Presentation of the Final Report

Localized Corrosion

Presented by

Peer Panel on Waste Package Materials Performance

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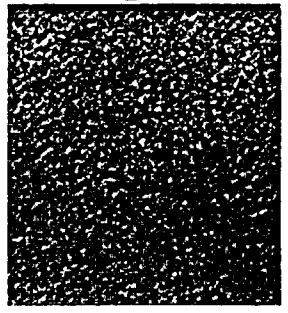
Main - 20

Localized Corrosion

Localized Corrosion – accelerated local attack resulting from the local breakdown of a protective passive film:

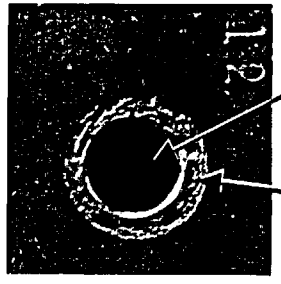
- Pitting corrosion – breakdown on a boldly exposed surface, usually associated with chloride ions in environment.
- Crevice corrosion – breakdown at an occluded region that has limited access to bulk environment.
- Intergranular corrosion – accelerated attack at grain boundaries associated with change in microstructure at grain boundaries (discussed in Potential Degradation Modes presentation).

Pitting in SS



from Metals Handbook, Vol. 13

Crevice Corrosion in SS



Alloy 22 and Ti Grade 7 are both extremely resistant to all forms of localized corrosion. However, Alloy 22 will crevice corrode under extreme conditions (high T, potential, and chloride concentration).

Localized Corrosion

Basis for Project design philosophy:

- Localized corrosion will not occur as long as the corrosion potential stays below some critical potential, i.e. if $\Delta E > 0$, where:

$$\Delta E = E_{crit} - E_{corr}$$

The Panel believes that this is an appropriate and conservative criterion if applied properly.

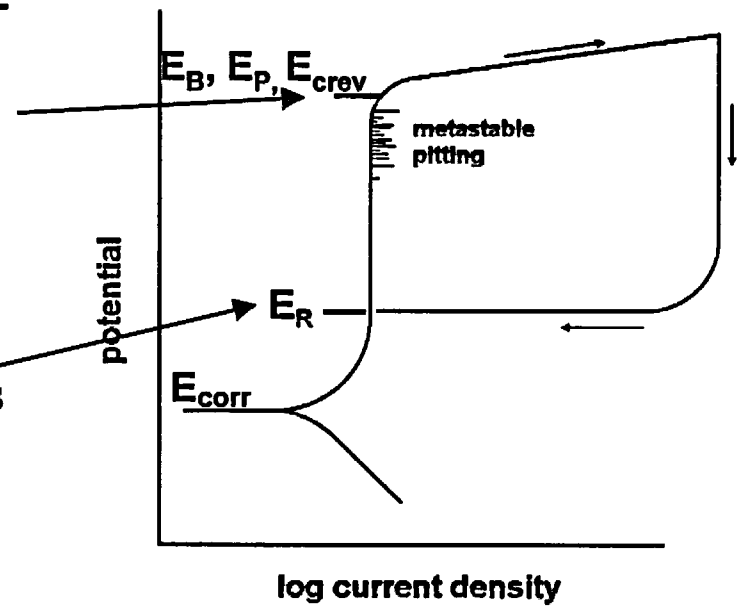
- Conservative measure of E_{crit}, such as the crevice repassivation potential, $E_{r,crev}$, should be used.
- E_{corr} should be measured and modeled separately from experiment used to determine E_{crit}.
- Environments more corrosive than those thought to be relevant should be studied to determine margin.

Critical Potentials in Localized Corrosion

Critical Potentials in Localized Corrosion

Breakdown Potential (pitting potential, crevice potential) is the potential at which the current increases dramatically during a potentiodynamic scan due to stable growth of localized corrosion.

Repassivation Potential (protection potential) is the potential at which the current drops during the reverse scan due to repassivation (or cessation of growth).



