

Thiocyanate adsorption onto ferrihydrite and its availability during the aging of ferrihydrite

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Thiocyanate (SCN^-) contamination results from many industrial sources such as coal processing and metal separation. Although SCN^- is less toxic than cyanide it is still harmful to aquatic organisms and humans [1]. The use of iron oxides to immobilise contaminants has been shown to be an effective treatment [2] but little is known about the removal of SCN^- by iron oxides.

Adsorption of SCN^- onto the surface of ferrihydrite and the availability of adsorbed SCN^- during the transformation of ferrihydrite were studied using macroscopic techniques complemented with Transmission Electron Microscopy (TEM). The preliminary results show that adsorption of SCN^- decreases as pH increases. Adsorption of SCN^- is strongly affected by the concentration of electrolyte with decrease in concentration of NaNO_3 leading to increase in SCN^- adsorption (Figure 1). This indicates that SCN^- adsorbs onto ferrihydrite as outer-sphere complexes.

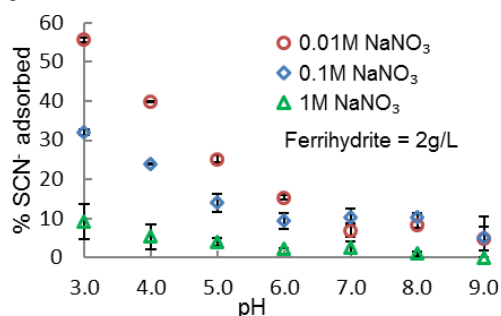


Figure 1: Macroscopic uptake of SCN^- as a function of pH and electrolyte concentration.

The adsorption isotherm reveals that adsorption capacity increases with increases in concentration of SCN^- . Within the studied range of SCN^- concentrations adsorption capacity is linearly proportional to the equilibrated concentration of SCN^- (Figure 2).

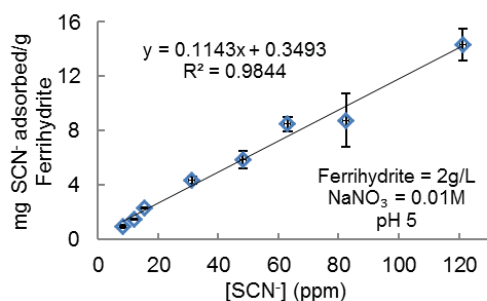


Figure 2: SCN^- adsorption isotherm.

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First-principle simulations of silver in hydrothermal fluids

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The knowledge of the speciation of coinage metals is a key element of the understanding of their transport in hydrothermal conditions and the formation of metal deposits from geological fluids. In saline brines, the main carrier of silver, solvated as silver cation Ag^+ , is the chloride anion Cl^- . Extrapolations from low temperature thermodynamical data, which suggest either AgCl_2^- [1] or AgCl_4^{3-} [2] as the dominant species at high temperature, lead to solubilities of Ag-bearing minerals that differ by two to three orders of magnitudes at elevated temperature. Molecular modelling can help putting constrains on these models. The interaction of silver or other coinage metals with water is, however, more complex than that of simple cations like Na^+ [3]. Moreover, at elevated temperatures, the hydrogen bond network of water is largely broken and its dielectric constant much lower than at ambient conditions, which questions the validity of empirical force-fields. First-Principles Molecular Dynamics (FPMD) makes no a priori assumption about the interactions and enables the description of such complex chemical systems.

We will first briefly discuss the FPMD description of supercritical water, with particular emphasis on the role of long-range dispersion interactions [4]. We will then present results from large scale FPMD simulations of silver solvation in aqueous solutions at ambient and elevated temperature, with various Cl^- contents. Modelled EXAFS signals will be compared to recently obtained experimental data. In agreement with very recent FPMD study using smaller samples [5], we find that AgCl_2^- and AgCl_3^{2-} species are stable at ambient conditions. We also find the AgCl_4^{3-} complex to be stable in our simulations. AgCl_2^- is found to be a linear complex while AgCl_3^{2-} is trigonal planar and AgCl_4^{3-} a distorted square planar complex. The largest complexes are, however, not stable at high temperature where only AgCl and AgCl_2^- complexes are found. These structures appear very fluxional. Transitions between these complexes at ambient temperature and chlorine exchange in AgCl_2^- at high temperature occur on a time-scale of about 10 picoseconds. The role of quadrupolar polarizability of Ag^+ in the stability and dynamics of these structures will be discussed.

[1] Akinfiev N.N. and Zotov A.V. (2001) *Geochem. Intern.* **39**, 990-1006. [2] Sverjensky D.A. *et al.* (1997) *Geochim. Cosmochim. Acta* **61**, 1359-1412. [3] Vuilleumier R. and Sprik M. (2001) *J. Chem. Phys.* **115**, 3454. [4] Jonchiere R. *et al.* (2011) *J. Chem. Phys.* **135**, 154503. [5] Liu X. *et al* (2012) *Chem. Geo.* **294**, 103-112.