The Influence of Radiation on Pit Solution Chemistry as it Pertains to the Transition from Metastable to Stable Pitting in Steels

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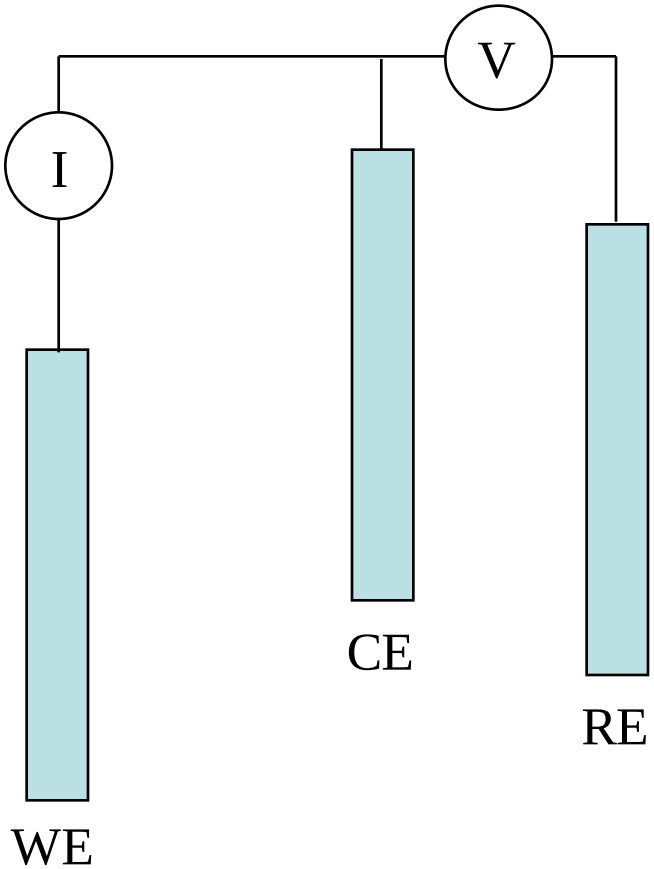
- Gustav Vaquez, GRA-PhD, LANL (Spring '05)

Overview

- Electrochemical Noise and the Hanford/SRS Corrosion Probe
- GEV to Correlate EN Current Data and Surface Damage.
- Influence of Radiation on EN.
- Analysis of Pit Solution Chemistry, Irradiated vs. Non-Irradiated.

Carbon steels in simulated alkaline waste solutions

Electrochemical Noise (EN)



