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Risk Based Corrosion Studies at SRS

EM Waste Processing Technical Exchange 2010

E.N. Hoffman

Senior Engineer A

Savannah River National Laboratory

November 17th, 2010

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

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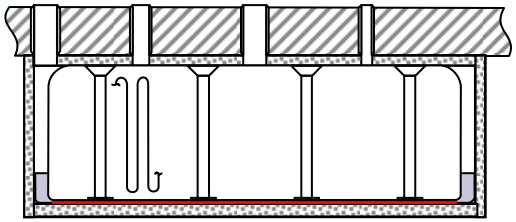
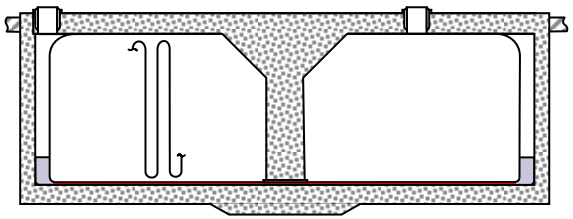
SRS Waste Tank Design and Fabrication

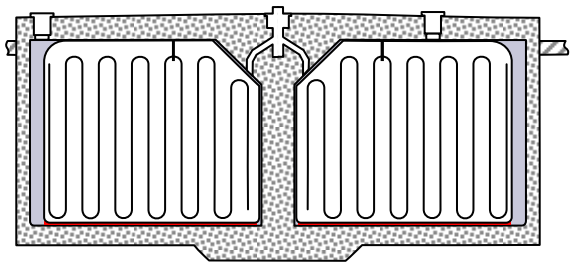


Type I
750 kgal
1951-1953



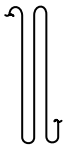
Type II

1.0 Mgal
1955-1956



Type III

1.3 Mgal
1966-1981



= cooling coil

TYPE I and II *(ASTM 285-B)*

- **Experienced stress corrosion cracking (SCC)**
- **2 have been closed; 22 scheduled for closure by 2017**
- **No active leak sites today**

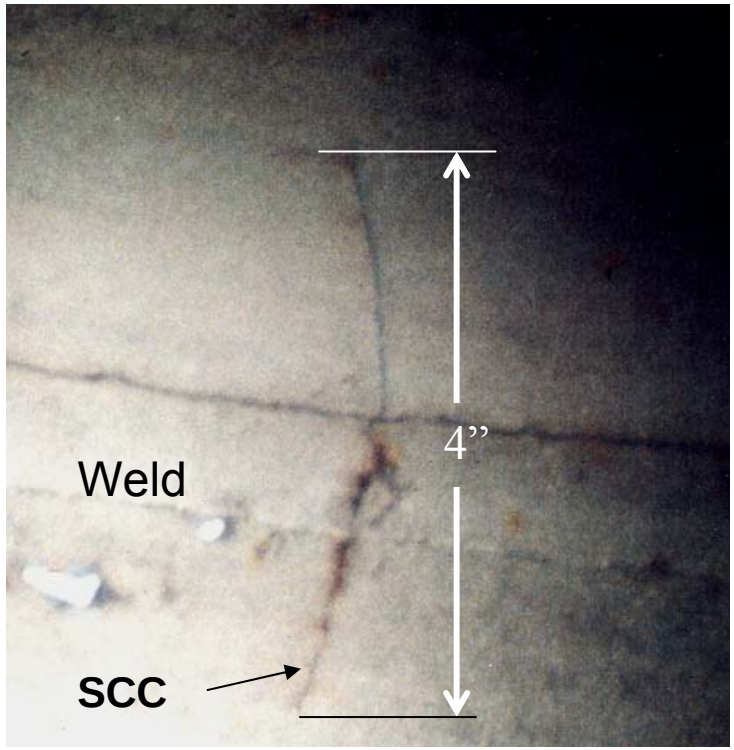
TYPE III *(ASTM A516-70 and A537 Class I)*