Conventional Wisdom: Localized corrosion can start to grow at potentials above E_B, and can continue to grow at potentials above E_R. Therefore, **resistant materials** have

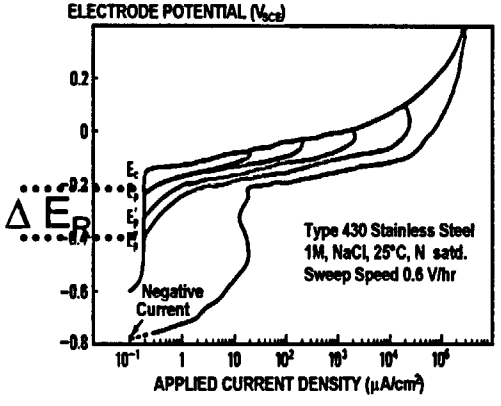
- **high values of: E_B, E_R, $(E_B - E_{corr})$, $(E_R - E_{corr})$**
- **low value of: $(E_B - E_R)$**

Critical Potentials in Localized Corrosion

- Crevice corrosion typically occurs more readily than pitting corrosion. Critical potentials related to crevice corrosion are lower:

$$E_{crev} < E_{pit} \qquad E_{r,crev} < E_{r,pit}$$

- Repassivation potentials depend on the extent of prior localized corrosion:



B. Wilde, in *Localized Corrosion*, R.W. Staehle, B.F. Brown, J. Kruger, and A. Agrawal, Eds., NACE-3, p. 342, NACE, Houston, TX, (1974).

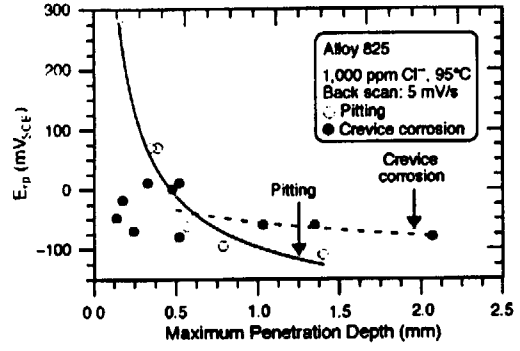


FIGURE 5. *Effect of prior pitting and crevice corrosion depth on E_{rp} for pitting and crevice corrosion for alloy 825 in 1,000 ppm Cl^- solution at 95°C.*

Dunn, Cragnolino and Sridhar, CNWRA

- **The most conservative critical potential is $E_{r,crev}$ generated from intentionally creviced samples with sufficient prior growth.**

Other Important Factors in Localized Corrosion

- The **composition of the environment** has a dominant effect on the susceptibility to localized corrosion.

  The susceptibility to localized corrosion increases with the logarithm of the **chloride** concentration. Chloride ions are present in Yucca Mountain.

  Oxyanions present in Yucca Mountain (**sulfates and nitrates**) have an inhibiting effect on localized corrosion.

- Localized corrosion will not occur at **temperatures** less than some critical value, either the critical pitting temperature or critical crevice temperature.

  Localized corrosion will only occur in a certain temperature range as the waste packages cool: below the value at which a liquid will form (related to the critical relative humidity for the surface contaminants) and above the critical temperature for localized corrosion.

- The **surface condition** can have a strong effect on localized corrosion. In general, the susceptibility to localized corrosion increases as the roughness of the surface finish increases. On the other hand, protective surface films can reduce the likelihood for localized corrosion.

