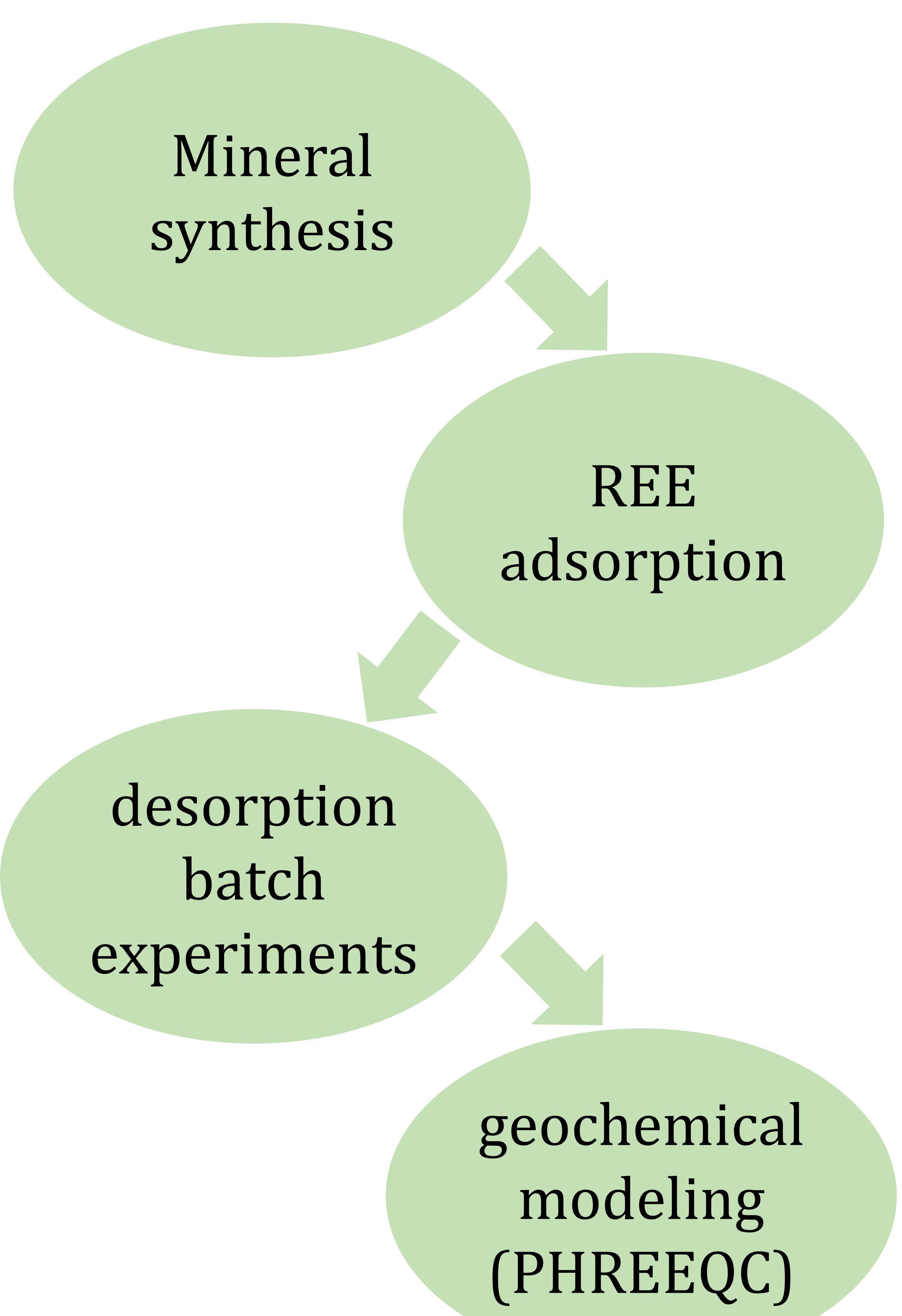
Environments where AMD is mixed with seawater, e.g. the Odiel estuary (south Europe), provide adequate conditions for REY adsorption onto schwertmannite.

Schwertmannite precipitates in AMD passive treatments.

Objectives

1) To study the capacity of schwertmannite to retain adsorbed REY at different pH
2) To determine the log K values for the desorption reactions.

