

ALLOY 22 - Ni-Cr-Mo-W-Fe - Thin Oxide Film Conferring Passivity

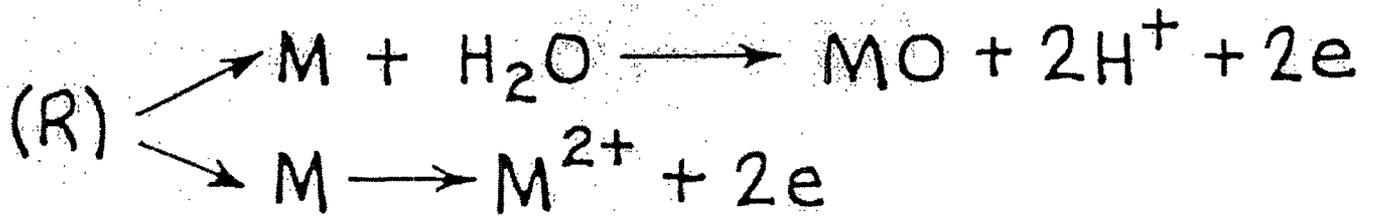
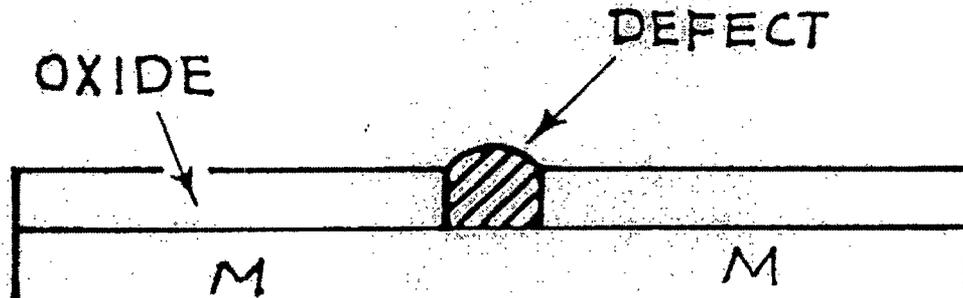
Ideal Conditions - Passive Current Flows - F_n - Oxide State & Environ.

Source of "PC" - uniform M^+ passage - non-uniform - oxide dissoln.

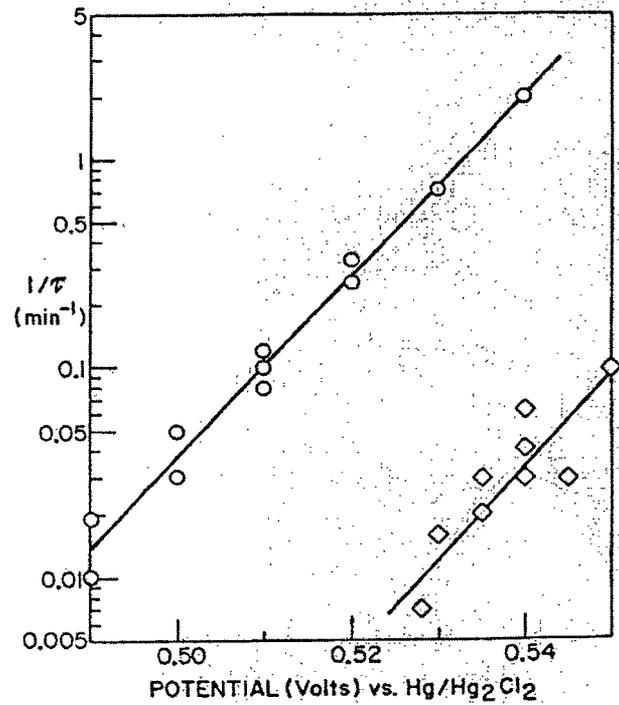
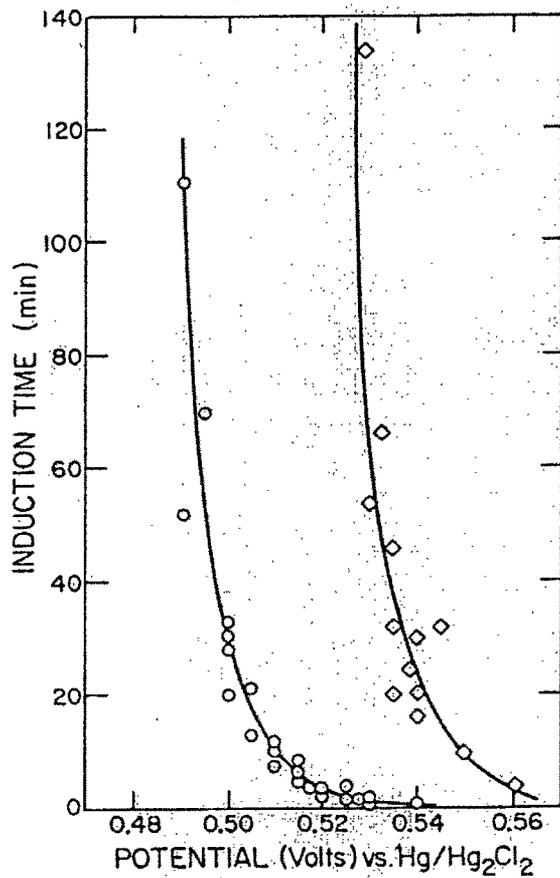
Suggest NUOD at defects which are not STATIC - 016/018 SIMS Ni

