

Coupling of dissolution and mass transport for pitting of nickel base alloys in solutions containing thiosulfate ions

Roger C Newman, Anotolie G Carcea and William Zhang

Department of Chemical Engineering and Applied Chemistry, University of Toronto

200 College Street, Toronto, ON, CANADA, M5S3E5

Stainless steels and nickel base alloys, not containing Mo, show pitting in sulfate solutions containing thiosulfate ions. Thiosulfate also catalyzes ordinary chloride pitting in such materials – that is, it occurs at lower potential, temperature, etc. This is due to the electroreduction of thiosulfate to an activating sulfur species. Alloyed Mo strongly inhibits such phenomena.

This paper is concerned with the effect of thiosulfate concentration, or rather sulfate[chloride] to thiosulfate concentration ratio. A long time ago, Garner and Newman proposed that such pitting could be predicted on the basis of such ratios, but recent data indicate that the ratio argument is really only valid for sulfate as the strong-acid anion. This is most likely due to the effect of anion charge. Sulfate and thiosulfate, being equally charged, mutually electromigrate into an incipient pit and preserve (at least initially) their concentration ratio in the bulk solution. Chloride and thiosulfate are differently charged, and thus there is a disproportionate enrichment of the doubly charged thiosulfate ion.

Studies of nuclear steam-generator alloys (600, 690, 800), show that indeed less thiosulfate is required to catalyze pitting in a chloride than in a sulfate solution. But the situation is complicated by the conversion of sulfate to bisulfate at the extreme pH values found in pits, and by decomposition and electroreduction of thiosulfate. Nevertheless, modeling based on the initial hypothesis shows good agreement with the experimental results.

The results of this study are relevant to the following scenario : sulfate ingress into the secondary side of nuclear steam generators leads to its reduction in magnetite-rich sludge piles at operating temperature, perhaps involving hydrazine; then during shutdown, air ingress reoxidizes the product 'FeS' to thiosulfate.