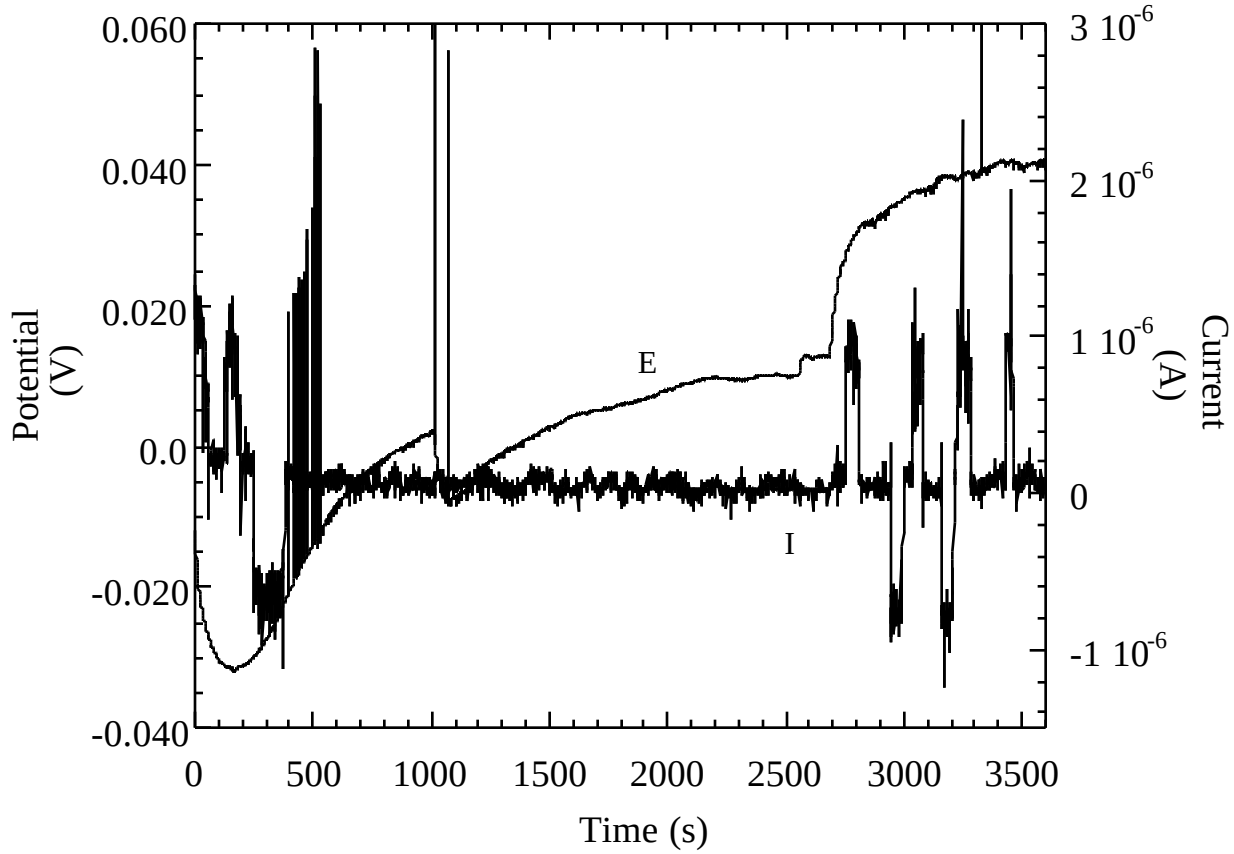
- Three nominally identical carbon steel electrodes
- Immersed in a simulated alkaline waste solution at OCP
- Flow control: 100ml/min
- Temperature control: 40° C
- Monitor current and potential for1 hr. per day for 5 days.

Correlation Between EN and Surface Damage Using Generalized Extreme Value Statistics

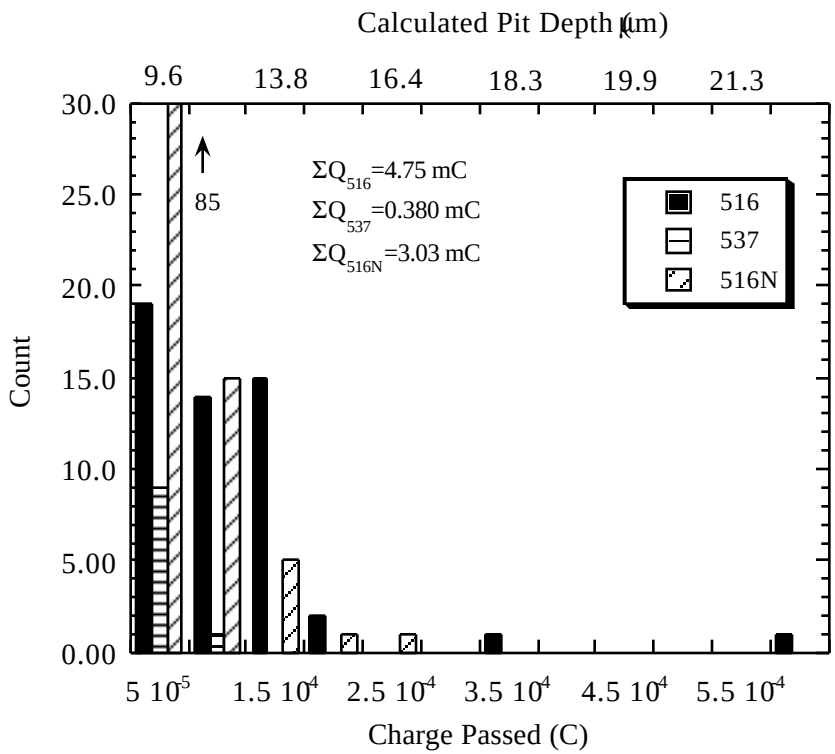
$$GEV(u,\alpha,k) = \exp\{-[1-k(x-u)/\alpha]^{1/k}\} \quad kx \leq \alpha + uk$$