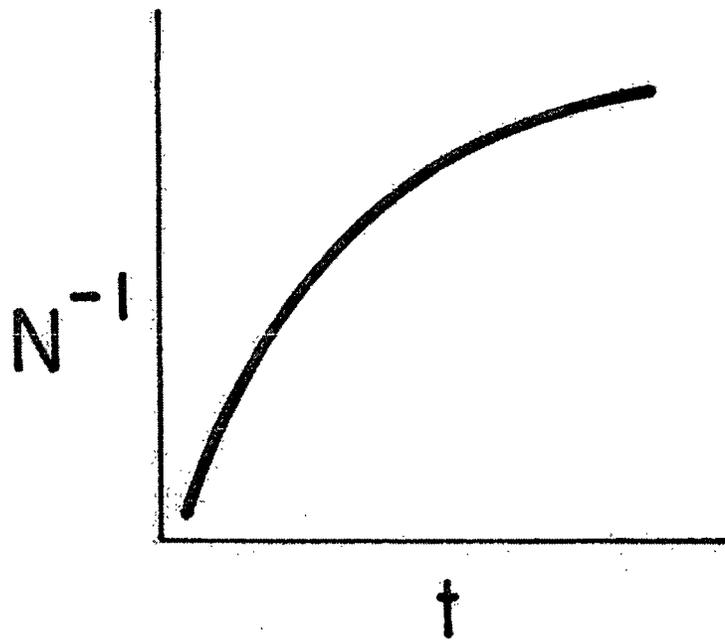
With time, # defects and PC decrease - but not "activity" at each defect