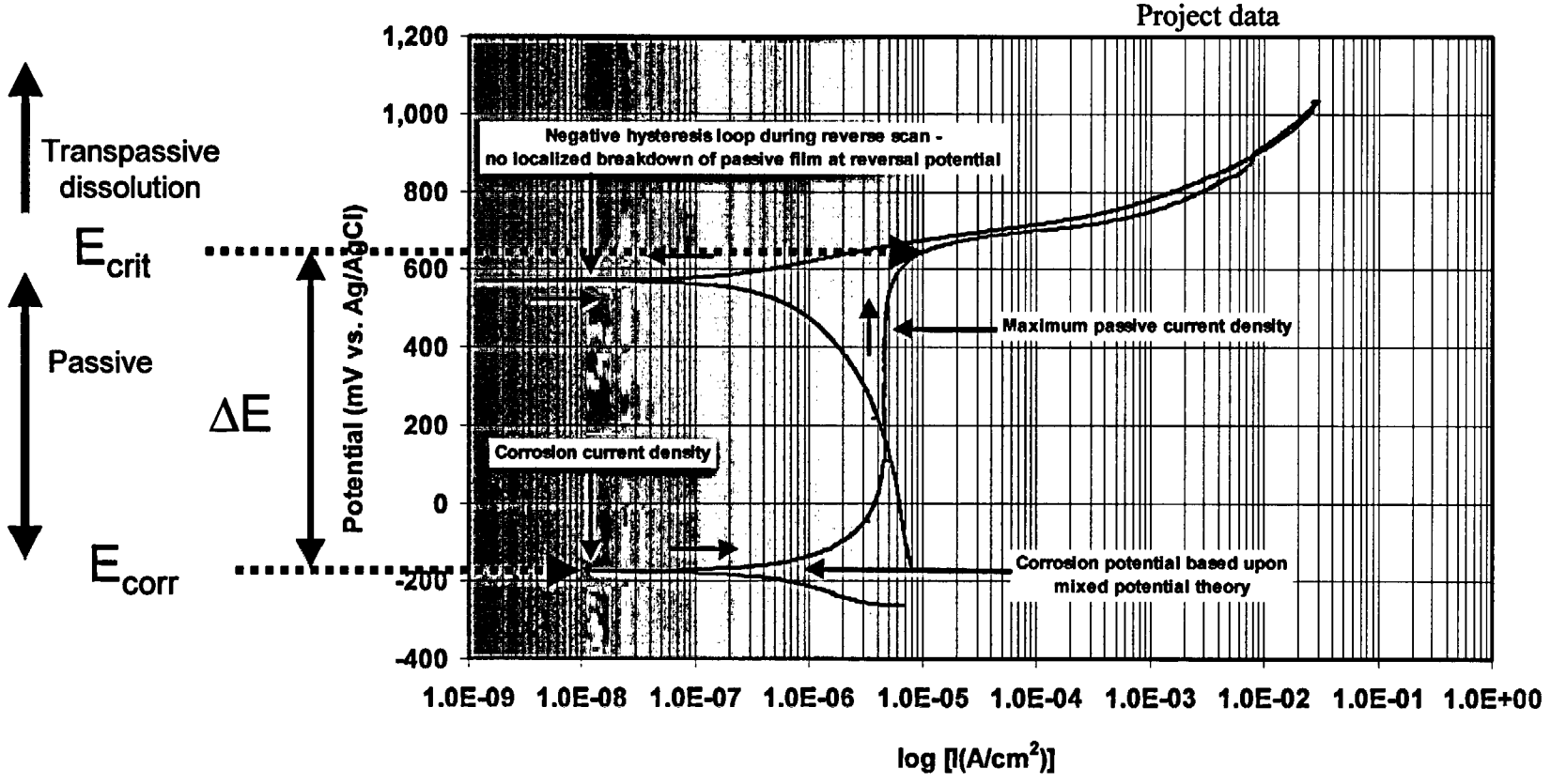
  There are no special plans for treatment of waste package surfaces; they will be the result of the sum of processing history.

Localized Corrosion - Project Approach

- The Project has performed two primary types of experiments related to localized corrosion: exposure in the LTCTF to various predicted or relevant environments and cyclic polarization.
- There has been **no evidence of localized corrosion** of Alloy 22 or Ti Gr 7 in the LTCTF environments over a period of as long as 4 years, which indicates a high resistance to localized corrosion in these environments.
- However, the corrosion potential has increased significantly (more below).
- The TSPA is based on ΔE determined by cyclic polarization on nominally uncreviced samples in these specific environments in which the alloys do not exhibit localized corrosion.
- As described in the Abstraction, the TSPA uses specific values from the cyclic polarization curves as E_{crit}.