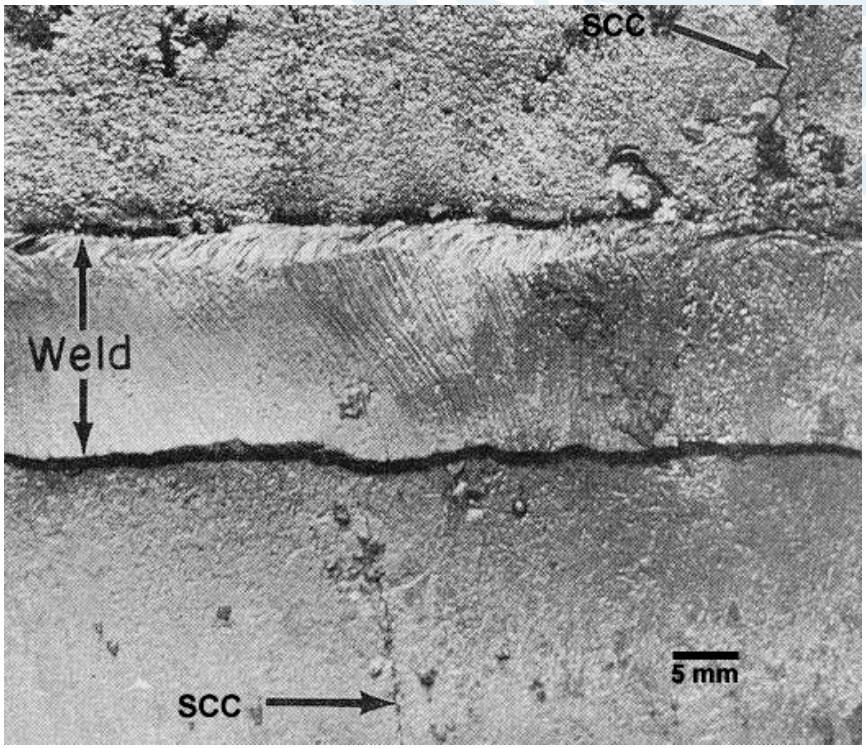
- **Post-fabrication relief of weld residual stresses**
- **Improved resistance to SCC and brittle fracture**
- **No leakage history**
- **Receives new waste**

Corrosion in SRS Waste Tanks

- **Types of Corrosion**
  - **Pitting:** Potential for localized corrosion due to nitrate, chloride, and sulfate ions.
    Tanks primarily susceptible: All types
  - **Stress Corrosion Cracking (SCC):** Hanford and SRS have had leaks in tanks due to nitrate-induced SCC.
    Tanks primarily susceptible: Type I and II
  - **General Corrosion:** Stored waste highly alkaline ($[OH^-] > \sim 0.1$ M) → general corrosion not significant.
    Tanks susceptible: none
- **Tank walls and cooling coils are at Risk for Corrosion in the regions of:**
  - Vapor space
  - Liquid/Air Interface space
  - Solution space

Stress Corrosion Cracking: Concentrated Waste Solutions



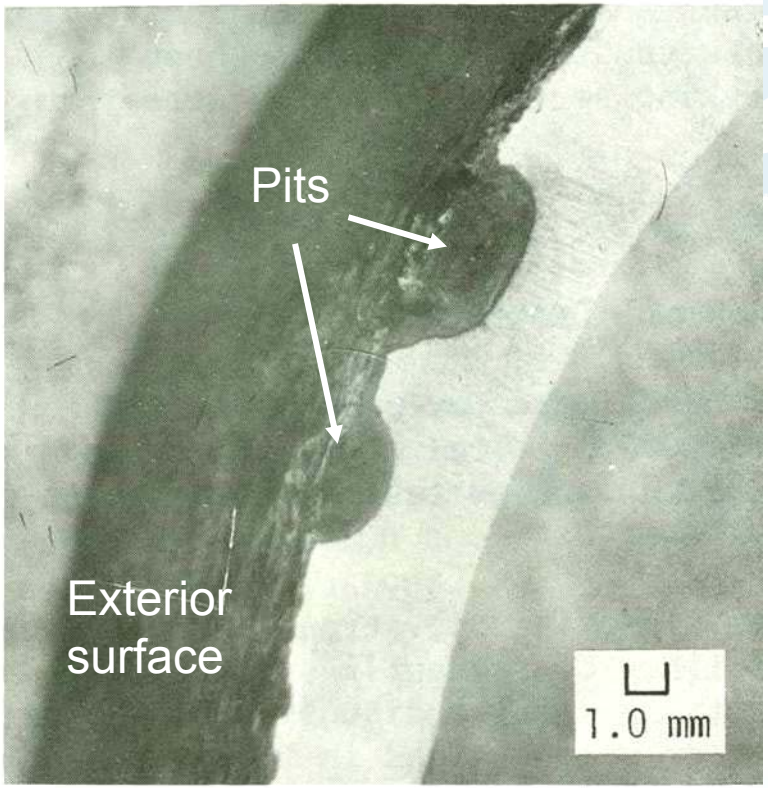


Stress corrosion cracks associated with fabrication welds in Tank 16 (Type II). Tank has been removed from service.