Strong Implications for Localized Corrosion - Perfection vs. Stability

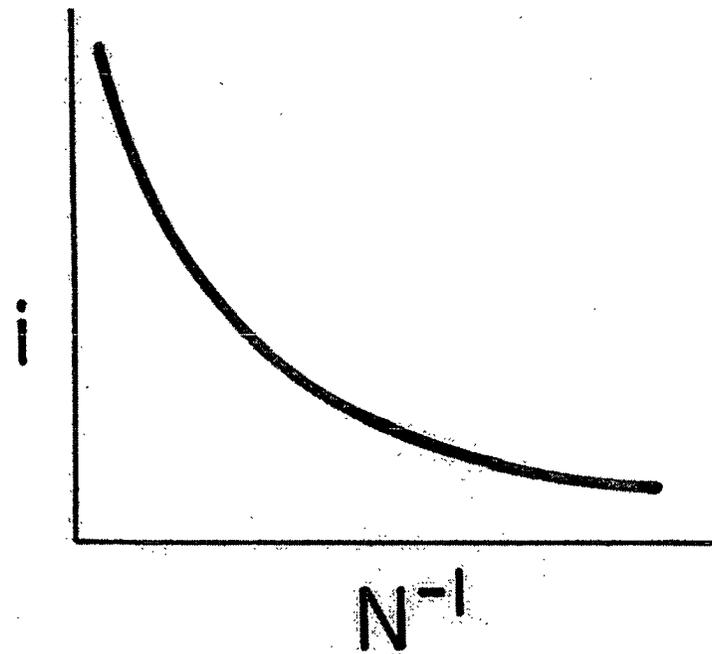


IF EVERYTHING IS EQUAL [METAL OR ALLOY COMPOSITION AND STRUCTURE, AGGRESSIVE ENVIRONMENT], THEN IT DOES NECESSAIRLY FOLLOW THAT THE MORE PERFECT AND DEFECT-FREE THE PASSIVE FILM, THE MORE RESISTANT IT IS TO LOCALIZED CORROSION.





$$N^{-1} \propto \log t$$



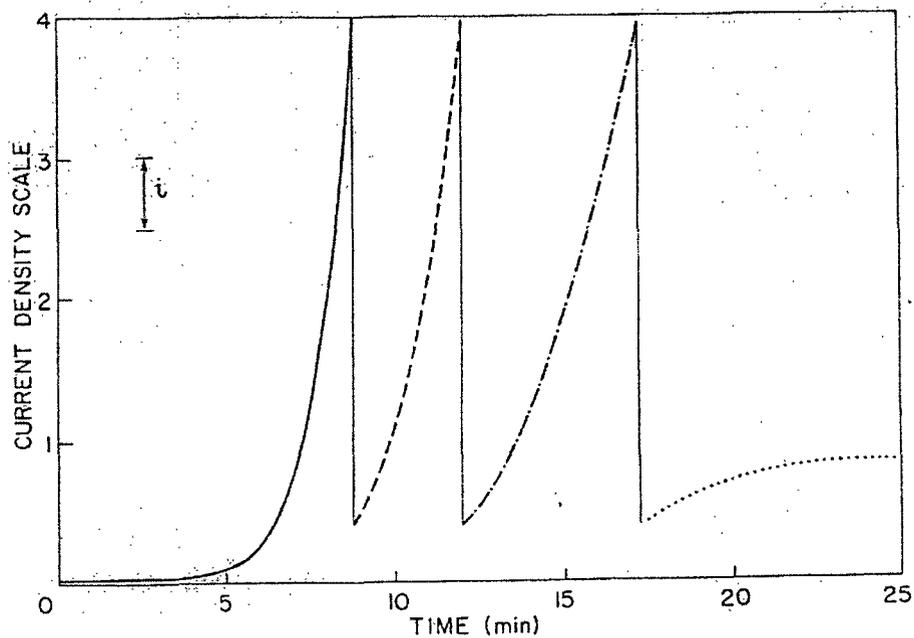
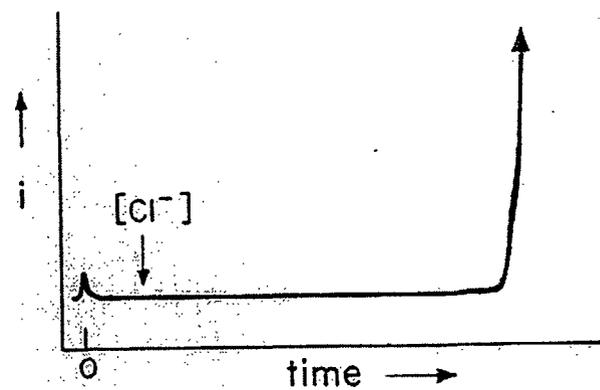
$$i \propto \exp - (N^{-1})$$

$$N^{-1} \propto -\log i$$

$$\therefore -\log i \propto \log t$$

Possible Experiments to be Performed with ALLOY 22:

- 1) Passive Film - Thickness, Composition, Structure, Fn. of Va, $t(a)$, A-.
- 2) Stability: CV, pot(l) step, OC and CR, $t(ind)$ in Cl, expand to F also.
- 3) Ni, Cr, Mo, W dissolve at different rates; time evolution of film.
- 4) Cl and F together have a massive detrimental effect [pH, other A-].
- 5) Local B & R in F results in substantial F incorporation into Ni POF.



