

Pitting Kinetics of Stainless Steels in Mixed or Concentrated Electrolytes

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Highly concentrated chloride solutions based on $MgCl_2$ or $CaCl_2$ cause apparently distinct pitting phenomena such as the appearance of comet-like streaks of etched material downstream of pits; this is due to a combination of a more aggressive pit environment (or less stringent repassivation criterion) in the concentrated solution, and higher viscosity that localizes the acid solution emerging from the pit. In such solutions the inhibition criteria are more strict.

The role of non-chloride anions in localized corrosion has become topical with the consideration of possible corrosion mechanisms in Yucca Mountain. Whilst there is no guarantee that nickel-base alloys and stainless steels obey the same rules, it is worthwhile to revisit published information on pitting of stainless steels and to present some unpublished results on the behavior of highly concentrated chloride solutions.

Nitrate and sulfate are the most important inhibitors of pitting. They seem to act in different ways, yet the common factor of mutual electromigration of anions into the pit or pit nucleus means that the concentration dependence of inhibition displays similarities for all anionic inhibitors.

Nitrate is a much better inhibitor at high than at low potentials. This leads to a phenomenon of anodic passivation of already initiated pits. Actually this is not unique to mixed electrolytes – near the critical pitting temperature (CPT) a similar behavior can be seen in pure chloride solution. Experimentation using artificial pits shows that nitrate is a much better inhibitor when an anodic salt film is present, and this led to the suggestion (by Newman and Ajjawi) that the low water activity within a hydrated salt film allows electroreduction of nitrate and/or redox reactions between Fe II and nitrate; of course if the latter is important, one can anticipate some differences between iron- and nickel-base systems.

Sulfate- and nitrate-containing systems differ in their response to potential when a salt film is already present. For nitrate, passivation occurs when the potential is made more positive, but in a certain range of chloride-to-sulfate ratio, sulfate causes passivation to occur directly from the salt-covered state *below* a critical potential. This can perhaps be understood in terms of a changing anionic composition of the salt layer with potential, although any such effect must be subtle, as a normal diffusion-limited behavior is always recorded – one supposes that different mixed salts would have different solubilities. Another factor to be considered is that the condition of the metal beneath the salt film has been shown to be one of continual passivation and reactivation, even in the absence of inhibitors.

Inhibitors are not always inhibitors. Around the CPT, sulfate causes pits to grow in a closed, crevice-like manner, and if the CPT is defined correctly, certain levels of sulfate reduce it quite substantially. Again there is an element of anodic passivation of pits, so that the unexpected aggressive effect of sulfate takes place over a range of potentials which is below that commonly used for CPT testing.