Treatment of redox in SR-Site solubility calculations

This memo is intended to clarify the reasoning behind the treatment of redox in the solubility calculations, as a response to the queries raised by SSM in a request for additional information (SSM2011-2426-4.7.2.i). In particular this Memo aims to clarify:

- The *reasoning* behind the assumption that chemical equilibrium between the corrosion products magnetite and goethite controls the redox in all cases for which solubility limits are valid.

- The relation of this assumption to the *evolution of the corroding canister insert* after different modes of canister failure.

- The effect of varying *redox state in the surrounding groundwater* on the redox potential in the canister.

Contents

1   Introduction

SSM asks for additional clarifications concerning the reasoning behind choosing to fix redox inside the canister according to the equilibrium reaction between magnetite and goethite. The requests are based on the suggestions from Trivedi (2012) and Baldwin and Hicks (2012). SSM indicates that further arguments are required than those found in the given references (SKB 2010a, p 97, Duro et al. 2006, p 16).

In SR-Site, the effect of the corrosion of the Fe insert is considered significant for the important groundwater parameters pH, Eh, dissolved $H_2(g)$ and $[Fe]_{aq}$. This is taken into account in the calculation of solubility limits, as described by Grivé et al. (2010). The reasoning and conceptual model behind this is described in section 2 below. It is also noted that the brief description given in the fuel and canister process report (SKB 2010a) does, in some respects, not correctly reflect the approach taken in SR-Site, as pointed out in Trivedi (2012). The full, and correct, description is given in Grivé et al. (2010) and in the SR-Site Data report (SKB 2010d, section 3.4), and summarised in this Memo. The brief text in the fuel and canister process report will be corrected with an erratum.

Furthermore, it is reiterated that in the SR-Site assessment, solubility limits are only considered for the conditions inside the canister (SKB 2010a, p 68): "The process is confined to the canister". No solubility limits are used to calculate radionuclide concentrations in groundwater outside the canister or in the buffer. In addition, in the scenarios where the bentonite buffer is eroded, no solubility limits are used – apart from the solubility limit for U (SKB 2010b, p 58).

It should also be mentioned that the amount of Fe present in an intact canister is very large: a BWR cast iron canister insert weighs 13700 kg (SKB 2010c, Table 3-1), and it has a large surface area available for reaction with intruding groundwater (ca 33 m^2: SKB 2010a, p 97 and SKB 2010c, pp 30–31). It has long been known that the redox potential of groundwater is strongly influenced by electron transfer reactions between Fe(II)/Fe(III) in the system (e.g. Goodwin 1982, Grenthe et al. 1992), and therefore Fe is considered a dominant redox-active element in most natural groundwater. It is thus assumed that the large amount of Fe inside the canister will act as a buffer against any possible deviations in redox potential in the incoming groundwater.

2   Assuming chemical equilibrium between magnetite and goethite: control of redox in the canister

The following is a clarification of the approach adopted in SR-Site in order to take into account the interaction between groundwater and a corroding Fe insert. The clarification is based on the description provided by Grivé et al. (2010, pp 19–21). The Simple Functions tool is used to calculate the Eh and $[Fe]_{aq}$ corresponding to the new chemical conditions which arise from groundwater interaction with a corroding canister, see further section 3.2 in Grivé et al. (2010). It should be noted that this interaction is complex, and that the Simple Functions Tool is not designed for calculating the complete change in groundwater chemistry. Rather, it is focused on the change related to the groundwater parameters most significantly affected by the corrosion of the Fe insert, namely pH, Eh, dissolved $H_2(g)$ and $[Fe]_{aq}$.

The reasoning is essentially based on equilibrium thermodynamics, and the main underlying assumption is that the solid – fluid system of the canister interior will reach equilibrium with regard to Fe chemistry. Under anoxic conditions, the insert is expected to corrode in two steps incorporating the change in Fe valence state in the system, from Fe(0) to an equilibrium between Fe(II) and Fe(III).

First, corrosion of cast iron produces magnetite according to the following reaction:

$$Fe(s) + 4 H_2O = Fe_3O_4(s) + 4 H_2(g) \qquad (1)$$

As is described in TR-10-46, page 97, the magnetite which is formed consists of two layers; the first forms quickly and adheres strongly to the iron surface. The second is a more loosely attached and more slowly formed layer. The rate of formation of this second layer is controlled by diffusion through the first magnetite layer.