QUESTION 2

[1] With time, oxide film may have fewer but "more active" defects, meaning that the critical potential will change.

[2] The electrolyte environment can change near the WP; special concern with [Cl] and [F] and influence CPP. F interferes with "later" passivation, Cl with initial stages; together, ability to interfere with all stages of passivation.

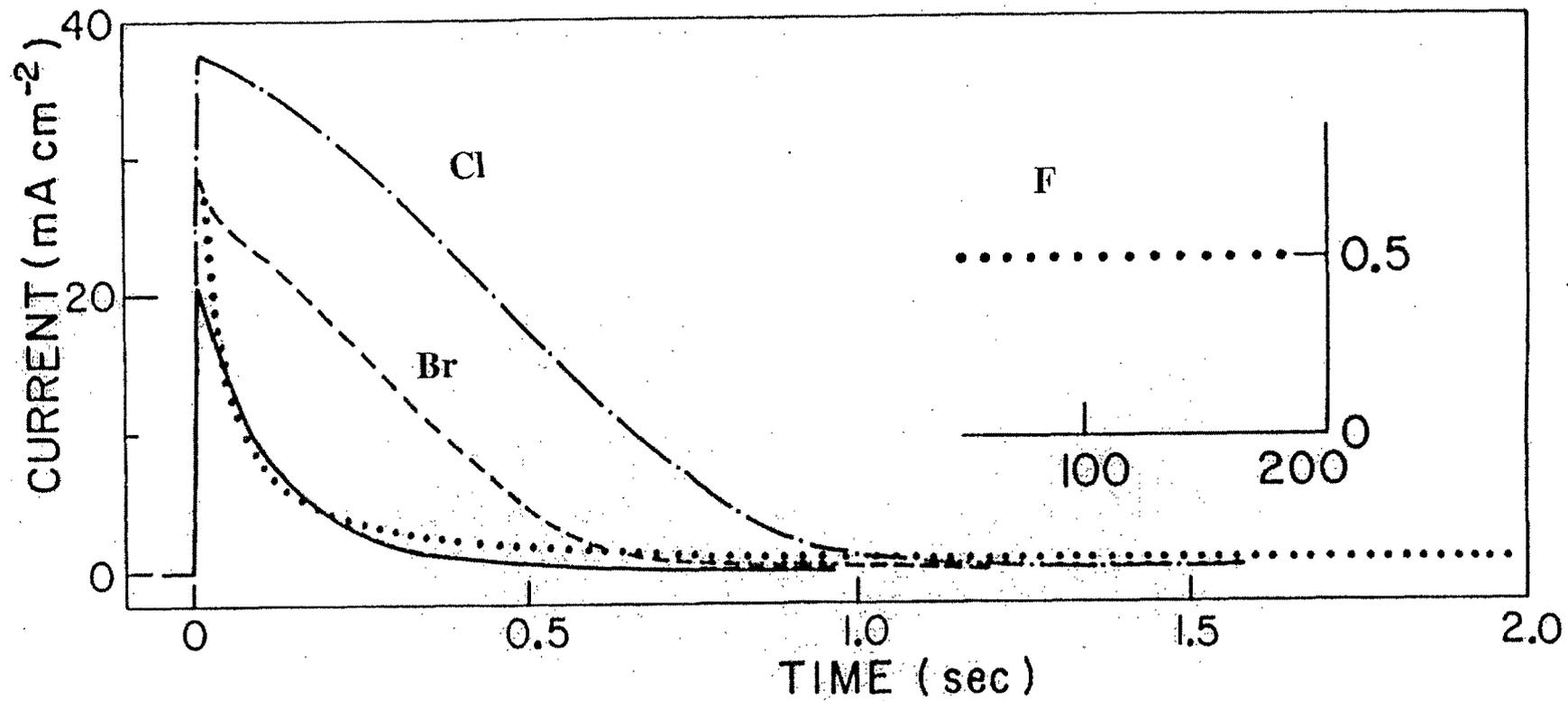
[3] Change in "complexing anion" conc. can greatly change the effective driving force, eg.:



