Challenges in the identification of redox reactive Fe(II) mineral phases in suboxic aquifer sediments

J.M. ZACHARA, T. PERETYAZHKO, J.P. MCKINLEY, CHONGXUAN LIU AND A.R. FELMY

Pacific Northwest National Laboratory, Richland, WA, USA

The kinetics of ^{99}Tc(VII) reduction, as the pertechnetate anion [$^{99}TcO_4^{2-}$ = 10^{-6} mol/L], were investigated in a series of suboxic aquifer sediments from the U.S. DOE, Hanford site exhibiting an average pH = 8. Reaction rates varied markedly displaying half-lives ranging from 2 to 110 d. Rate constants did not normalize to extractable Fe(II) concentration. The heterogeneous reaction products, as identified by EXAFS analysis, were adsorbed ^{99}Tc(IV) clusters (n = 2-4) that did not vary in size with reduction rate. Iron was not observed in the second coordination sphere. The Fe mineralogy of the sediments was investigated using a combination of chemical extraction, x-ray diffraction, variable temperature Mossbauer spectroscopy, and analytical electron microscopies; revealing the presence of a complex Fe(II) mineral suite containing variable concentrations of pyroxenes, siderite, Fe(II)-phyllosilicates (smectites, illites, and mica), and magnetite. Direct correlations between ^{99}Tc reaction rates and Fe(II) mineralogy were not evident. The most reactive sediment was titrated with higher levels of ^{99}Tc (10^{-4} mol/L), with the distribution of Fe(II) mineral phases monitored by Mossbauer spectroscopy after ^{99}Tc(VII) reaction. Spectral peak positions for siderite at 4.5 K decreased during titration from 29% to 6% of the total area, transforming to those of Fe(III) oxide, providing presumptive evidence that siderite was one of several reactive phases. Additionally, ^{99}Tc(VII)-oxidized sediment was screened by digital autoradiography to identify ^{99}Tc(IV)-containing mineral phases. These phases were manipulated for analysis by electron microprobe and micro-x-ray diffraction. A significant fraction of the ^{99}Tc(IV)-containing phases were Fe-micas as observed in a previous investigation with sediments from another location. Residual siderite did not appear to contain ^{99}Tc(IV). We conclude with a discussion of: i.) the challenges involved in the identification of redox active phases using macroscopic and microscopic techniques and ii.) kinetic versus thermodynamic controls on redox reactivity in mineralogically heterogeneous subsurface sediments.

Evaluation of rock properties and rock structures in the micron-range with sub-micron X-ray Computed Tomography

G. ZACHER[1]*, M. HALISCH[2], O. BRUNKE[1] AND T. MAYER[1]

[1]GE Sensing & Inspection Technologies GmbH, Niels-Bohr-Str. 7, 31515 Wunstorf, Germany

[2]Leibniz Institute for Applied Geophysics, Stilleweg 2, 30655 Hannover, Germany

In recent years high resolution X-ray Computed Tomography (CT) for geological purposes contribute increasing value to the quantitative analysis of rock properties. Especially spatial distribution of minerals, pores and fractures are extremely important in the evaluation of reservoir properties. The possibility to visualize a whole plug volume in a non-destructive way and to use the same plug for further analysis is undoubtedly currently the most valuable feature of this new type of rock analysis and will be a new area for routine application of high resolution X-ray CT in the near future.

The paper outlines new developments in hard- and software requirements for high resolution CT. It showcases several geological applications.

The results were performed with the phoenix nanotom and recently phoenix nanotom m, the first 180 kV nanofocus CT system tailored specifically for extremely high resolution scans of samples up to 240 mm in diameter and weighing up to 3 kg with voxel-resolutions down to <300 nm. These characteristics with respect to spatial resolution principally allow CT measurements which valuably complement many absorption contrast setups at synchrotron radiation facilities (Withers 2007 [1]; Brunke *et al*. 2008 [2]; Kastner *et al*. 2010 [3]).

[1] Brunke *et. al*. (2008) „Comparison between x-ray tube-based and synchrotron radiation-based μCT" in Developments in X-Ray Tomography VI, edited by Stuart R. Stock, *Proceedings of SPIE*, Vol. **7078**. [2] Withers (2007) "X-ray nanotomography", *Materials Today,* **10(12)**, 26-34. [3] Kastner *et. al*. (2010) "A comparative study of high resolution cone beam X-ray tomography and synchrotron tomography applied to Fe- and Al-alloys", in *NDT & E Int*. vol **43**, pages 599-605.