

Use of Crevice Scaling Laws to Investigate Local Hydrogen Uptake in Model Occluded Sites

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A damaging role of hydrogen is postulated in the mechanism for environment-assisted cracking (EAC) of many engineering alloys. Over 30 years ago, potential-pH diagram analysis demonstrated that the occluded geometry of a crack tip, crevice, or pit could enhance both hydrolytic acidification and promote ohmic potential drop. The resulting hydrogen overpotential created a situation where net hydrogen production and a high hydrogen fugacity were thermodynamically assured at an occluded site. The potential and pH of the bulk solution outside the pit or crack precluded such high hydrogen fugacities on external surfaces away from the occluded site. In these cases, local occluded site charging can occur without bulk external hydrogen charging. However, near-surface hydrogen concentrations within crack tips and pits were not quantified.

Early attempts to quantify crack tip and occluded site hydrogen concentrations focused on permeation experiments in bulk analogs of crack tip solutions at appropriate potentials representative of the crack tip or pit bottom potential. Alternatively, rules governing the relationship between hydrogen production rate and diffusible hydrogen concentration, derived from permeation experiments, were used in combination with scratch-repassivation data. The transient reduction of water kinetics were taken to simulate hydrogen production rates at transiently bare crack tips. Problems with these approaches include the inherent uncertainty concerning local hydrogen production rates as well as difficulty in duplicating surface films, near-surface trap state densities, and near-surface alloy compositions. These issues create difficulty in quantifying exact hydrogen concentrations at crack tips or within crevices and pits.

In this study, two approaches have been used to overcome many of the experimental difficulties inherent to the problem of local crack tip or pit hydrogen analysis. First, crevice scaling laws have been implemented to enable duplication of occluded site conditions representative of a small pit or crevice in larger sized model pits more assessable to hydrogen measurements. The scaling laws were developed using computer simulations developed by Jason Lee and Robert Kelly. Various crevice geometries were simulated using actual experimental parameters to determine a relationship between critical depths, representing activation and hydrogen production, and gap size. Potential versus depth data from the simulations were used to produce a graph of x_{crit}^2 vs. gap, which was determined to be the working scaling law for our system.

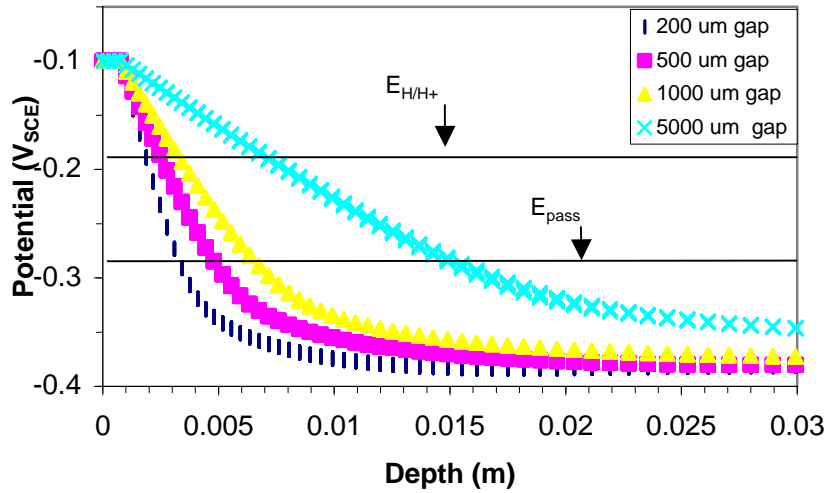


Figure 1: Simulated potential profiles for a rectangular crevice. $i_{crit} = 10^{-2} \text{ A/cm}^2$, $E_{pass} = -0.32 \text{ V}_{SCE}$, $E_{H/H+} = -0.215 \text{ V}_{SCE}$.