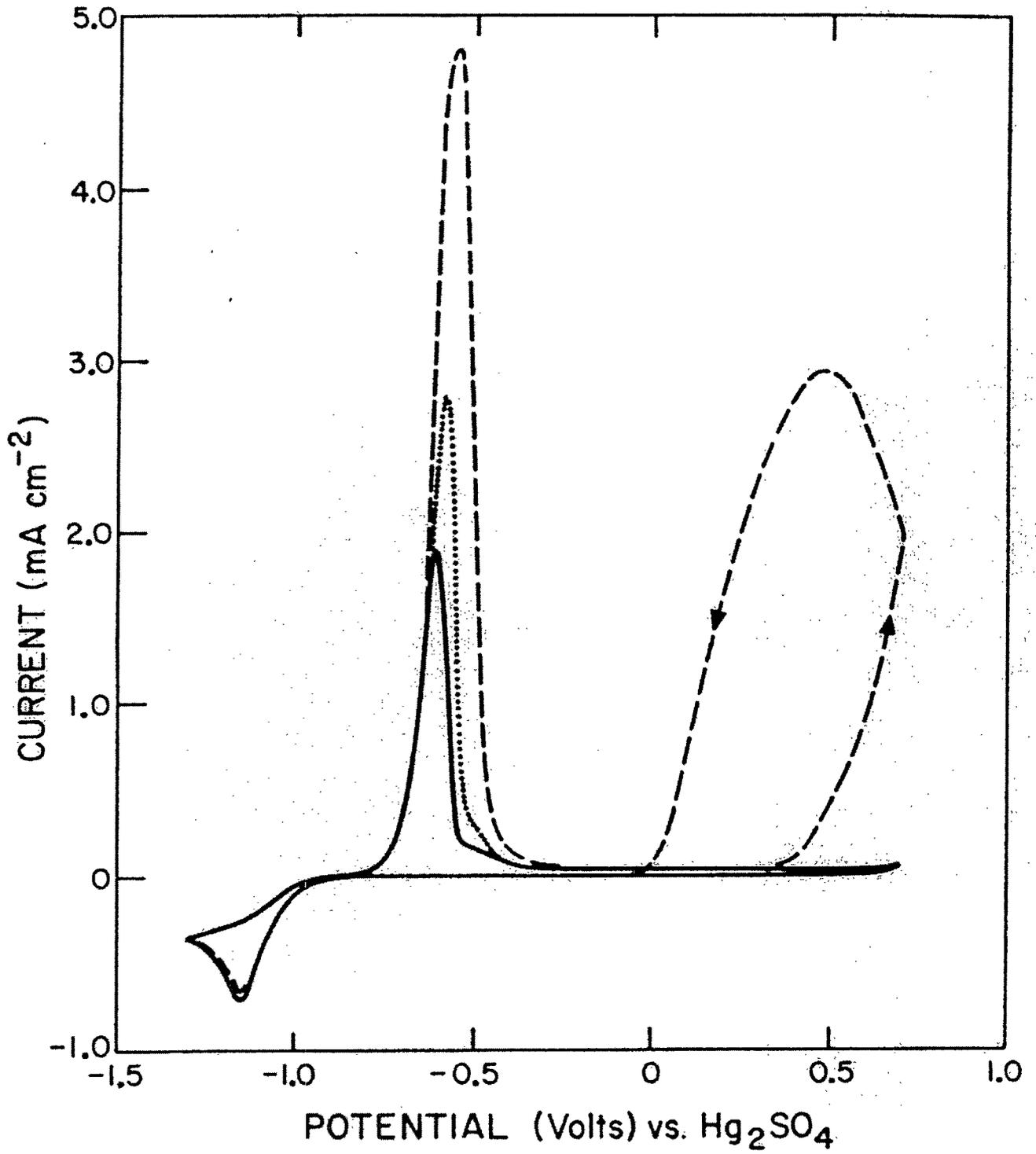
F and Cl have strong complexing abilities with cations.

