

1.6.P02

Transformation of Fe(III)-hydroxide to more stable phases at conditions representative of hydrothermal solutions

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Fe(III)-oxides and hydroxides are present in nearly all geological environments and even small quantities on fractures or on sediment surfaces are visible by their strong colour. Their high surface area, their small particle size and their reactivity makes them important in the uptake and retention of trace components, including organic compounds such as pesticides and fertilisers as well as heavy metals and radionuclides. Transformation from one phase to another has the potential of releasing adsorbed or incorporated material back to the fluid phase. Thus, parameters describing phase transformation and their dependence on solution conditions are necessary before accurate predictive models can be made for contamination risk assessment.

We studied the transformation of ferrihydrite to goethite and hematite during exposure to saline solutions at 70° C. Changes in morphology, structure and particle size were monitored using atomic force microscopy (AFM) and X-ray diffraction (XRD) with Rietveld refinement. We examined phase transformation in solutions with pH 4, 7, 9 and 12, in solutions where silica was absent, where dissolved silica was added before treatment but after precipitation of the ferrihydrite and where dissolved silica was added before precipitation began. Silica is a known inhibitor of amorphous Fe-hydroxide transformation but the effect of high salinity is not well documented.

Goethite was favoured at low and high pH, as expected from published work. Hematite was preferred in the middle ranges. Transformation was complete after a few days in silica free solutions, but took longer when silica was present. Higher salinity had little effect on transformation in the silica free solutions but seemed to enhance transformation when silica was present over what was expected from published work on rinsed synthetic solids. When the solution was supersaturated with respect to silica, allowing the formation of colloidal particles, the ferrihydrite precipitated on them and was not transformed, even after many days of treatment.

These observations confirm that silica retards the transformation of ferrihydrite, even at higher salinity so in nature, ferrihydrite that precipitates on a silica substrate is not as likely to transform as that precipitating in a free solution in the laboratory. Thus, contaminants immobilised by Fe(III)-hydroxides in a saline environment where silica is present, such as the leachate from a landfill percolating through soil, for example, is likely to be more stable than predicted by laboratory data derived from pure, synthetic systems.

1.6.P03

Study on the heterogeneity of surface energy of Titania nanoparticles by means of probe gas adsorption isotherms

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Since the photocatalytic activity of anatase is discovered by Fujishima in 1972, Titania nanoparticles has recently attracted a great deal of attention in the field of environmental engineering. The material properties, including congregation pattern, surface reactivity, adsorption behavior, are determined by surface energetic heterogeneity of particles. In this study, three samples of lab-synthesized nanoparticles of anatase and rutile were analyzed by the means of N₂ adsorption isotherms. And INTEG method[1], FHH method [2] were employed to process the low-pressure segments of the adsorption isotherms in order to obtain the adsorption energy distribution and fractal dimension, respectively. It is found that the fractal dimension is determined by the size of particles. The values of fractal dimension of anatase and rutile particles with diameter of 40nm are 2.65 and 2.69 respectively, while that of anatase particles with diameter of 300-600nm are 2.46. It is also discovered that the adsorption energy distribution (AED) is controlled by the mineral composition and the shape of crystals, and is not influenced by the particle size. The AED of anatase particles with diameter of 40nm is similar to those of 300-600 micron, and can be distinguished from the AED of rutile particles with diameter of 40nm. By combining the AFM observation, the peaks of higher energy and lower energy in the AED of anatase (Figure 1) could be assigned to {101} surfaces and {110}, {100} surfaces, respectively. There is also a peak of much higher surface energy (13kJ/mol), which is attributed to the defects in the crystal.

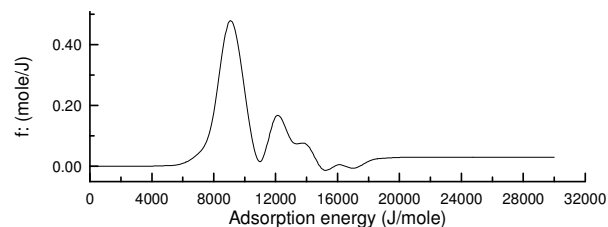


Figure 1 AED of rutile particles with diameter of 40 nm

References

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[2] Jaroniec M. 1995, *Langmuir* **11**, 2316-2317.