

In-situ X-ray Absorption Spectroscopy to study the Structure of Hydrothermal Aqueous Sulfate Solutions

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Hydrothermal aqueous salt solution play an important role in geochemistry for the understanding of the ore deposit formation as well as in the supercritical water oxidation (SCWO) and the supercritical water gasification (SCWG), which use hot compressed water as a process medium. At the Paul Scherrer Institut a SCWG process was developed [1], which turns various kinds of wet biomass into synthetic natural gas. One big task in the SCWG and SCWO is the salt separation from the process stream to recover nutrients such as P, S, K and Na and to avoid problems such as blocking of the apparatus or poisoning of catalysts used in the SCWG. For optimizing such processes and understanding the solution chemistry, especially solubility of salts, a detailed knowledge on the phase behavior and microscopic structure of salt solutions is needed. Water changes its structure at elevated pressures and temperatures drastically, with strong impact on dissolved matter. Specifically, the solubility of salts in hydrothermal water may decrease strongly when approaching the conditions of the critical point of pure water (374°C, 22.1 MPa). Especially for sulfate solutions this behavior is known [2]. One possible effect is the formation of ion pairs under or close to supercritical conditions. Extended X-ray absorption fine structure (EXAFS) measurements can provide insight into the microscopic structure of solutions as they yield a direct measurement of atomic distances. Up to now the ion pair formation has been studied for systems containing ions with, on the energy scale, high absorption edges. Studies with the lowest energy were performed at the Ca-K-edge (4038.5 eV) [4]. Performing such measurements for light elements, such as sulfur or phosphorus is challenging, as the absorption edges are at low X-ray energies with intrinsically small penetration depth of a few tens of microns. Due to this small penetration depth the thickness of the X-ray windows and the path length in the fluid are critical issues. Here, we present a design of X-ray windows and a cell, which are suitable to perform measurements at the S-K-edge (2482 eV). The windows are 18 µm thick diamond membranes (Diamond Materials, Freiburg, Germany) which are supported by a diamond ring on a titanium holder. The free aperture is 100 µm. The path length in the solution can be adjusted to values between 25 and 240 µm using different spacers, which are also used for the axial alignment. The cell is sealed with copper O-rings and was designed for temperatures up to 400°C and pressures up to 300 bar. The solution is flushed through the cell using a high pressure syringe pump (ISCO). The pressure is controlled with a back pressure valve. At the PHOENIX beamline (Swiss Light Source, Switzerland) with its high photon flux and microfocussed beam at low energies it was possible to perform measurements of a K₂SO₄ solution (5% w/w) at a pressure of 300 bar up to a temperature of 297°C.

[1] F. Vogel, Catalytic conversion of high-moisture biomass to synthetic natural gas in supercritical water. In: Handbook of Green Chemistry, P. Anastas (Series Editor), Volume 2 Heterogeneous Catalysis, R. Crabtree (Volume Editor), Wiley-VCH, Weinheim, chapter 12, 281-324, 2009.

[2] V.M. Valyashko, Chapter 15 - Phase equilibria of water-salt systems at high temperatures and pressures. In: Aqueous Systems at Elevated Temperatures and Pressures, D. A. Palmer, R. Fernández-Prini, and A. H. Harvey (Editors), Academic Press, London, 597-641, 2004.

[3] T.M. Seward et al., Geochim. Cosmochim. Acta, 63, 16, 2409-2418, 1999.

[4] J. Fulton et al., Rev. Sci. Instrum., 75, 12, 5228-5231, 2004.

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