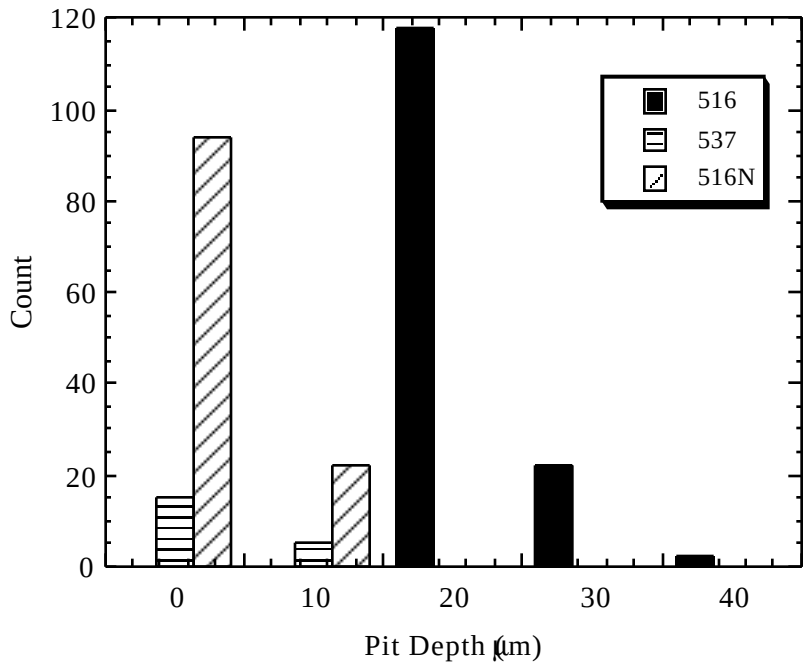
- Combines Gumbel, Frechet, Weibull distributions
- Models distribution "tail" ... leads to thresholding of data
- Small sample sizes (40-120 events)