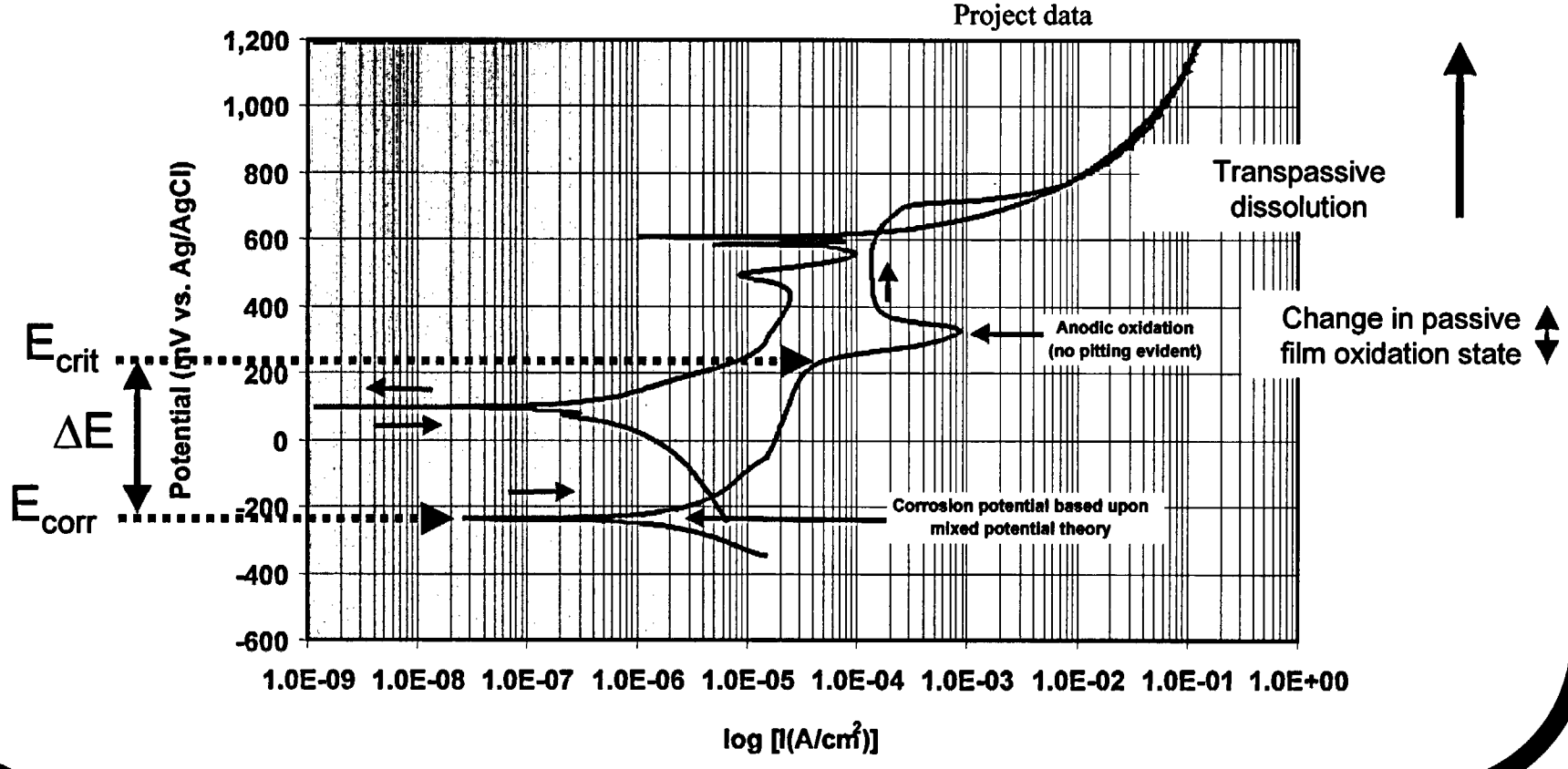
Localized Corrosion - Project Approach

Alloy 22 in SAW at 90°C



Localized Corrosion - Project Approach

Alloy 22 in SCW at 90°C
Alloy C-22 in SCW at 90 Centigrade



Localized Corrosion - Project Approach

- The TSPA is based on ΔE determined from potentiodynamic polarization curves in the few expected or relevant environments.
- Experimental data were fitted to determine dependencies on certain variables:

  For Alloy 22:

  $$\Delta E(mV) = 1260 - 0.313\ T + 8.15 \log[Cl^-] - 188\ pH + 11.8\ pH^2 + \varepsilon$$

  For Ti Gr 7:

  $$\Delta E(mV) = 2050 - 1.17\ T + 14.1 \log[Cl^-] - 48.9\ pH + \varepsilon$$

- According to these equations, ΔE will be > 0 for both alloys for a wide range of values of the variables. Therefore, localized corrosion is predicted never to occur.
- Note the weak dependence on temperature and chloride concentration, and lack of consideration of the effect of inhibiting oxyanions.

Localized Corrosion - Project Approach

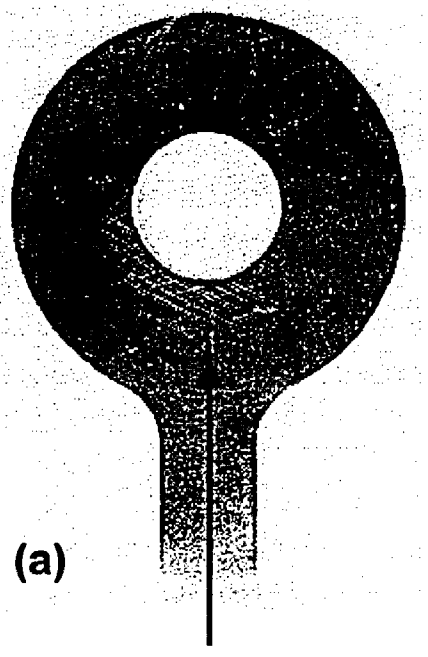
- Problems with Project approach:
  - Samples used in potentiodynamic experiments were nominally **uncreviced.**
  - **Alloys do not exhibit localized corrosion in tested environments – E_{crit} is not related to localized corrosion.** In other words, the model for localized corrosion is based on data that are unrelated to localized corrosion.
  - Does not allow extrapolation to other environments in which localized corrosion is possible.
  - E_{corr} values (zero current potentials in polarization curves) are **not indicative of long term corrosion potential.**