Pitting Corrosion: Dilute Waste Solutions

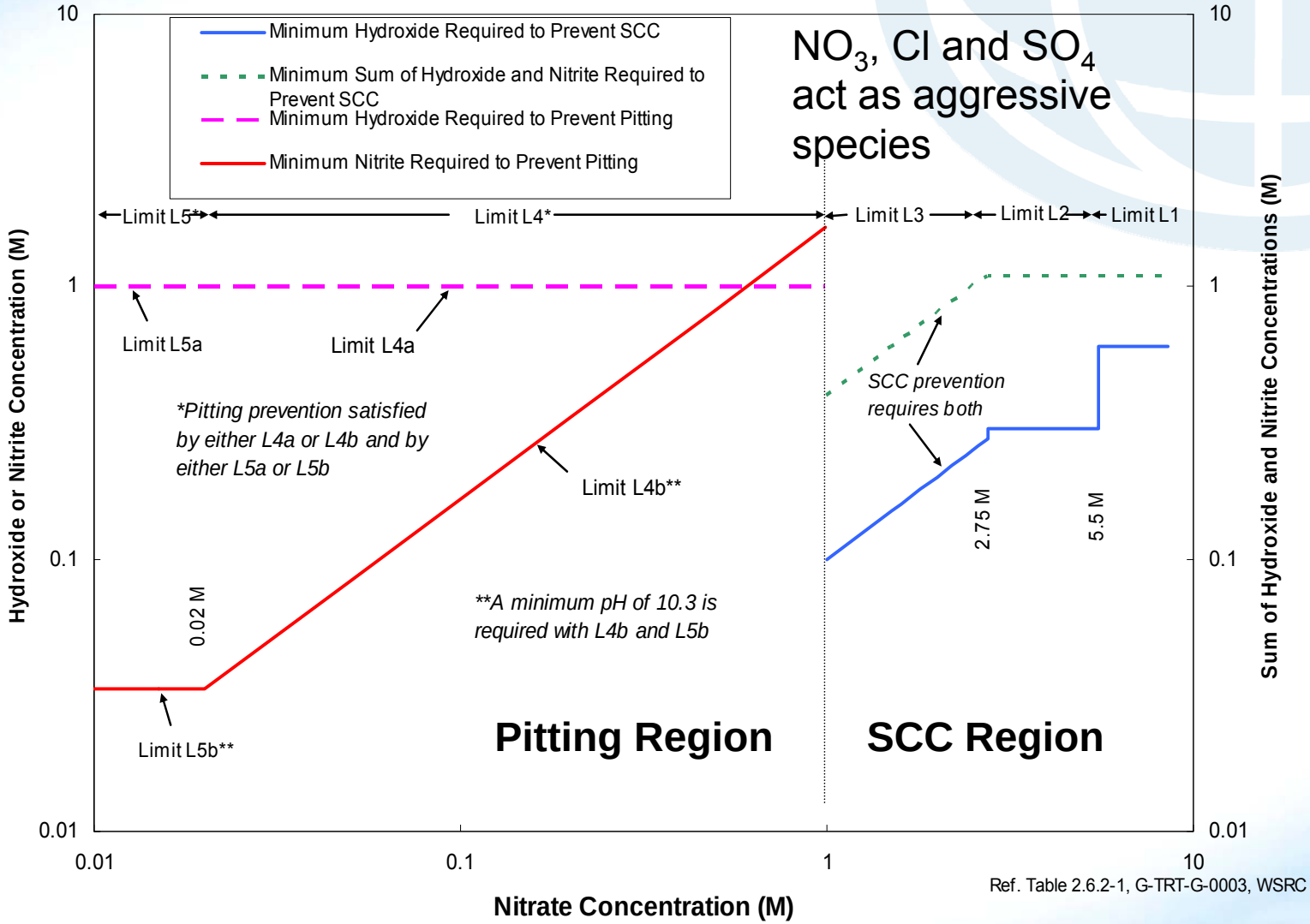
- **Failure of Cooling Coils in Type I Waste Tanks at SRS**
  - **Material: Carbon steel pipe**
  - **Sludge removal operations in the 1960's**
  - **Caused by dilution of waste, lowering hydroxide concentration**
  - **Coil segment removed for laboratory investigation**