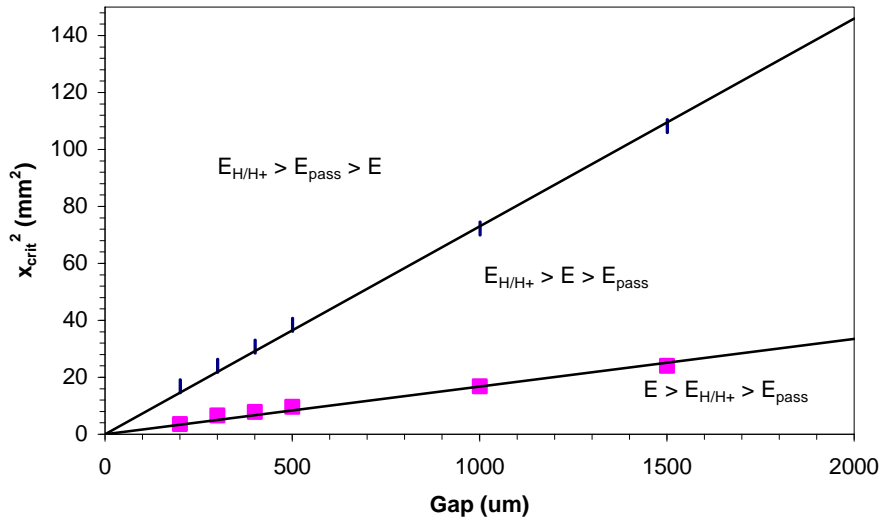


Figure 2: Simulated x_{crit}^2 vs. gap data for a rectangular crevice. $i_{crit} = 10^{-2} \text{ A/cm}^2$, $E_{pass} = -0.32 \text{ V}_{SCE}$, $E_{H/H+} = -0.215 \text{ V}_{SCE}$.

Second, a variety of hydrogen probes with enhanced combinations of lateral and depth resolution, as well as great sensitivity to hydrogen concentration have been utilized. These include thermal desorption spectroscopy and nuclear reaction analysis. These techniques have been applied to the study of local hydrogen uptake in PH 13-8 Mo stainless steel (H1050 condition, $\sigma_{ys} = 1241 \text{ MPa}$, $K_{IC} = 96\text{-}165 \text{ MPa m}$) with and without model localized corrosion sites. The studies were conducted on the metal exposed to solutions of HCl (simulating large chemistry changes

within the occluded site), H₂SO₄ (simulating a crevice environment with no metal dissolution or pH change), and H₂SO₄ plus dissolved iron, chromium, and nickel ions (simulating a crevice environment after metal dissolution). Each of these systems exhibits an active-passive transition. Thermal desorption spectroscopy was used to determine room temperature hydrogen diffusivity in this alloy in order to effectively charge samples with uniform hydrogen concentrations at various potentials along the polarization curves for PH 13-8 Mo exposed to 0.1M HCl and 5M H₂SO₄ with dissolved metal ions. Hydrogen uptake has been investigated under conditions where bulk hydrogen charging occurs at cathodic potentials, under local pitting conditions, as well as under conditions promoting crevice depassivation and surface activation. Local hydrogen concentrations in the stainless steel alloy are measured in conjunction with global electrochemical parameters, and global hydrogen production rates.

Experiments in model occluded sites are augmented with micro-pH and potential probe measurement of local crevice potential and pH. A model pit with a diameter of 1500 μm and a depth of 40 mm exhibited a potential drop of 160 mV over the length of the pit with a surface hold potential of -0.60V_{Hg/Hg₂SO₄} in 5M H₂SO₄ with dissolved metal ions.

Future work includes sectioning the model pits and analyzing them using thermal desorption spectroscopy in order to determine local hydrogen concentration as a function of depth. Nuclear reaction analysis will also be employed on samples held at various potentials to determine how passivity, active dissolution with concurrent hydrogen production, and net cathodic polarization affect local hydrogen concentration profiles.

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