Electrochemical Noise Data



Comparison of Charge Passed and EN Data

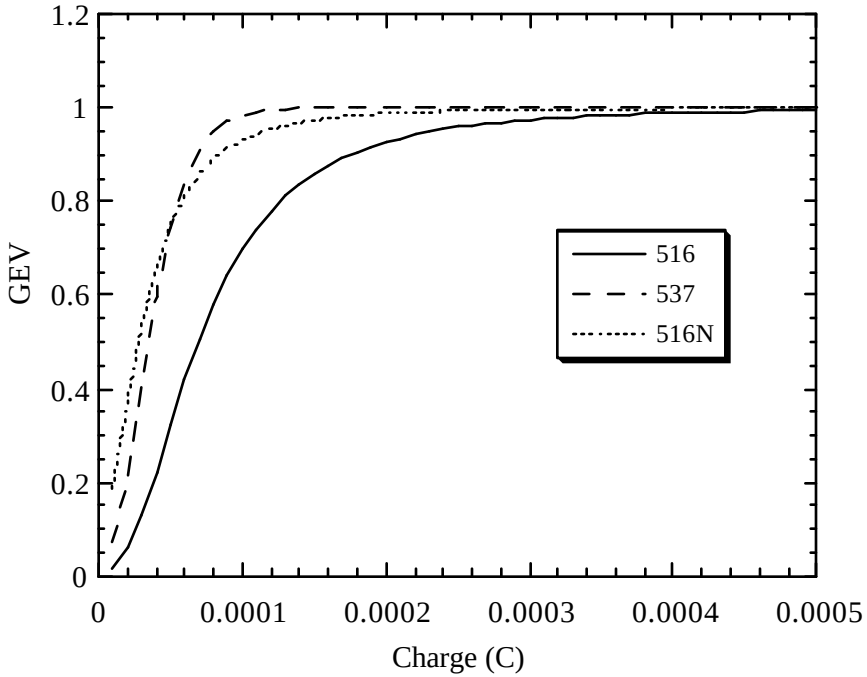




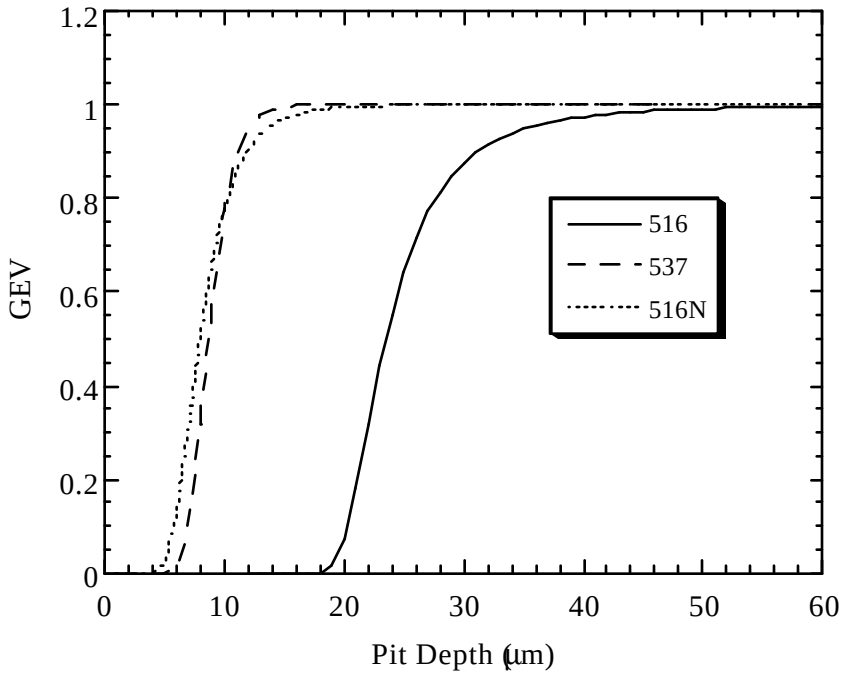
Chloride/Nitrate/Nitrite Simulated Waste Solution pH 14 @ 40° C

Correlation Between EN and Surface Damage Using Generalized Extreme Value Statistics

EN - charge passed



Pit Depth



Using GEV 1:1 correlation between electrochemical noise and pitting events

Is there An Influence of irradiation on Pitting Corrosion?

Summary of potentiodynamic polarization data taken at the UF Radiation Chemistry Lab. Data with and without g radiation are presented. Each data set represents the average of six separate experiments.

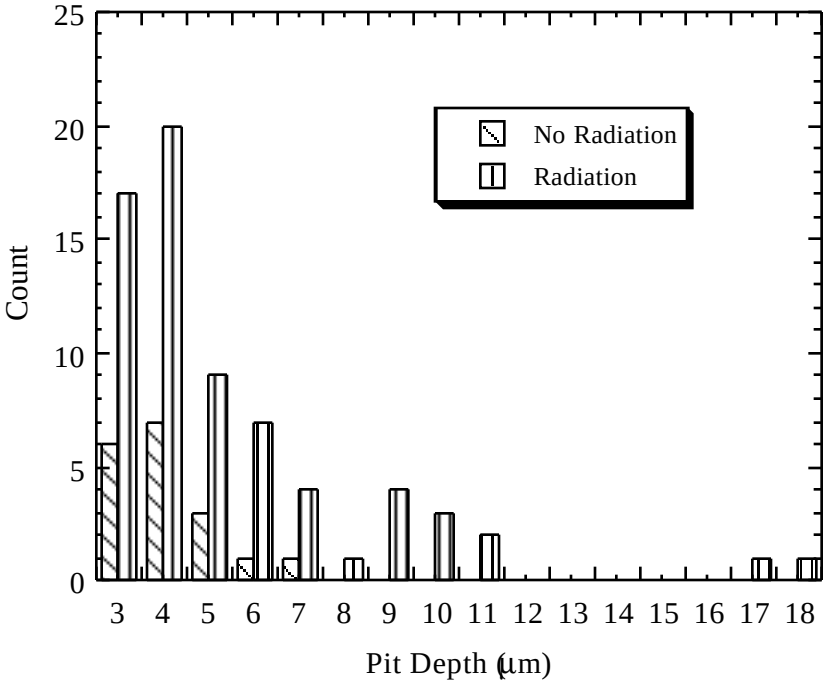
	In Radiation Field*	Without Radiation Field
OCP (V)	-0.41± 0.090	-0.30 ± 0.03
I_{corr} (A/cm^2)	5.2 ± 1.l x 10^{-7}	2.3 ± 1.6 x 10^{-7}
I_{pass} (A/cm^2)	1.7 ± 0.3 x 10^{-6}	5.9 ± 2.6 x 10^{-7}
E_{pit} (V)	0.44 ± 0.12	0.46 ± 0.06
E_{rp} (V)	-0.73 ± 0.20	-0.70 ± 0.16