Chemistry control program needed to mitigate and prevent SCC and pitting



Cooling coil section showing two pits

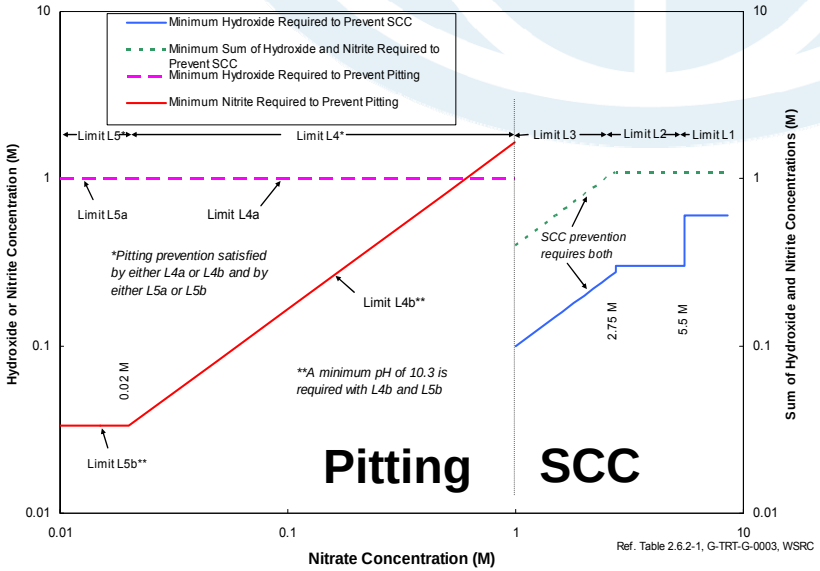
Current Chemistry Controls



Ref. Table 2.6.2-1, G-TRT-G-0003, WSRC

Challenges and Opportunities for Improved Control

- Current control program minimum nitrite limit below 1.0 M developed based on focused experimentation in the dilute range below 0.1 M.
- Refine corrosion control across 1.0 M nitrate threshold for operational efficiency.
- Current experimental approach utilizes statistics to account for variation in the experimental response.



Objectives and Statistical Design

Objectives

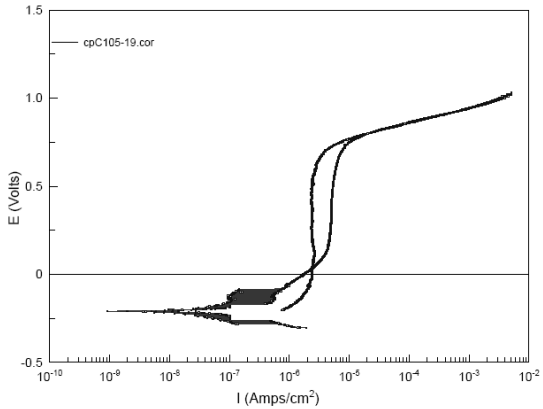
- Utilize statistical methods to reduce conservatism in current chemistry control program.
- Express nitrite inhibitor limits in terms of pitting risk on waste tank steel.