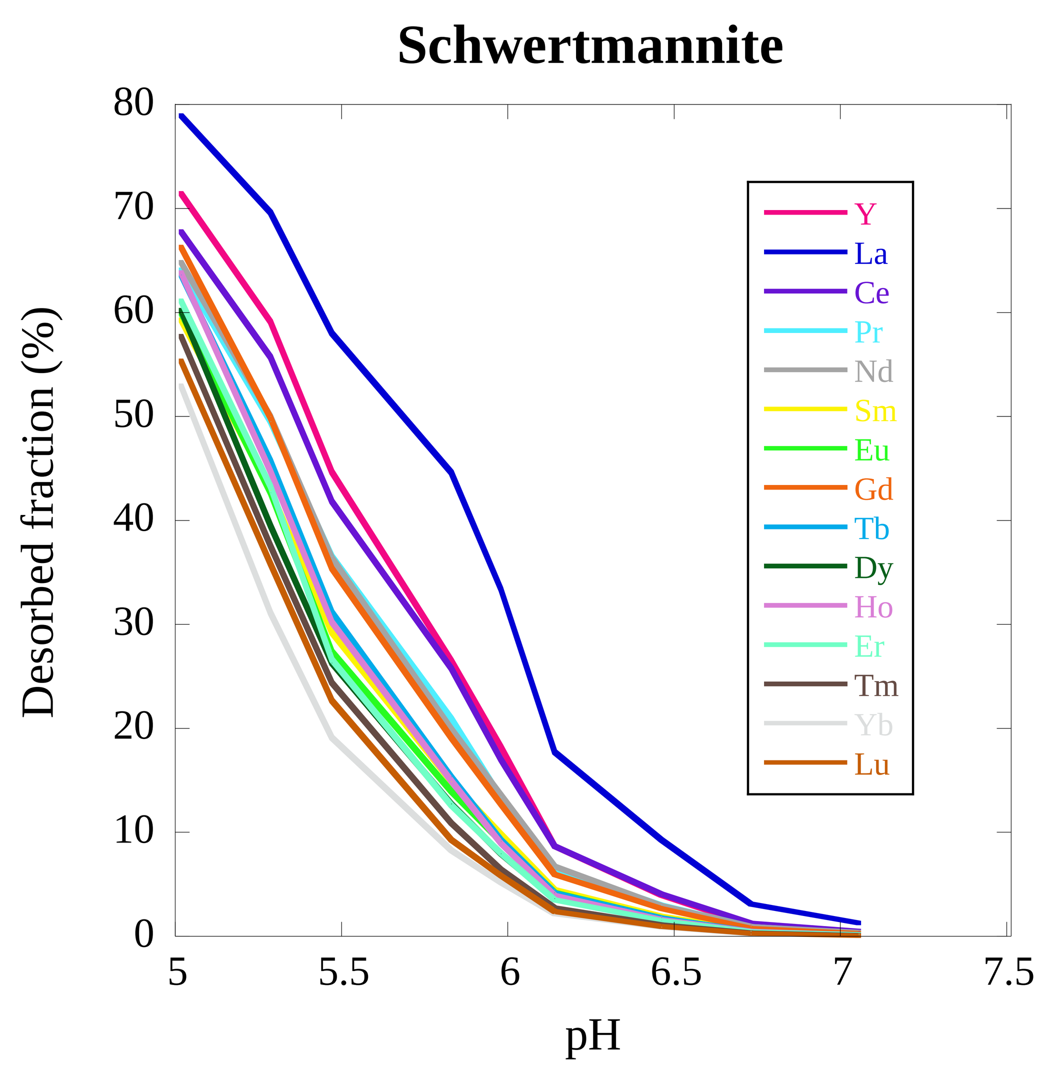
Methodology



Results & discussion

Desorbed fraction

Results from the single point batch experiments showed that the REY retention on schwertmannite is highly dependent on pH. 55 - 80% of the adsorbed REY is released back into the water at pH of ~5, whereas at pH of ~6.5 – 7 the release is less than 5%.
Moreover, heavy REE are less desorbed than light REE.



Experimental results: desorbed REY fraction as a function of pH.