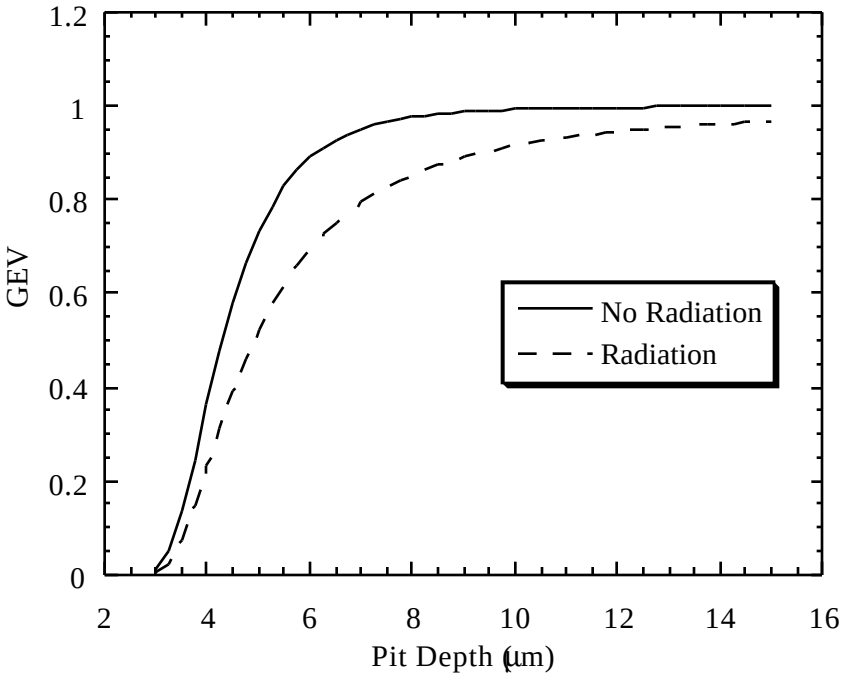
A516; Chloride/Nitrate Solution @ 40° C

* Co^{60} γ radiation, 1.5x10^6 rads/h

Influence of Radiation on Pit Depth

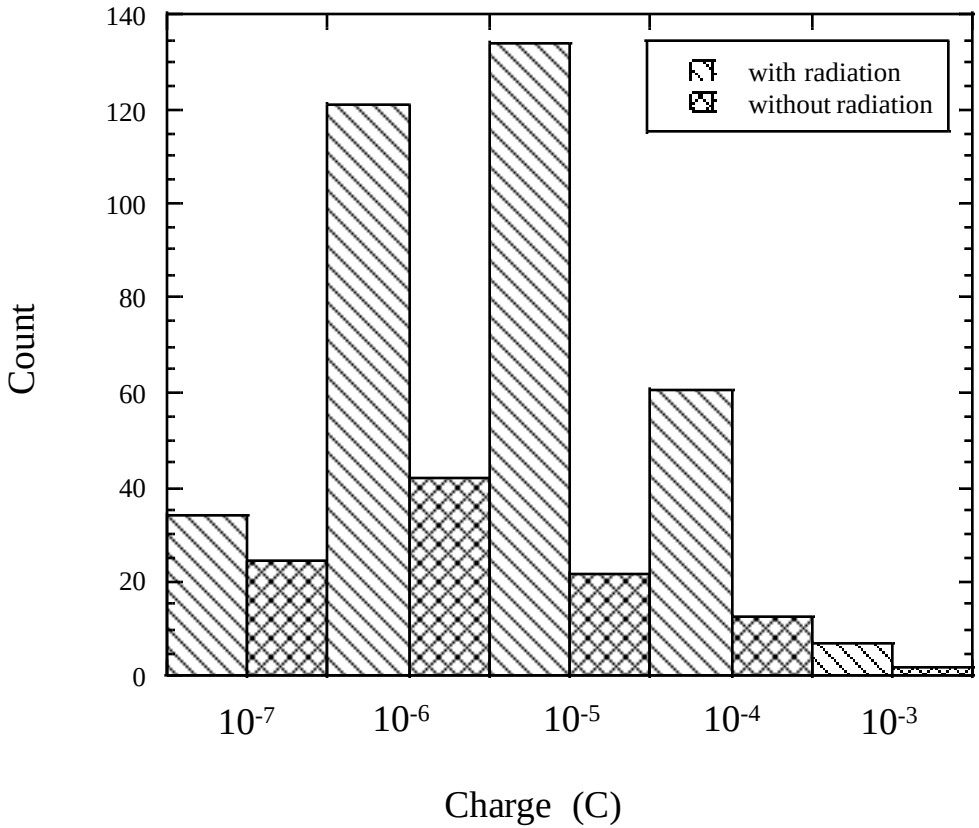
A516





Irradiation results in larger corrosion pits

Influence of Radiation on EN

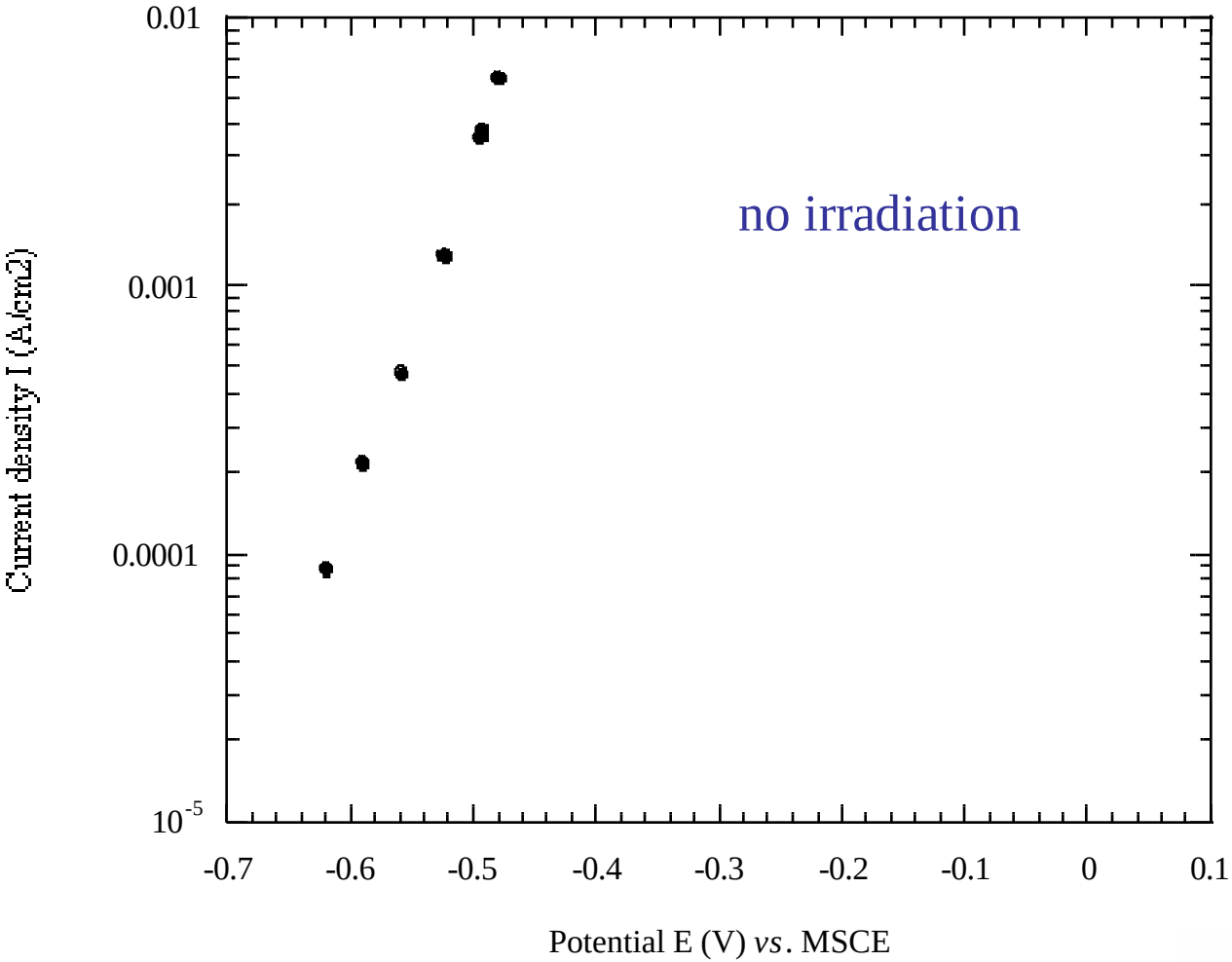


0.95 Quantile:

no rad. 69.5 mC

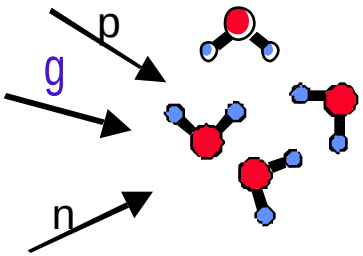
rad. 122.5 mC