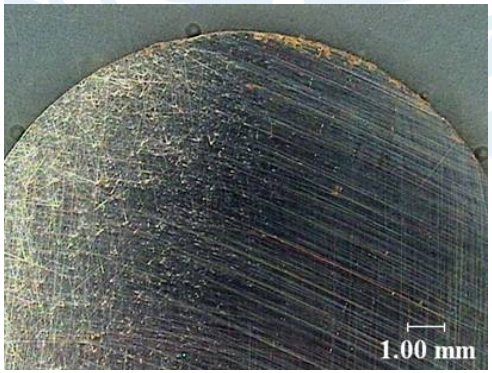
Statistical Design

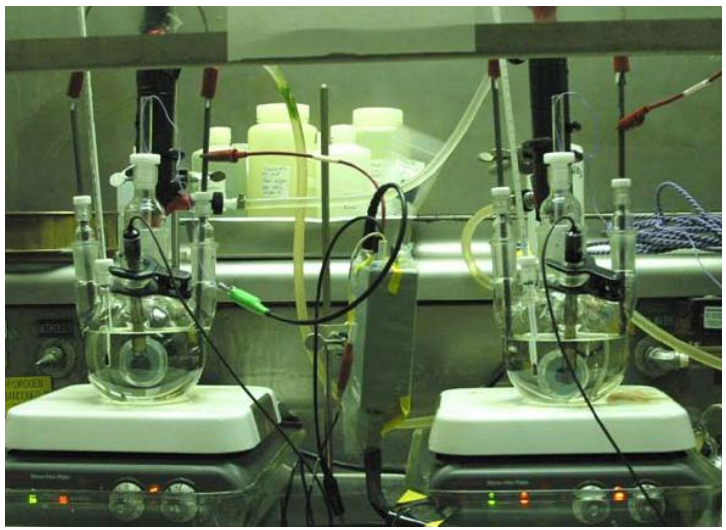
- Design space of $0.02\ M \leq [NO_3^-] \leq 1.0\ M$
- Temperature = 40 °C, pH = 10
- Binary outcomes: pitting vs. no pitting

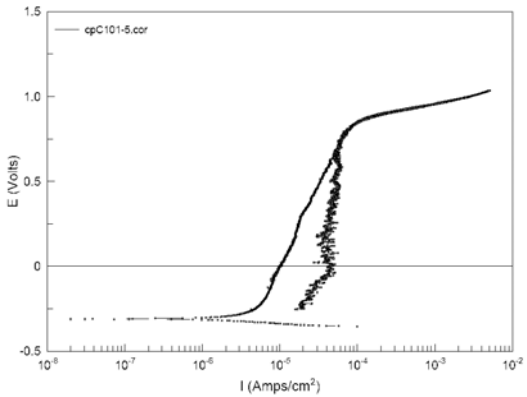
Experimental Approach

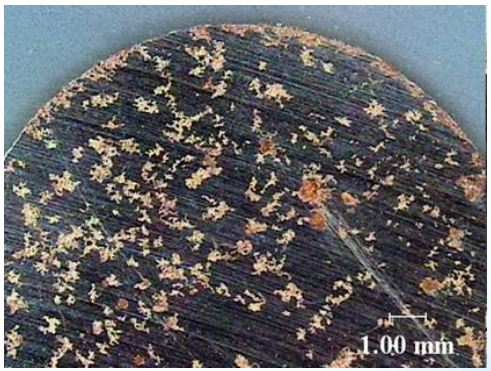
- Electrochemical cyclic potentiodynamic polarization (CPP) testing is used to accelerate the corrosion response.
- A potential is applied and the current response is measured leading to a CPP curve.



