

Effects of Sulphide and Chloride Concentrations on the Morphology and Growth Kinetics of Sulphide Films during Copper Corrosion in Anaerobic Aqueous Solutions

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Abstract

Containers with an outer copper shell have been proposed and designed for high level nuclear waste disposal in Sweden, Finland and Canada since copper is highly corrosion resistant in anaerobic groundwater. In the anaerobic groundwater anticipated in a Swedish repository, the only significant threat to the long-term durability of the container is corrosion by sulphide from mineral dissolution and/or microbial activity involving sulphate-reducing bacteria. Our research objective is to characterize the effects of sulphide and chloride concentrations on the morphology and growth kinetics of copper sulphide films in aqueous sulphide-containing solutions.

The ratio of these two concentrations, as well as their absolute values, appears to have a significant effect on the properties of the Cu_2S film formed. When the $[\text{SH}^-]$ is low (i.e. 5×10^{-5} mol/L), the film has a cellular structure and its growth kinetics appear to be linear and controlled primarily by SH^- diffusion in the aqueous solution. This implies that the film is not protective (up to an exposure time of ~4000h). However, when $[\text{SH}^-] > 5 \times 10^{-4}$ 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 film indicating it is protective.

When $[\text{Cl}^-]$ is low (i.e., 0.1 mol/L), the film appears compact, obeys a parabolic growth law, and is controlled mainly by Cu^+ diffusion in the

film indicating the film is protective under these conditions. However, when $[\text{Cl}^-] > 1.0$ mol/L, the film becomes porous, and at extremely high $[\text{Cl}^-]$ (i.e., 5 mol/L), grows two-dimensionally with pores between plates. This 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 SH^- diffusion in the bulk of the aqueous solution and CuCl_2^- diffusion in the pores of the cellular sulphide film. These long-term experiments show that the sulphide film changes from compact to porous when $[\text{Cl}^-]/[\text{SH}^-] \geq 1000$ under stagnant conditions, suggesting that this ratio might be an important factor controlling the morphology and properties of the film.

To investigate the importance of this ratio, the structure and properties of the film are being investigated under controlled-convective conditions in solutions, when this ratio ranges from 100 to 100000. Available results indicate that, under controlled convective conditions the film is always compact for a concentration ratio > 1000 , suggesting that the SH^- flux may be the key factor determining the morphology and properties of sulphide films.

Keywords: Copper; Corrosion; Sulphide; Film growth kinetics, Flux.

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