Structural transformations of As-sorbed Fe(III) (oxyhydr)oxides during alkali extraction of As
K.F. Wang a, P.E. Holm b, C.M. van Genuchten a
a Department of Geochemistry, Geological Survey of Denmark and Greenland, 1350 Copenhagen, Denmark
b Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

Arsenic-bearing water treatment residues (As-WTRs) are generated from Fe-based groundwater treatment. This waste by-product has traditionally been overlooked for resource recovery presumably due to the high toxicity of As. Recently, the European Commission has classified As-bearing compounds as having a critical supply risk. Consequently, As-WTRs represent a local source of As that can offset current methods of producing As compounds, including mining. Converting As-WTRs to valuable As compounds first requires As separation from the solid Fe matrix, which can be done by simply increasing pH. However, increasing pH also promotes Fe precipitate crystallization, which might limit reuse of the Fe solids in water treatment applications due to the expected decrease in reactive specific surface area. Therefore, to maximize the resource recovery potential of As-WTRs, it is essential to understand how alkali extraction of As alters the structure of the Fe(III) (oxyhydr)oxide sorbent.

This presentation reports results from experiments using NaOH to release As(V), as the main As species detected in As-WTRs, from synthetic 2-line ferrihydrite (2LFh) and field sludge obtained from existing As treatment plants. Macroscopic measurements of As extraction efficiency (i.e., % As released) are combined with synchrotron-based Fe and As K-edge EXAFS data to identify solid phase transformations during As extraction.

The results indicated that As release from 2LFh was largely controlled by NaOH concentration and was tightly coupled to goethite transformation. At 1 h of reaction, NaOH levels of 0.01 M (pH ≈ 12) released only 25% of sorbed As (left column in Figure 1), with little goethite detected by Fe K-edge EXAFS LCFs (middle and right columns in Figure 1). However, 1 M NaOH (pH ≈ 14) released >95% of sorbed As and 75% of the initial solid transformed to goethite. This result implies an optimal NaOH concentration that effectively extracts As, but does not promote significant Fe phase crystallization. Interestingly, the field sludge showed more resistance to As release and Fe transformation than synthetic As-sorbed 2LFh over identical conditions, which suggests that major co-occurring species in field sludge (e.g., Ca, Mg, P, Si) and other phases (e.g., CaCO3) play a complicated role on As release and Fe phase transformation during alkali extraction.
Figure 1. Impact of NaOH concentration and reaction time on As release (left column) and Fe transformation (middle and right columns) using As(V)-sorbed 2LFh (top data) and field sludge (bottom data). The output of Fe K-edge EXAFS LCFs (red dotted lines) are overlain on the data (solid black lines) in the middle panel. The EXAFS LCFs were performed with the references given at the top of the middle panel. The field sludge was collected directly from the sludge storage area of an As treatment plant in India.