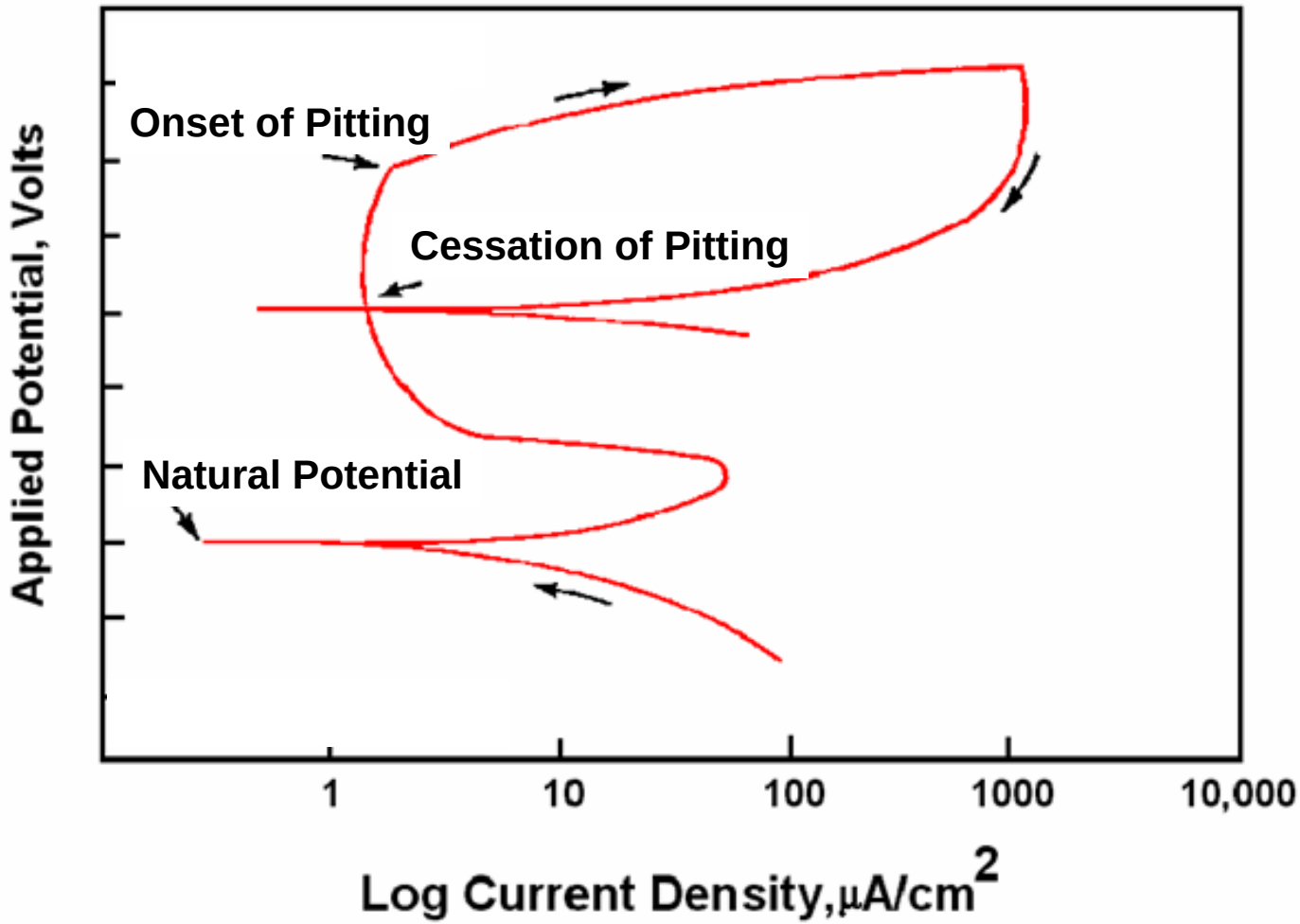




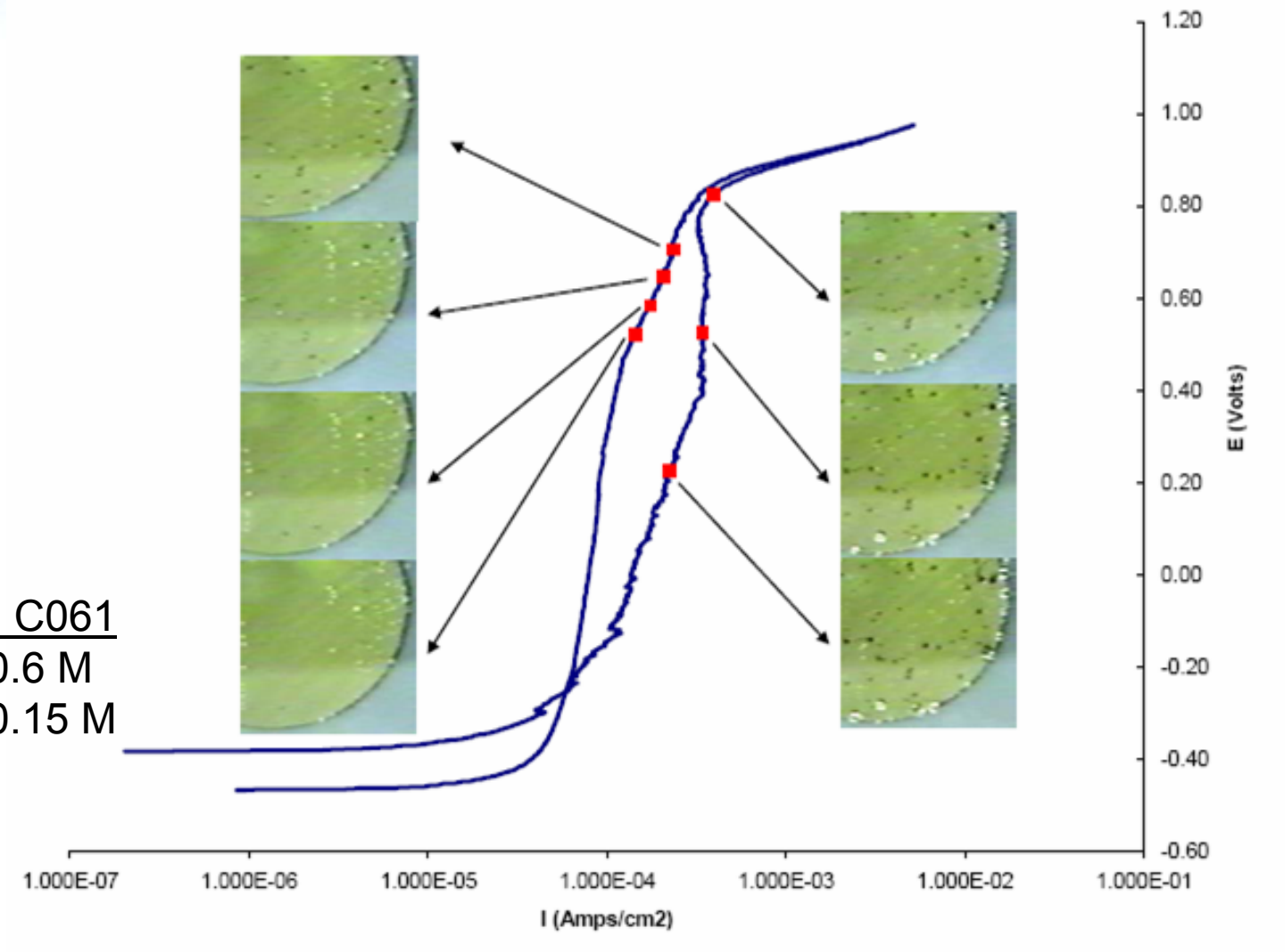




Cyclic Polarization Scan