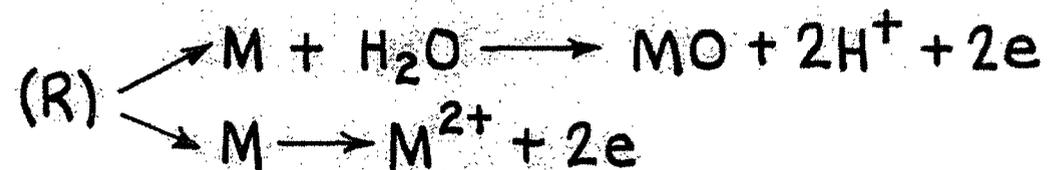
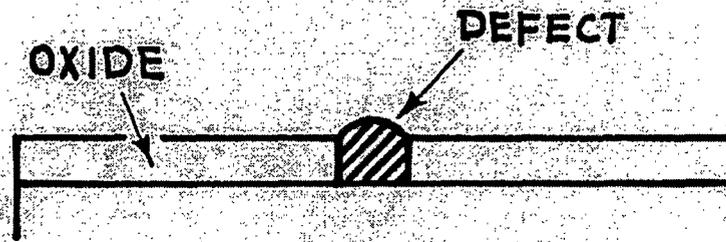
Something like this will mean a great increase in driving force for dissolution and possibly localized corrosion.

[4] Not only do we need a high OC "V", but cathodic counter reaction must be able to sustain the localized corrosion: H₂, O₂, red[n], etc. Effect of temperature on anodic and cathodic reactions, solubility, complexes, chemical dissolution, oxide?

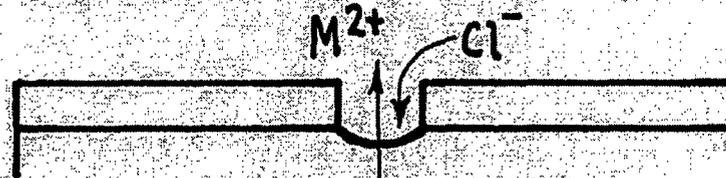


HYSTERESIS EFFECTS: DIFFERENCE B/W E(pn) &E(pp)