Model description

In the desorption reactions, n aqueous protons are exchanged with the sorbed REE complex (RSO_4^+, R is equivalent to each REE):

$$(XO)_nRSO_4^{1-n} + nH^+ \leftrightharpoons RSO_4^+ + nXOH$$

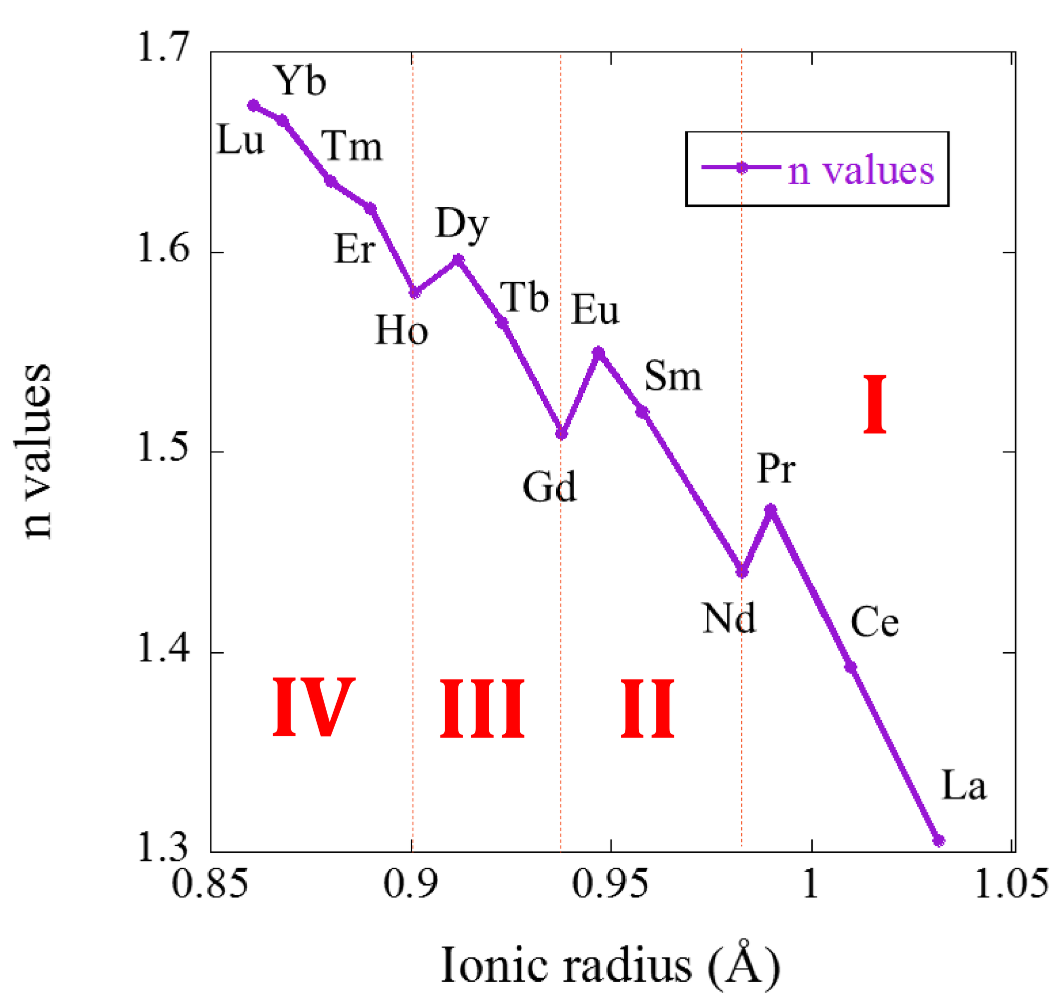
In monodentate complexes, one surface site adsorbs an aqueous complex (n=1) whereas in bidentate complexes two sites are used (n=2).

The reactions are:

$$XORSO_4^0 + H^+ \leftrightharpoons RSO_4^+ + ROH \qquad K_R$$

$$(XO)_2RSO_4^- + 2H^+ \leftrightharpoons RSO_4^+ + 2XOH \quad K_R$$

However, the derived n values (≈ 1.5) suggest the occurrence of both monodentate and bidentate complexes.

