A calorimetric analysis of sulfate adsorption on ferrihydrites: the influence of aluminum substitution

NADINE KABENGI [1,2*] AND ALIREZA NAMAYANDEH [2, 3]

[1] Georgia State University, Department of Geosciences, Atlanta, GA 30303 USA (kabengi@gsu.edu)
[2] Georgia State University, Department of Chemistry, Atlanta, GA 30303, United States
[3] Virginia Tech, Department of Geosciences, Blacksburg, VA 24061, United States (anamayandeh@vt.edu)

The substitution of aluminum (Al) in the ferrihydrite structure impacts its structure, composition, and sorptive properties. Herein we report on a well-resolved calorimetric study on the influence of Al on sulfate adsorption and reversibility. Microcalorimetry experiments were conducted at pHs 3.0 and 5.6, along with a detailed characterization of all samples. By using the total energies of the calorimetric peaks associated with the displacement of probe ions known to undergo completely reversible reactions (as determined by the congruence of their thermal signature in terms of reactions times, peaks areas and enthalpies), we have obtained quantitative insights into the properties of the surface charge, as well as the adsortion and irreversibility of sulfate with 0, 12 and 24 mol % Al. We hypothesized that increasing Al% increases defect sites and these tend to be mostly singly coordinated which favor inner-sphere complexation, and which was observed. in situ calorimetric measurements are excellent probes of surfaces. They allow for the continuous monitoring, with high sensitivity and accuracy, of changes in chemical reactivity due to small transformations in underlying structures.