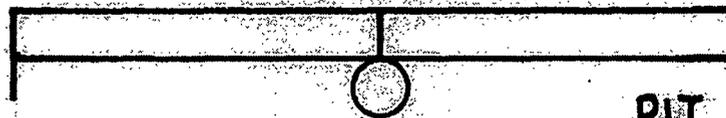




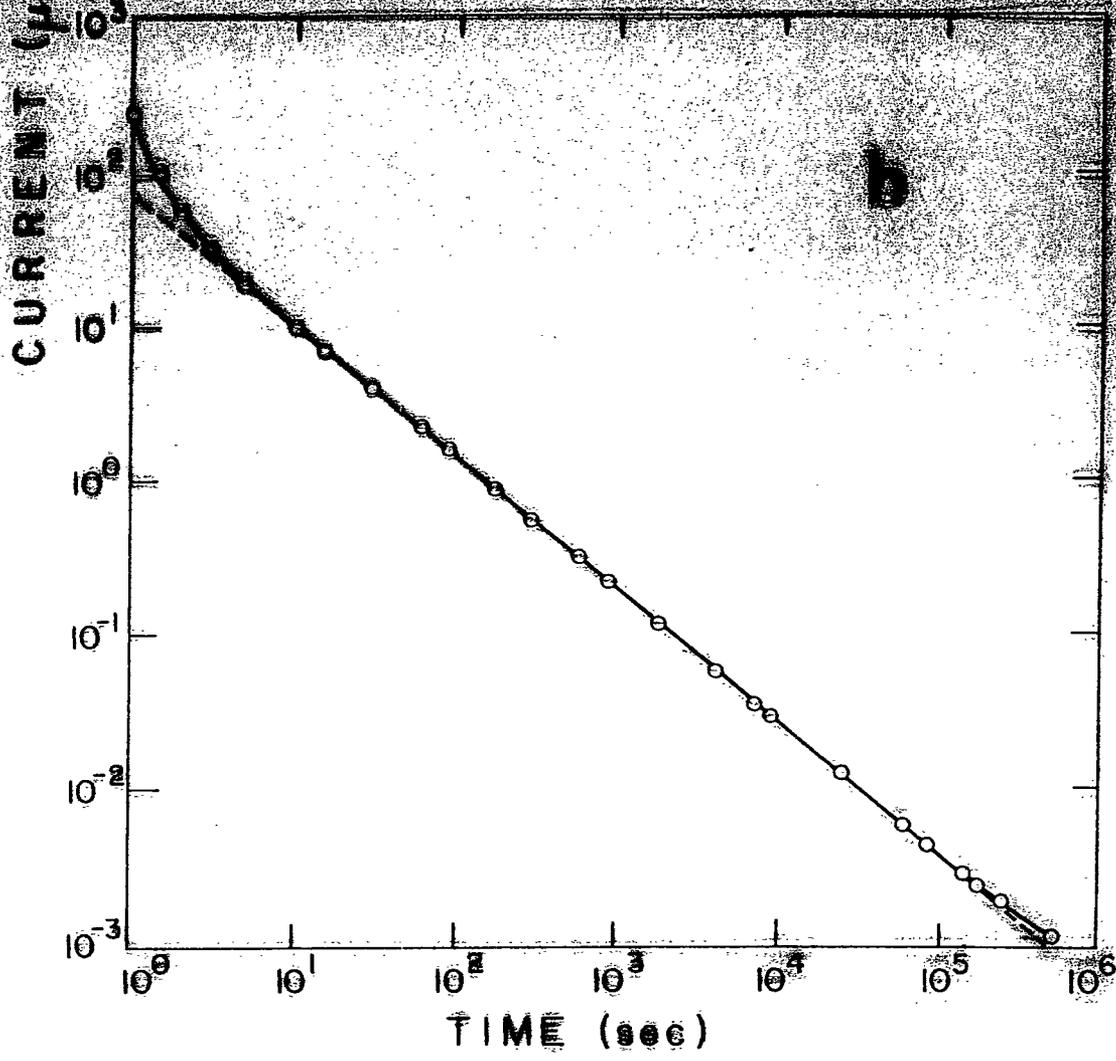
Cl^- MIGRATES AND INTERFERES WITH REPAIR



\therefore MORE METAL DISSOLVES AND MORE Cl^- MIGRATES



PIT DEVELOPMENT



MacDougall 7/20/01

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International Workshop on Long-Term Extrapolation of Passive Behavior

Question N°1: On the effects of long-term passive dissolution

Premise:

- **The Alloy 22 surface is passivated**
- **The passive layer is thermodynamically stable and self repairing Passive corrosion is uniform and proceeds at a rate $\leq 0.1 \mu\text{m}/\text{year}$**
 - \Rightarrow **times $\geq 10^5$ years for penetration of the 2cm thick WP wall (when localized corrosion is not expected).**

What will happen after several hundreds or even thousands of years, assuming the passive corrosion penetration has reached a substantial depth ($> 10\mu\text{m}$)?

Question N°2 : On the long-term preservation of conditions preventing localized corrosion

Premise:

The open circuit potential at the package surface stays significantly more negative than the critical potential for stable localized corrosion.

Mechanisms that may cause initiation and propagation of localized corrosion (not amenable to description in terms of a critical potential).

- **Passive film breakdown caused by impurity segregation (e.g. S) at the alloy-passive film interface (this can occur at potentials below the critical potential for stable pitting).**
- **Local depassivation by aggressive ions (e.g. F⁻) (interactions with specific defects of the passive film?)**

Experiments and/or theoretical treatment to investigate the above issues.

- **Same as for question N°1: laboratory studies of the passive behavior of Alloy 22 with increasing amounts of impurities (e.g. S)**
- **Study of the mechanisms of local depassivation by ions other than Cl⁻ (e.g. F⁻)**