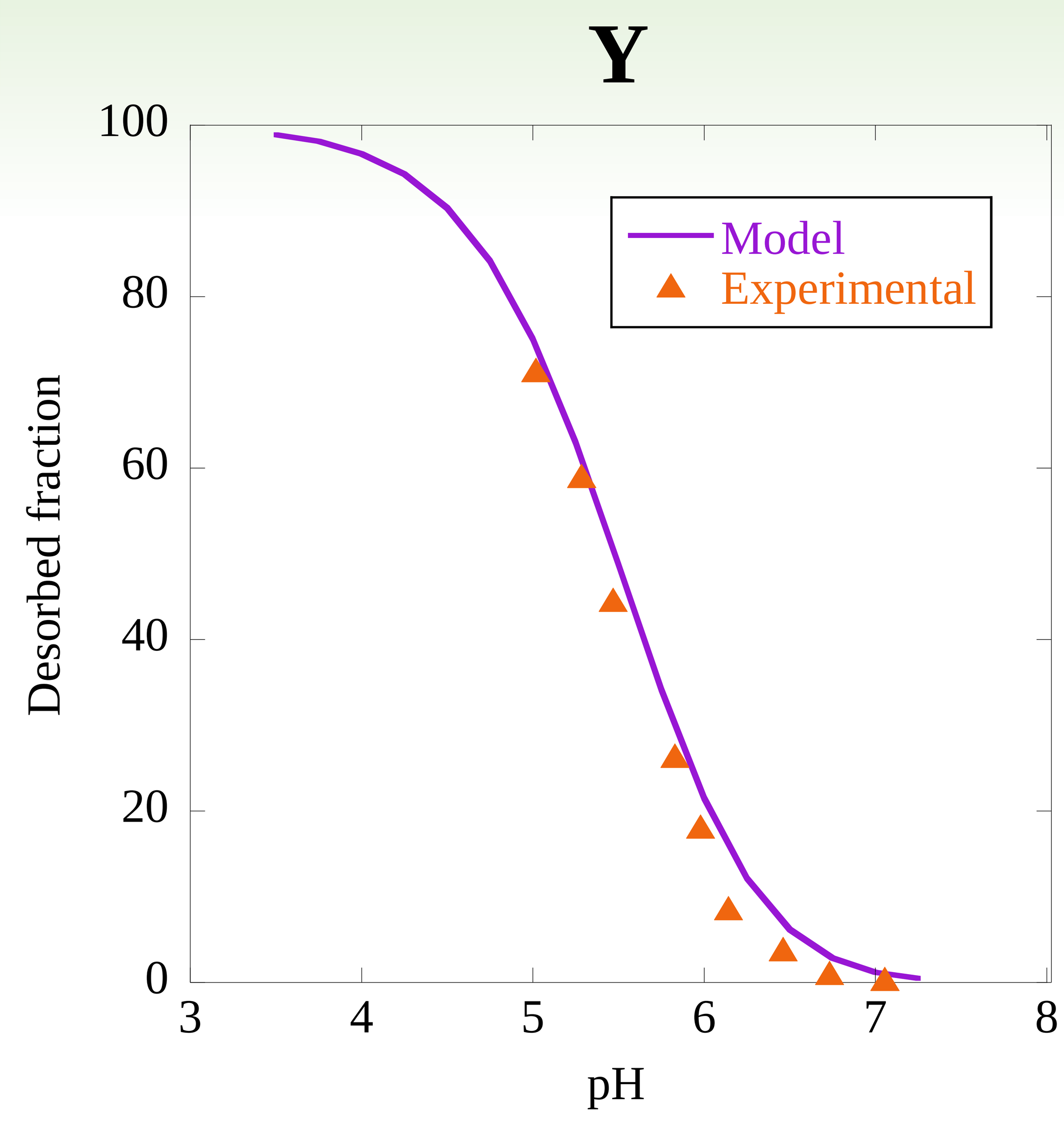


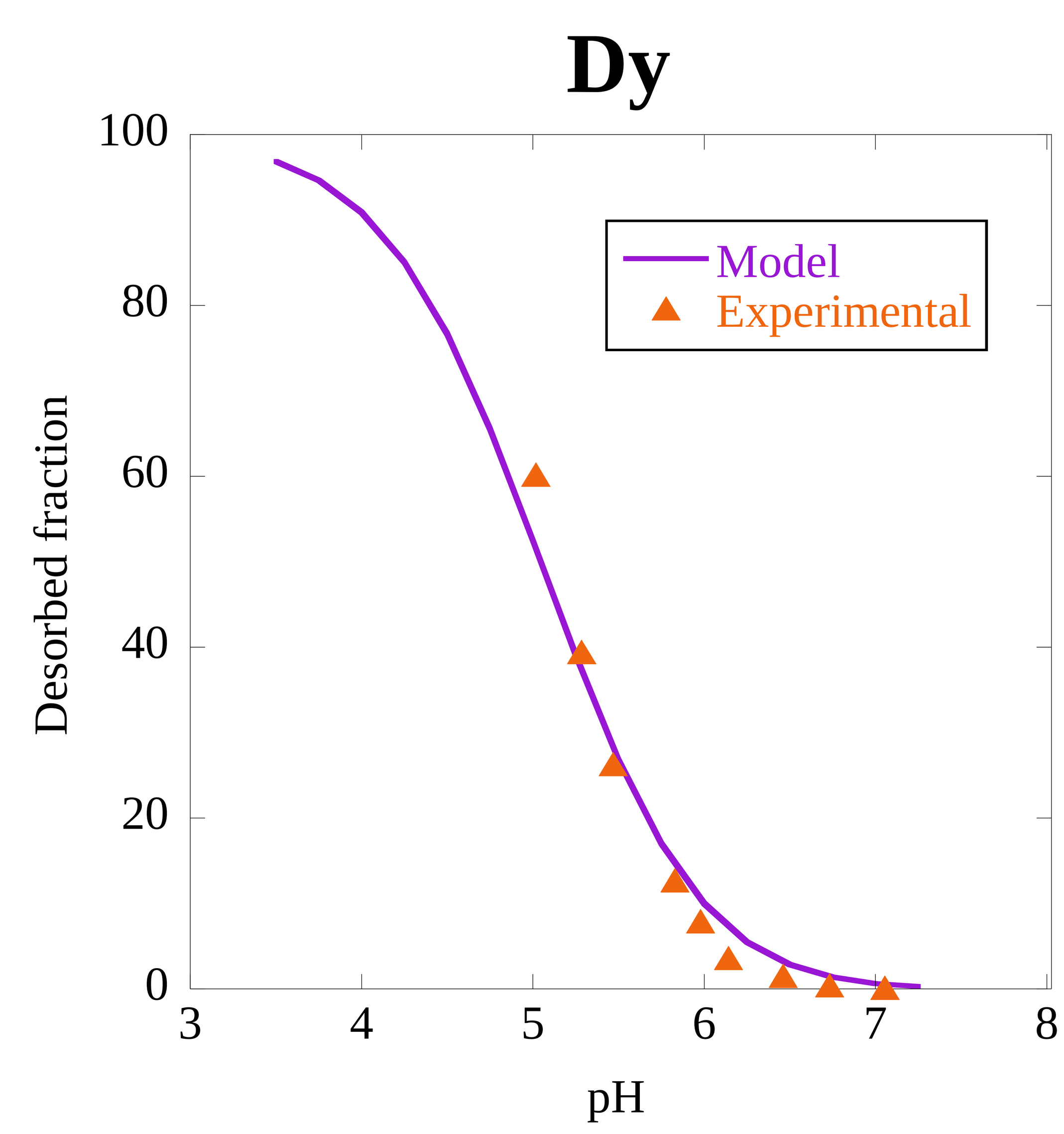
n values as a function of REE ionic radius.

PHREEQC modelling

Both reactions have an equilibrium constant associated (K_R) for each REE that can be obtained with the experimental data from the desorption experiments.

To validate the equilibrium constants, a geochemical model have been performed using PHREEQC code, and logK values from both reactions. These are the results for Y and Dy:





Model and experimental desorbed REY fraction as a function of pH: a) Y and b) Dy.

What's next?

The next step is to analyze, using synchrotron radiation at the ESRF facilites, the schwertmannite obtained from the desorption experiments to validate that both bindings (monodentate and bidentate) are occurring.

Acknowledgements

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