Analysis of Pit Current Density - Pit Polarization Curve

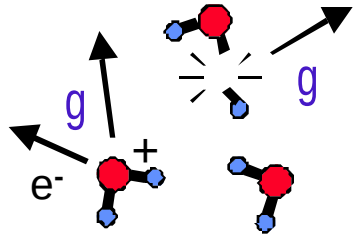


Background: Water Radiolysis Events

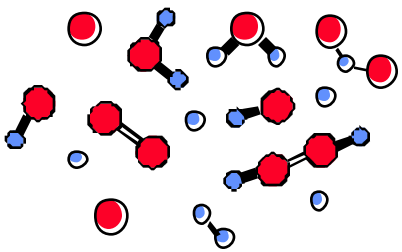
Primary species: e^-_{aq}, H_3O^+, OH, H, H_2



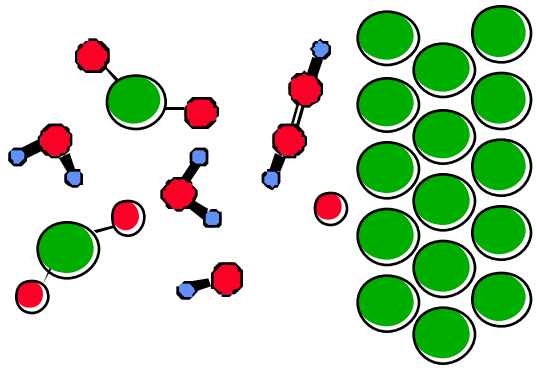
1. **Particles irradiate water**



2. **Radiolysis/Ionization**



3. **Diffusion/Recombination**



4. **Direct Corrosion?**

$$e^- + e^- \rightarrow \mathbf{H_2} + 2\,OH^-$$
$$e^-_{aq} + H^+_{aq} \rightarrow H$$
$$e^-_{aq} + H \rightarrow \mathbf{H_2} + OH^-$$
$$e^-_{aq} + OH \rightarrow OH^-$$
$$e^-_{aq} + \mathbf{H_2O_2} \rightarrow OH^- + OH$$
$$H + H \rightarrow \mathbf{H_2}$$
$$OH + H \rightarrow \mathbf{H_2O}$$
$$H + \mathbf{H_2O_2} \rightarrow \mathbf{H_2O} + OH$$
$$OH + OH \rightarrow \mathbf{H_2O_2}$$
$$H_3O^+ + OH^- \rightarrow \mathbf{H_2O}$$

