Nickel adsorption on chalk and calcite: Pure synthesised vs biogenic material

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Because of their high reactivity and wide occurrence, calcite bearing rocks are good candidates to be used as sorbents for removing heavy metals from aqueous solutions, and the properties of synthetic calcite are often used to predict the properties of these rocks. However, pure synthetic calcite is a questionable model for natural material, especially because most natural calcite is biogenic and has impurities associated with its surface.

Our aim was to investigate the extent of Ni adsorption on synthetic calcite and compare it with results on chalk, rock that consists of >96% $CaCO_3$, mostly as <1 μm biogenic crystals. Batch sorption experiments were performed in calcite or chalk equilibrated solutions at atmospheric CO_2 partial pressure, ranging pH (7.7–8.8) and 25 °C. To describe the data, a surface complexation model was used and Ni surface stability constants were calculated with FITEQL 4.0.

The results showed that Ni uptake by chalk follows roughly the same pattern as on calcite. Adsorption increased with increasing pH and surface area. However, the difference in Ni sorption density ($\mu mol \cdot m^{-2}$) for chalk and calcite suggests that BET surface area is not a good estimate for reactive surface area in porous biogenic carbonates.

The surface complexation model provides a good fit for the data. Although all samples are composed mainly of calcite, their stability constants are quite different: $\log K_{Ni} = -0.50$ and -0.43 for the chalk from two locations compared with $\log K_{Ni} = -1.12$ for calcite [1]. This can be explained by the presence of organic compounds and clay particles on the chalk surface, which were detected by XPS for both chalk samples. Including montmorillonite into the model resulted in $\log K_{Ni}$ values for chalk closer to those of synthetic calcite.

The data show that trace amounts of polysaccharides and clays on the chalk surface must be considered for accurate modelling of heavy metal behaviour and that ideal solids are quite probably not trustworthy for predicting the behaviour of natural materials.

[1] Belova et al. (2014), *J. Contam. Hydrol.* **170**, 1-9.