

The Corrosion of Copper Nuclear Waste Containers in Anaerobic Aqueous Sulphide Solutions

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Abstract

Since copper is generally accepted to be thermodynamically stable in the anaerobic saline groundwaters anticipated in a Swedish nuclear waste repository, it has been selected as the corrosion-resistant material for the fabrication of nuclear fuel waste containers. The only corrosion threat to the durability of these containers is attack by sulphide derived from either mineral dissolution or/and microbial activities. The aim of the present study is to determine the growth mechanism of copper sulphide films in aqueous sulphide-containing solutions, and particularly to characterize the influences of sulphide and groundwater chloride on the film growth kinetics and film properties.

The corrosion process is monitored using corrosion potential and electrochemical impedance spectroscopy (EIS) measurements. Experiments are conducted in anaerobic sulphide solutions in the concentration range from 5×10^{-5} mol/L to 10^{-3} mol/L in the presence of various concentrations of chloride for exposure periods up to 4000 hours (~167 days). SEM equipped with a focused ion beam (FIB) is used to produce cross-sectioned corroded specimens and energy dispersive X-ray spectroscopy (EDS) to identify film composition. X-ray photoelectron spectroscopy (XPS), and micro X-ray diffraction (μ XRD) are used to characterize the surface composition and the nature of the sulphide phases present on the corroded copper surfaces.

The results show that the corrosion product is a single layer Cu_2S film, formed by an outward growth mechanism controlled by a combination of Cu^+ diffusion in the film and SH^- diffusion in solution. When the sulphide concentration is low (i.e. 5×10^{-5} mol/L), the film has a cellular structure and its growth kinetics appear to be linear. The film growth process is controlled primarily by SH^- diffusion in the aqueous solution, implying that the sulphide film is not protective under these conditions up to an exposure time of ~ 4000h. However, when the sulphide concentration is $> 5 \times 10^{-4}$ mol/L, the film appears compact, and its growth obeys a parabolic law. In this case, film growth is controlled mainly by Cu^+ diffusion in the sulphide film indicating the film is partially protective under these conditions.

When the chloride concentration is low (i.e. 0.1 mol/L), it does not appear to influence the sulphide growth significantly. However, when the chloride concentration is > 0.5 mol/L, EIS spectra exhibit three time constants indicating a detectable influence on the sulphide film properties. The detection of a high frequency response, not seen at lower chloride concentrations, implies that localized corrosion may be occurring on the copper surface. However, no obvious pits are found in subsequent surface analyses. Moreover, the sulphide film experiences two-dimensional preferential growth with pores between plates when the chloride concentration is extremely high (i.e. 5 mol/L). The well-defined high frequency impedance response clearly indicates that the film is non-protective for exposure periods up to 1691 h

(~71 days). Under these conditions, the film growth process appears to be controlled by a combination of SH^- diffusion in the bulk of the aqueous solution and CuCl_2^- in the pores of the cellular sulphide film.

Whether the structure and properties of the sulphide films formed in anaerobic aqueous sulphide solutions containing chloride are determined by the sulphide flux at the film/electrolyte interface or the ratio of chloride and sulphide concentrations is significant for the safety assessment of nuclear waste containers. Further investigations to clarify these issues are on-going.

Keywords: Copper; Corrosion; Sulphide; Electrochemical impedance spectroscopy; Film growth kinetics.

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