RAPID COMMUNICATION

Some scientific considerations on the article: 'Scientific basis for corrosion of copper in water and implications for canister lifetimes' published by F. King and C. Lilja

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There has for the past 30 years been a debate regarding whether corrosion of copper can occur in anoxic water. In short the debate has been between experiments showing that corrosion of copper can occur and theory that predicts that it will not occur. The thermodynamics of copper corrosion, particularly, that copper cannot corrode in anoxic water, is a fundamental prerequisite for the Swedish repository concept for spent nuclear fuel developed by the Swedish Nuclear Fuel and Waste Management Company (SKB). Thus, in 1986 and subsequently Hultquist and co-workers experimentally confirmed that corrosion of copper can occur in some conditions. However, this research is generally assumed to be incorrect, most recently by a paper by King and Lilja in this journal. In this article I will develop the argument that Hultquist's work should not be so disregarded.

Keywords: Corrosion, Copper, Anoxic water

Introduction

In the Swedish repository concept (KBS-3) the spent nuclear fuel will be deposited 500 m down in the bedrock and placed in copper canisters that are embedded in bentonite clay. The water at a depth of 500 m is anoxic so the critical question is: 'does corrosion of copper occur in water without dissolved oxygen?' The likelihood for the corrosion of copper under such repository conditions was the subject of a scientific evaluation published in 1978.[1] The report is signed by nine of the members, but one of the members Professor Wranglen of the Royal Institute of Technology submitted a dissenting report where he argued regarding the canister material that: 'Allowance must be made, for example, for the existence of heretofore unknown processes of ageing and material destruction'. In 1986, Hultquist claim he found such a 'heretofore unknown process' and published experimental results of hydrogen evolution from de-aerated water in the presence of pure copper.[2] In the following few years, a number of researchers attempted to repeat Hultquist's results, in particular Simpson *et al.*[3] and Erikson *et al.*;[4,5] however, they were unsuccessful. At this stage most experimental and thermodynamic evidence supported the view that copper is immune to corrosion in anoxic water. Of course if copper was found to corrode in anoxic water, it would alter the basis for selection of a suitable canister material for unprocessed nuclear waste over geological timescales. Hultquist and co-workers have during the latest years repeated the original study under much more carefully controlled conditions and repeatedly observed hydrogen evolution.[6–8] Importantly, in 2010–2011, the Swedish Radiation Safety Authority commissioned additional experimental research that successfully replicated Hultquist's later results[9] and theoretical work that provided a possible thermodynamic explanation for the observed phenomenon.[10] However, and unfortunately, the article 'Scientific basis for corrosion of copper in water and implications for canister lifetimes' published in 'Corrosion Engineering, Science and Technology' 2011 by King and Lilja[11] has not fully considered the possibility of copper corrosion in anoxic water. Since this would significantly impact upon the overall findings and implications of their paper I will here develop the argument that anoxic copper corrosion should not be so disregarded in these studies.

Commentary

The most serious problems with King and Lilja's paper are that they: ignore known flaws in the papers that they select to rebut the argument concerning copper corrosion in pure water, and ignore SKB's own commissioned studies on copper corrosion in the underground Aspö laboratory that report unusually high corrosion rates. Thus, Eriksen's[4,5] attempt to repeat Hultquist's work was clearly compromised by the presence of air (i.e. oxygen and nitrogen) in the Gas Chromatograph spectrum, and indeed this was pointed out by Chuah[12] at a seminar also attended by King and Lilja who

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therefore should have been aware of this. The study of Simpson *et al.*[3] used flowing N_2 gas with a ppm level of oxygen, which is not an appropriate approach when trying to detect hydrogen evolution from a slow corrosion process such as anoxic copper corrosion.[2,6] More importantly, perhaps none of the results from the prototype studies in the underground repository, such as the Minican and LOT projects[13,14] were mentioned in their paper which is strange, because the measured corrosion rate greatly exceeded (by at least 1000 times) the claimed corrosion rate of 1 nm/year. Although it might be argued that the experimental protocols in the underground test were in error, the measured corrosion rates, from 1·5 cm/year (Ref. 15) to a few micrometres per year (three orders of magnitude higher than the value quoted in King and Lilja's paper), deserve consideration. Another troublesome result in the Minican study was that anoxic conditions were confirmed (Table 6-1 in Ref. 13) and still, corrosion rates of μm per year were measured (Fig. 6–33 in Ref. 13). The Swedish Radiation Safety Authority (SSM) evaluated the scientific quality of these prototype studies commenting that SKB tended to either neglect undesirable results that went counter to their arguments (Minican study) or delayed the reporting of such results (LOT study).[15]

Summary

Since 1986 there has been an extensive discussion regarding whether corrosion of copper in anoxic water is possible. There are theoretical arguments that support both sides of the discussion; however, the experimental evidence increasingly supports the fact that copper will, under some circumstances, corrode in pure, oxygen free, water. So the question of whether copper is a suitable canister material for spent nuclear fuel should have been settled by prototype studies in the underground Aspö laboratory where SKB has in their Minican study measured a corrosion rate of the order of micrometres in anoxic water. These results should have put doubt into the discussion of the overall immunity of copper canisters in such an environment. It is important for full public confidence in the Swedish nuclear waste repository (and indeed all others of a similar nature) that all possible mechanisms for corrosion of the primary biological barrier (copper in this case) are taken into account. Unfortunately, the article by King and Lilja disregards all contradictory evidence of this nature throwing doubt on the robustness of the entire system.

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Authors Queries

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