A XANES study of Zn and Fe(II) chloride complexes in hypersaline brines

W. LIU[1], B. ETSCHMANN[1], G. FORAN[2], M. SHELLEY[3] AND J. BRUGGER[4]

[1] CSIRO Exploration and Mining, Australia; weihua.liu@csiro.au; barbara.etschmann@csiro.au
[2] Australian National Beamline Facility, Photon Factory, Japan; foran@anbf2.kek.jp
[3] Research School of Earth Sciences, The Australian National University, Mike.Shelley@anu.edu.au
[4] Adelaide University and South Australian Museum, Brugger.Joel@saugov.sa.gov.au

The development of numerical modelling of reactive transport relies on the availability of thermodynamic properties for the solid, surface, aqueous and vapour species stable at the conditions of interest. The lack of experimental studies and comprehensive activity-composition models severely limits the predictability of these models in systems involving highly saline fluids or low-density volatile-rich fluids.

In this study we try to obtain formation constants for the aqueous complexes of transition metals from series of synchrotron XANES spectra obtained on solutions containing a constant amount of the metal of interest and variable concentrations of a ligand. The method relies on a non-linear least-squares approach, with full distribution of species calculations based on a complete thermodynamic model for the experimental system under consideration. The technique is particularly suitable for following octahedral to tetrahedral transitions among weak chlorocomplexes of transition metals.

Zn *K*-edge XANES spectra of acidified Zn bearing NaCl solutions have been measured at 25°C. The systematic change of the XANES spectra with increasing Cl concentration indicates the coordination change of Zn chloride complexes from octahedral to tetrahedral structure. The log K for the $ZnCl_{3\ (octahedral)}^{-} + Cl^{-} = ZnCl_{4\ (tetrahedral)}^{2-}$ reaction at 25˚C is retrieved within error of the accepted literature value. The same method were applied to study speciation of Fe(II)-chloride complexes in 0.4-15 m LiCl solutions at 25˚C and 150˚C. The result shows that tetrahedral Fe(II) chlorocomplexes ($FeCl_{4\ (tetrahedral)}^{2-}$) predominate at high chloride concentration solutions, and the stability of this tetrahedral complex increases with increasing temperature. This study confirms that tetrahedral chloride complexes play an important role in Zn and Fe transport in hypersaline brines especially at elevated temperatures, and shows that XANES is well suited to study systems that are difficult to study with other techniques such as UV-Vis spectrophotometric method.