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Electrochemical aspects of stress corrosion cracking of Ni-Cr-Fe alloys in acid sulfate solutions relevant to nuclear steam generators

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It is well known that the alloys used for nuclear steam-generator tubing can suffer from stress corrosion cracking (SCC) in faulted secondary-side chemistry. Sulfate is a common contaminant, and is commonly thought to play a specific role in such cracking, as distinct from chloride or other strong-acid anions. In fact, the evidence for this proposition is less conclusive than is commonly supposed - it is an intriguing idea that sulfate is reduced to an aggressive form of sulfur with an intermediate oxidation state between sulfate and sulfide, thus promoting SCC, but direct evidence for this is lacking. Few if any studies have varied sulfate and chloride in a systematic way, keeping the potential and other variables constant.

The present research has multiple aims related to the acid-sulfate type of SCC in Alloys 600 and 800. One is the issue already identified – how specific is this cracking to sulfate as a contaminant, and what is the role of reduced forms of sulfur? More generally, we refer to work carried out more than 30 years ago by J.F. Newman at the CEGB laboratories [1] in the UK. He showed that a convenient test solution, for static autoclaves, was an acid sulfate blend that incorporated $FeSO_4$ in the mixture. Upon heating, a Schikorr type of reaction occurred, coating the test sample with magnetite and evolving hydrogen. The residual liquid was essentially a $NaHSO_4$ solution (which is not particularly acid at high temperature, owing to the suppressed second dissociation of sulfuric acid). In our work, we have used this and related test protocols to arrive at some fairly general conclusions:

- Alloy 800, a kind of high-alloy stainless steel, seems to be more susceptible to cold work than Alloy 600, a nickel-base alloy, in such solutions.
- In highly acidic solution, the alloys have comparable susceptibility to SCC, but as the solution is diluted (less acidic), the 800 alloy clearly shows its superiority over Alloy 600. This is probably due to the higher Cr content of Alloy 800, but other factors may be at play, and a mechanistic analysis is under way.

1. J.F. Newman, "Stress Corrosion of Alloys 600 and 690 in Acidic Sulfate Solutions at Elevated Temperatures," NP-3043 (Palo Alto, CA: EPRI, 1983).