

References and comments given by researchers at KTH to the panel members for the scientific workshop on copper corrosion mechanisms.

(The workshop will be arranged by the Swedish National Council for Nuclear Waste, 16 Nov. 2009)

The KBS-3 model was based on the assumption of thermodynamic immunity of copper in pure water. In Ref. [1], Chapter 10, page 10:3, it is stated that “Copper is the noblest of the common engineering materials. It is thermodynamically stable in pure water. This means that the corrosion of copper in the groundwater will be determined by supply of corrosive substances dissolved in the water. These substances are preliminary dissolved oxygen and, for reducing groundwater conditions, dissolved sulphide.”

In practice “anoxic water” includes all water environments with more dissolved hydrogen (H_2) than dissolved oxygen (O_2). Theoretically, the borderline situation with equal amount of dissolved H_2 and O_2 in equilibrium with water is represented by a line in the Pourbaix diagram. According to Nernst equation, this corresponds to a gas phase with a total pressure of 10^{-28} bar. This could colloquially be regarded as water without dissolved gases. Anoxic water gives a rather low redox potential compared to water in contact with air. However, below this redox potential line in the Pourbaix diagram both monovalent and divalent corrosion products are thermodynamically expected to form on copper. This has been known at least since 1920, when Walter Nernst was awarded with the Nobel Prize in chemistry. With this background information, the starting point and statement in Ref. [1] quoted above is even more surprising.

The company SKB AB claims that the following peer reviewed publications are being conducted in anoxic or O_2 -free water solutions, Refs. [2,3].

- Reference [2] is based on the experiments presented in the SKB report [4]. A prerequisite to detect hydrogen evolution from mild corrosion such as copper corrosion in pure water is that negligible O_2 -gas is present. This was known already 20 year ago. A high O_2 -gas content was detected in the SKB report [4], see Figure 2, which disqualifies the study as concerning corrosion in O_2 -free water. In spite of this fact this report was the basis of a “scientific evidence” published in Corrosion Science [2] with the conclusion that no copper corrosion takes place in O_2 -free water. A question that should be asked is why this information about O_2 -gas detection seen in Fig. 2 in Ref [4] was omitted in Ref. [2].

- Flowing nitrogen gas was used in Ref. [3] but such an experimental arrangement would not be accepted today as being an anoxic exposure. Even the purest nitrogen gas contains a few ppm O_2 -gas, thus it could never ensure an O_2 -free environment. This was already pointed out by G. Hultquist et al. 1989, see Ref. [6].

Refs. [5-7, 9-11] report experiments with hydrogen detection in gas phase, copper metal and corrosion product. This means that water corrodes copper under formation of

a hydrogen-containing corrosion product under sufficiently anoxic conditions. It should be pointed out that in Fig. 2b in Ref. [5] two different calibration curves are shown where the higher response is used in Fig. 2c. It has turned out that the curve with the lower response is valid. For example, a hydrogen probe output of 400 mV from the commercial probe used, corresponds to a hydrogen pressure of roughly one mbar.

Ref. [8] gives an alternative explanation to the results presented in Ref. [7]. However, this alternative explanation has earlier been ruled out by us, as well as in Ref. [9].

The Swedish Radiation Safety Authority, SSM, has asked us to make a scientific comment to the BRITE-report, which was initiated by SSM. This report scrutinizes only Ref. [9]. Our scientific comments will be sent to the panel members later.

Concluding remarks

Refs [2,3] can not be regarded as being performed under anoxic conditions. In most of our referred papers we discuss a hydrogen-containing copper corrosion product and during the later years, it has turned out that this product most likely is an amorphous hydroxide, CuOH. This monovalent hydroxide converts rather easily to copper oxide, especially when exposed to air, as discussed in Ref. [9]. It may be pointed out that our findings do not imply any changes regarding the known thermodynamic data of copper corrosion products.

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