But:

- The Project is aware of data generated at other labs, and finds that these data generally support Project view that the alloys are resistant to localized corrosion.
- Project subcontractors are doing other work, and **the Project has started to address the shortcomings in their approach to localized corrosion.**

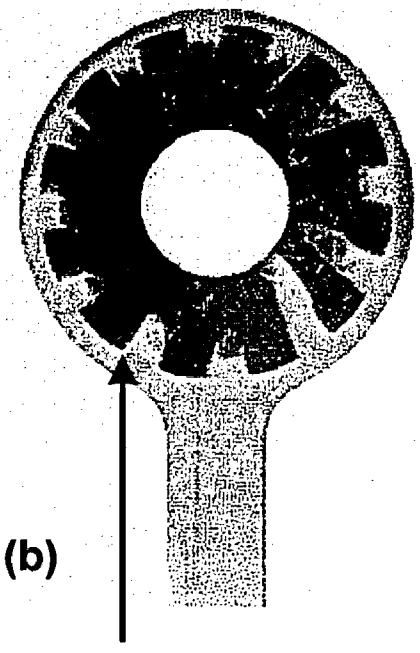
No Crevice Corrosion in BSW, but Crevice Corrosion Observed in Concentrated Chloride-Only Solution

Alloy 22 Crevices
Ceramic Washer
Ramped to 550 mV
~ 100°C BSW



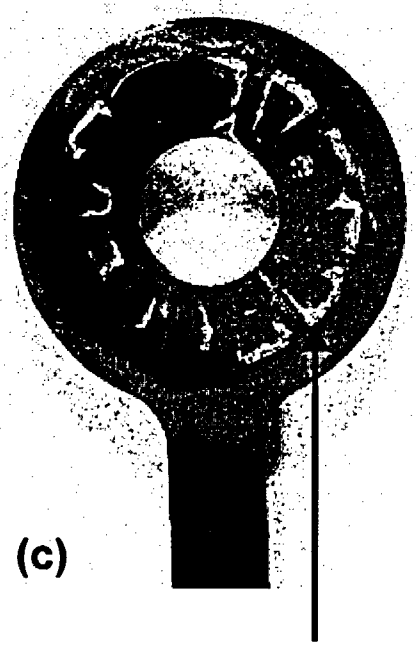
No crevice attack

Alloy 22 Crevices
Teflon Washer
Ramped to 800 mV
~ 110°C BSW



Stain but no crevice attack in BSW

Alloy 22 Crevices
Ceramic Washer