Primary radiolysis reaction:

$$OH + OH \xrightarrow{k_1} H_2O_2 \quad k_1 = 4.5x10^9 \ sec^{-1}$$

In the presence of corrosion products rad. results in Fe^{+3}:

$$OH + Fe^{+2} \rightarrow Fe^{+3} + OH^-$$

$$H_2O_2 + Fe^{+2} \text{ ® } Fe^{+3} + OH + OH^-$$

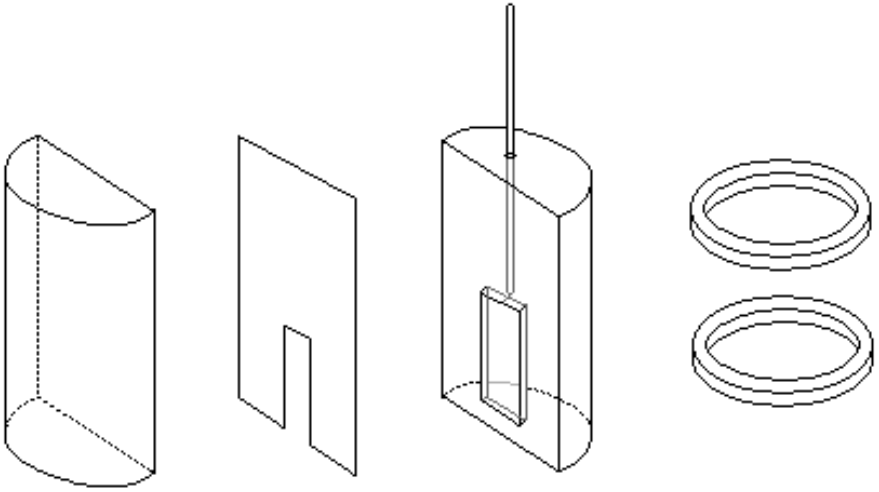
$$HO_2 + Fe^{+2} \rightarrow Fe^{+3} + H_2O_2$$

Why this is important, acidification stabilizes pitting:

$$Fe^{+2} + 2H_2O \rightarrow FeOH^+ + H^+ \ ; \ \text{pH} = 4.74 - 1/2\log\left(Fe^{+2}\right)$$

$$Fe^{+3} + 3H_2O \rightarrow Fe_2(OH)_2^{+4} + 2H^+ \ ; \ pH = 1.6 - 1/3\log\left(Fe^{+3}\right)$$

Analysis of Pit Solution Chemistry



A B C D

Sample No.	Pit Volume (mL)	Con. Fe^{3+} (ppm)	Fe^{3+} (ng) in pit volume	Con. Cl^- (ppm)	Cl^- (µg) in pit volume	Fe^{3+}/Cl^-
With radiation						
1	0.00208	0.139	57.4	8.57	2.93	19.5×10^{-3}
2	0.00188	0.331	132.0	32.3	6.95	19.0×10^{-3}
3	0.00201	0.163	73.2	17.4	3.30	22.2×10^{-3}
Without radiation						
4	0.00182	0.846	439.0	10.7	6.01	73.0×10^{-3}
5	0.00179	2.16	912.0	4.49	1.59	573.0×10^{-3}
6	0.00211	0.0357	17.9	5.11	2.45	7.31×10^{-3}

Conclusions

- GEV Work on Carbon Steel
  - 1:1 Correlation between EN and Pitting Damage
  - Irradiation Increases EN and Pit Depth.

  ..... these results indicate GEV analysis using current thresholding can be used to quantitative evaluate Hanford/SRS EN data

- Preliminary solution Analysis From Artificial Pits
  - As yet, no Clear Influence on Solution Chemistry (limited population)

Current and Future Directions

- Additional Carbon Steel Work (fall '05 completion).
  - Solution Analysis Experiments with/without Irradiation.
  - Pit Polarization Curves During Irradiation.
- Work on Austenitics (SS 316L) in Acid Chloride (INEEL)
  - Influence of Passive Film on Metastable Pitting (G. Vasquez).
    - film rupture; straining electrode experiments
    - oxide transport properties ?