

# Thermodynamic description of Fe(II) solubility and hydrolysis in dilute to concentrated KCl systems

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Due to the extensive use of metallic iron as container material (mostly as cast iron and steel), this material as well as its corrosion products are expected to strongly impact the geochemical conditions (pH,  $E_h$ ) in the near-field of potential repositories for nuclear waste disposal. To improve scientific understanding of the redox conditions to be expected under repository conditions in case of water intrusion, an accurate knowledge of the speciation and thermodynamic stability of the phases expected to form is crucial. Despite the large number of studies investigating the aquatic chemistry of iron, the data reported for chloride-rich alkaline and hyperalkaline systems is very limited. Within the framework of the *Thermodynamic Database* (TDB) project of the *Nuclear Energy Agency* (NEA), no thermodynamic data for several iron(II) compounds and aqueous species relevant in reducing, alkaline conditions (e.g.,  $\text{Fe}(\text{OH})_2(\text{cr})$ ,  $\text{Fe}(\text{OH})_2(\text{aq})$ ,  $\text{Fe}(\text{OH})_3^-$ ) were selected up to date, mostly due to insufficient solid phase characterization in solubility studies and resulting uncertainties.

Contributing to an improved description of iron thermodynamics, this presentation will focus on the Fe(II) solubility and hydrolysis in dilute to concentrated salt systems. Undersaturation solubility experiments with well-defined ferrous hydroxide ( $\text{Fe}(\text{OH})_2(\text{cr})$ ) and hibbingite ( $\text{Fe}_2(\text{OH})_3\text{Cl}(\text{cr})$ ) solid phases were conducted in glove boxes under argon atmosphere ( $< 2$  ppm  $\text{O}_2$ ) in 0.01 M to 4.0 M KCl solutions in near-neutral to alkaline pH conditions. In addition, analogue experiments were performed within 0.1 M to 4.0 M KOH solutions to investigate the formation of anionic Fe(II)-OH species. Solid phases were characterized by XRD before and after the experiments.  $E_h$  and pH conditions were monitored over the course of several months as well as the aqueous iron concentration using ICP-MS. Experimental data will be presented together with a new thermodynamic SIT activity model allowing a robust description of the  $\text{Fe}^{2+}$ - $\text{K}^+$ - $\text{H}^+$ - $\text{OH}^-$ - $\text{Cl}^-$ - $\text{H}_2\text{O}(\text{l})$  system also under saline conditions. Implications for the Fe corrosion phases potentially controlling redox under repository relevant conditions will be discussed.

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