350 mV for 2 hours
~ 100°C 4M NaCl

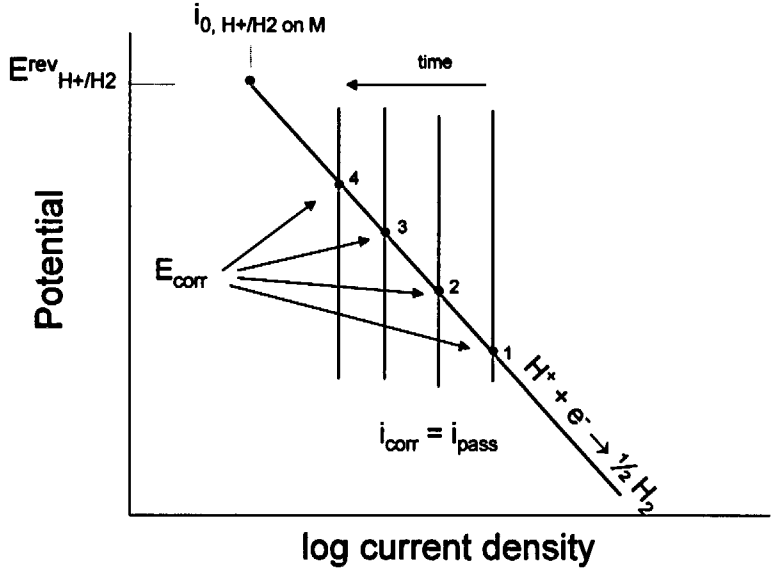


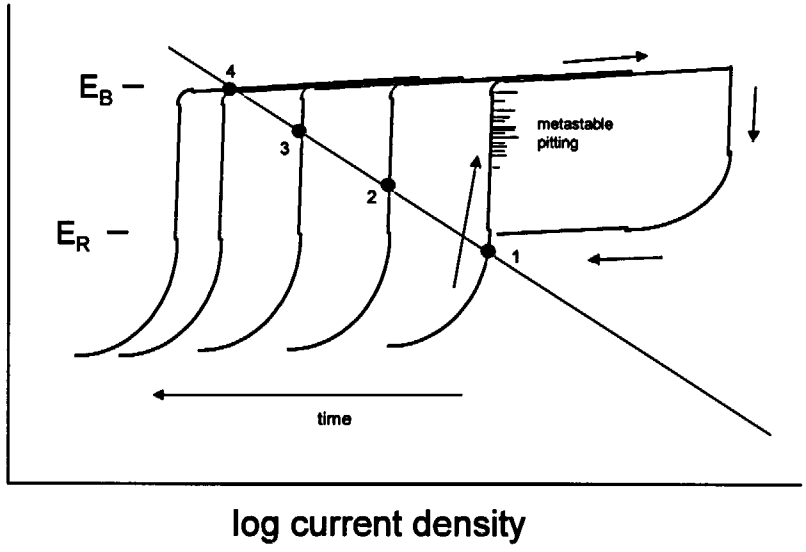
Severe crevice attack of sample

In the case of (a) and (c) above, the potential was increased until a current density of 5 mA cm^{-2} was achieved.

Project data

Localized Corrosion - Ennoblement

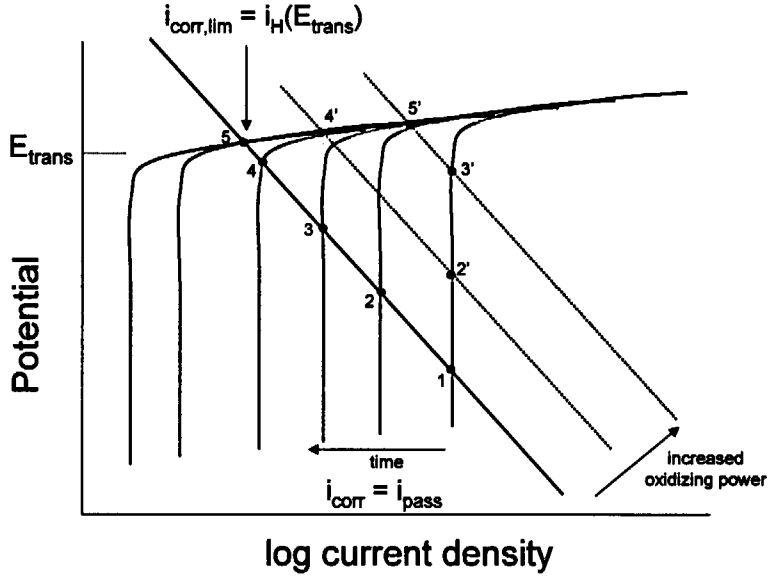




Improvement in passivity leads to **passivity induced ennoblement (PIE)** - increase in E_{corr}, assuming no changes in cathodic kinetics. Decrease in i_{corr} accompanies PIE.

PIE is limited at breakdown potential if localized corrosion is possible, but sustained localized corrosion would not be possible because of limit of cathodic reaction.