In a second step, magnetite is expected to react with water and an oxidant to form a phase containing Fe(III). The thermodynamically most stable Fe(III) mineral under these conditions is hematite (Duro et al. 2006, p 16, Navrotsky et al. 2008). However, in solubility calculations it is customary to take into account the Ostwald ripening effect (also called the Ostwald Step Rule), which means that the phase first formed is not the most stable phase but rather a kinetically favoured, less stable precursor (for a discussion regarding this see Duro et al. (2006, p 46). In the case of Fe(III)-containing oxides, there are a number of possible phases which could form. Of these it is recognised that goethite (α-FeOOH) is the most common and also most stable oxyhydroxide (e.g. van der Zee et al. 2003, Navrotsky et al. 2008). Ferrihydrate, $Fe(OH)_3$, is a poorly ordered Fe oxyhydroxide which is less thermodynamically stable than goethite; this phase is, however, not expected to play a role as important as that of goethite under the relevant conditions. It has been shown that in the presence of dissolved Fe(II), the rate of ferrihydrate transformation into goethite is rapid (Yee et al. 2006). Therefore, the continued corrosion of magnetite, which will occur in the presence of oxidants (e.g. oxygen), is expected to proceed according to the reactions given in Grivé et al. (2010, p 20):

$$Fe_3O_4 + 1.5H_2O + 0.25O_2(g) = 3FeOOH \qquad (2)$$

The equilibrium constants of the following reactions are then used in the calculation of Eh and pO$_2$:

$$3Fe^{2+} + 3H2O + 0.5O_2(g) = Fe_3O_4 + 6H^+ \qquad (3)$$

$$Fe^{2+} + 1.5H_2O + 0.25O_2(g) = FeOOH + 2H^+ \qquad (4)$$
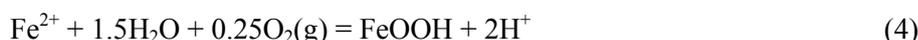
This calculation is based on the assumption that the two iron minerals expected to be in contact with the water inside the canister are magnetite and goethite, and that the system has reached equilibrium. Figure 3-4 in Grivé et al. (2010) describes this equilibrium. Given the Eh and pH, this equilibrium allows calculation of $[Fe]_{aq}$. It should also be noted that as long as there is still metallic iron in the canister, the equilibrium $Fe(s)/Fe_3O_4(s)$ will also be operative inside the canister and cause e.g. reduction of radionuclides (as in Zero Valent Iron barriers).

Using the magnetite/goethite equilibrium rather than the magnetite/hematite equilibrium, as described by Duro et al. (2006), results in a slightly higher Eh of the system due to goethite being more soluble and therefore somewhat elevating the amount of Fe (III) in solution.

3   Evolution of the corroding canister insert

As stated in the introduction (section 1), the amount of Fe available is expected to act like a buffer against deviations in Eh of incoming water. This is expected to be true for the duration of the time period which the safety assessment has to cover. The corrosion process is described as occurring in two steps: first conversion of Fe(0) to magnetite, then the adjustment towards equilibrium between magnetite and goethite. The first step is expected to continuously introduce magnetite to the system, at a rate controlled by ion transport across the adherent layer of magnetite. The continuously formed magnetite is precipitated as a loose layer with poor adhesion. The corrosion rate of the iron insert is

slow enough to ensure that this will continue for a very long time (SKB 2010a, p 97, SKB 2010d, p 103). The chemistry of the incoming water is expected to change as a result of the interaction with the corrosion products; as described, the parameters most affected are pH, Eh, dissolved $H_2(g)$ and $[Fe]_{aq}$. Over time, the evolution of the Fe corrosion products might be expected to involve a dehydration of goethite and the crystallisation of hematite; this however will take a long time, and will have the effect of lowering the Eh somewhat.

4   Effect of redox state in the surrounding groundwater

The effect of the redox state in the surrounding groundwater is not significant for the redox conditions inside the canister as long as the corrosion of the Fe insert is ongoing. As stated in the introduction (section 1), the amount of Fe available is very large and is expected to buffer against deviations in Eh of incoming water. The iron corrosion products are expected to control the redox potential for all timescales relevant for the safety assessment (SKB 2010d, p 103). This is because of the large amount of iron, the large surface area available for solid-fluid interaction, and the relatively slow renewal of the fluid volume inside the canister. Therefore, it is expected that there will be enough time for water to adjust to the new chemical conditions, given that even in the erosion-corrosion scenario (with comparatively high flow rate), the flow rate in the deposition hole is still less than 1 m^3/year (SKB 2010b, Table 4-3). In the shear load scenario, when solubility limits are used, the buffer is still intact, and the water turn-over rate in the canister is much lower. Thus, the relation between flow rate inside the canister and reaction rate (influenced by surface area/volume ratio) form the basis for the assumption that the system will reach equilibrium. The redox state of the incoming groundwater is therefore expected to change as a consequence of the reactions described in section 2. In scenarios where the only solubility limit considered is that of U, the redox buffering of iron is still valid.

5   Summary

Solubility limits are only used for the conditions inside the canister. The amount of Fe inside the canister is very large and is expected to act as a redox buffer for the duration of the assessment period. The Eh inside the canister is determined using the pH of incoming water and the equilibrium between magnetite and goethite. This choice is based on current knowledge of Fe oxide formation and redox controlling reactions in natural systems. The redox state of surrounding groundwater is not relevant for solubility calculations, since these are only performed for the canister interior, and the Eh of the water entering the canister is expected to be buffered by the Fe corrosion products.

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