Localized Corrosion - Ennoblement

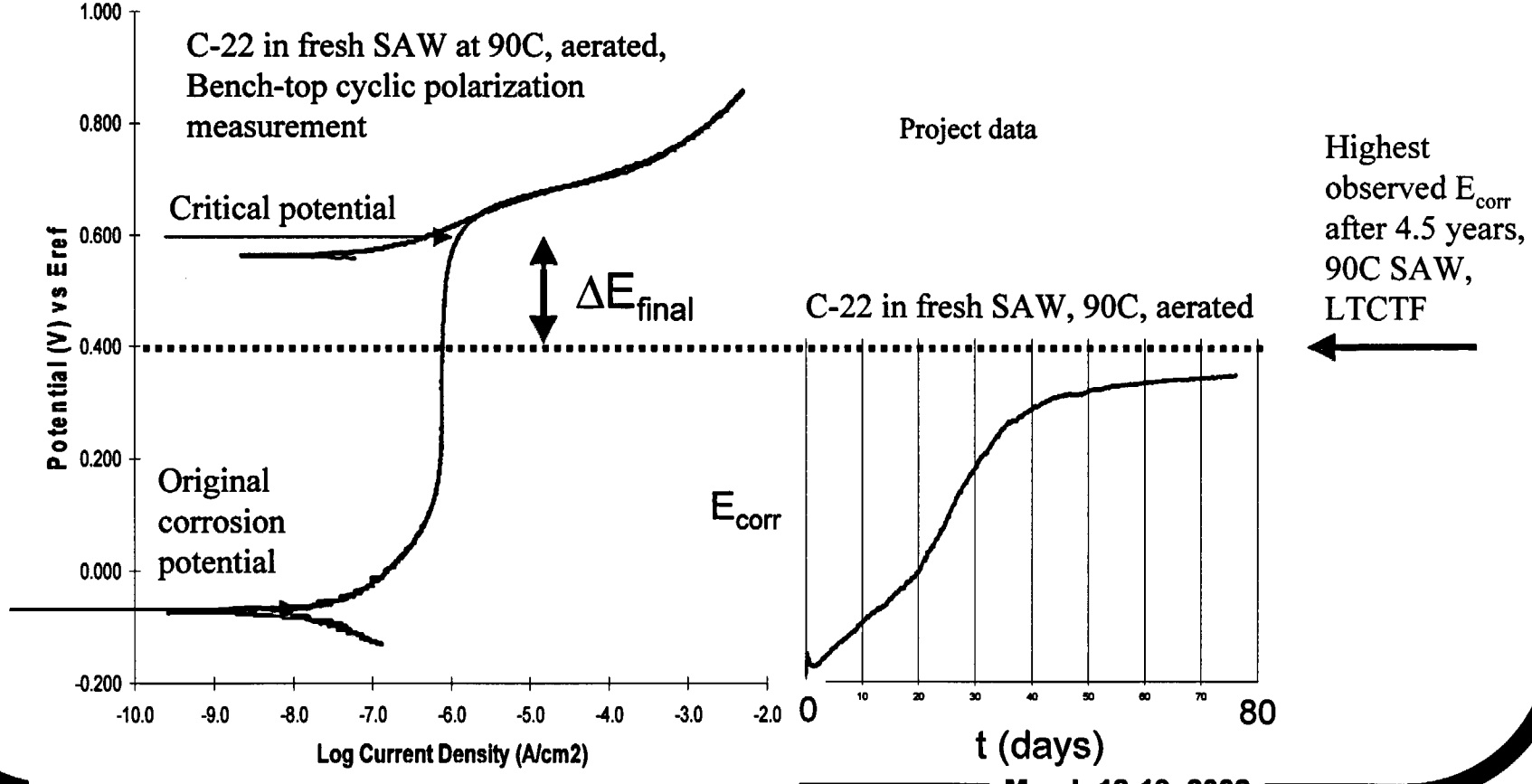


- PIE is limited by transpassive potential if breakdown is caused by transpassivity.
- Transpassive dissolution might lead to oscillations between points 5 and 4.
- Condition is susceptible to transpassive dissolution if kinetics are enhanced or a new cathodic reaction is available, such as reduction of peroxide generated by radiolysis.
- **There are implications of PIE on ΔE criterion.**

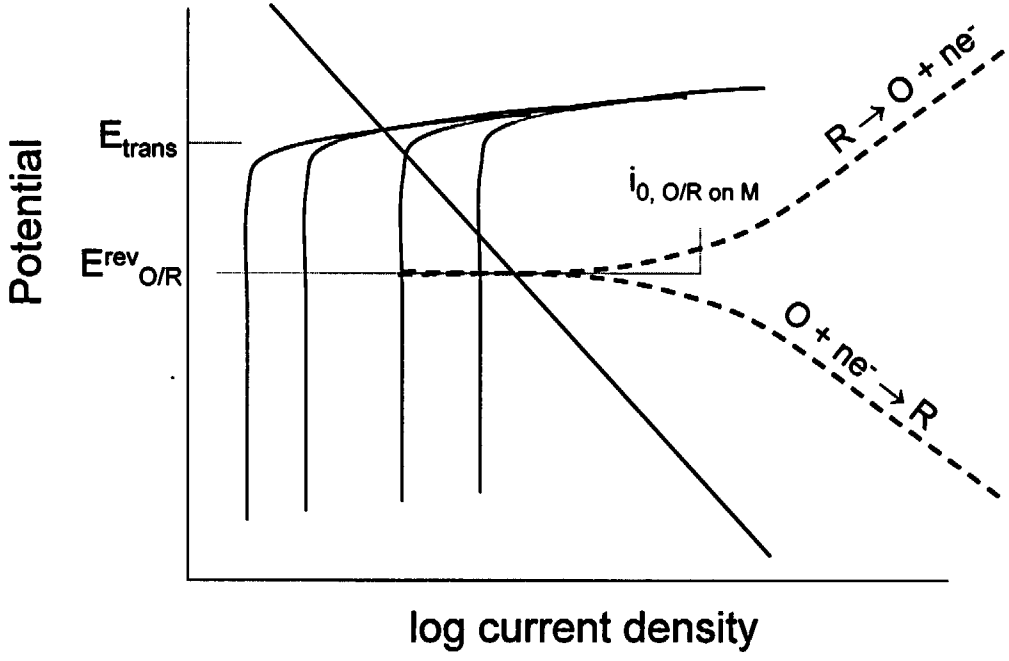
Localized Corrosion - Ennoblement

The project has measured E_{corr} to have increased by about 500 mV after 4.5 years in various solutions in the Long Term Corrosion Test Facility.

No localized corrosion was found, and the potential remained below the transpassive potential and close to the potential for Pt in that solution.



Localized Corrosion - Ennoblement



The corrosion potential might be pinned at a value below a critical potential if the solution contains a redox reaction with an exchange current density that becomes large relative to the passive current density as the passive current density decreases. Based on the potential of Pt, this seems to be happening over long times in SAW.

ΔE might get small with time, but that is not bad if E_{corr} stays below a conservative E_{crit}, such as $E_{r,crev}$.

Localized Corrosion Growth- Project Approach

- The Project has a model for the prediction of localized corrosion growth, but it is irrelevant to TSPA because localized corrosion is predicted never to initiate.
- The current model predicts that localized corrosion in Alloy 22 or Ti Gr 7, once initiated, would grow at a constant rate over a distributed range of values.
- This is a very conservative model that over-predicts the penetration rate of localized corrosion since it is known that the rate of localized corrosion will usually slow with time (varies approximately with $t^{1/2}$).
- Localized corrosion is autocatalytic, and tends to propagate once initiated. However, pits and crevices can spontaneously die or cease growing. This might be more important for crevice corrosion in a moist dust environment because of cathodic limitations. The arrest of localized corrosion has not been considered by the Project.

Localized Corrosion - Panel Recommendations

1. The ΔE design criterion is appropriate and conservative if applied properly. The Project should take a more rigorous approach to the determination of the critical potentials:
   - The Project should use $E_{r,crev}$ from intentionally creviced samples that have undergone sufficient attack as the value of E_{crit}.
   - The Project should measure and model E_{corr} separately.
2. The Project should test under aggressive conditions in which the alloys are susceptible to localized corrosion. Extrapolation of E_{crit} and E_{corr} to any environment of interest would then be possible.

Localized Corrosion - Panel Recommendations

3. Temperature is a critical factor in localized corrosion with higher temperatures being more likely to cause localized corrosion. $E_{r,crev}$ and E_{corr} values should be determined at higher temperatures and most particularly at all temperatures to which the waste packages might be exposed in the presence of an aqueous layer.

4. Studies of localized corrosion propagation and arrest should be undertaken to supplement work on initiation because these factors will control the accumulated extent of damage from localized corrosion should it occur. More realistic models should be developed.

5. The effects of metal surface condition on localized corrosion should be examined as surface condition also can have a large influence.

6. Testing should be performed under all metallurgical conditions that might enhance susceptibility, such as welded structures.

Localized Corrosion - Panel Recommendations

7. Environments containing possible oxidizing agents, such as peroxide or ferric ions, should be investigated. The possible effects of radiolysis should be reevaluated for the current waste package design and expected condition of spent fuel. Oxidizing agents will increase the corrosion potential and thus the likelihood for localized corrosion.

8. Localized corrosion (crevice corrosion in particular) should be studied in the environments that are most relevant for the external metal surfaces:

   - moist dust on the metal surface
   - scale and deposits on the metal surface