In-situ Monitoring of Corrosion Evolution during CPP



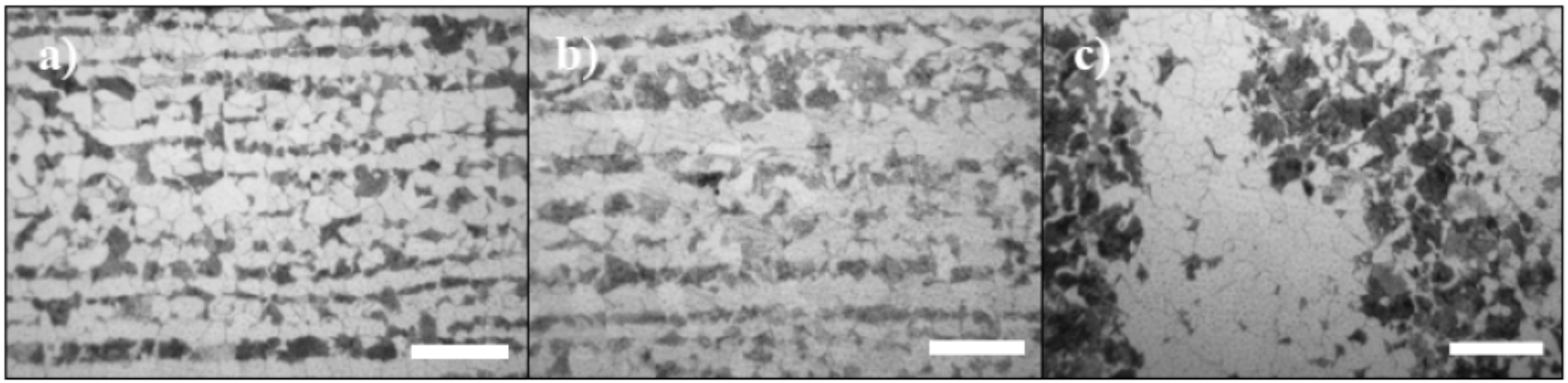
Solution C061

NO_3^- = 0.6 M

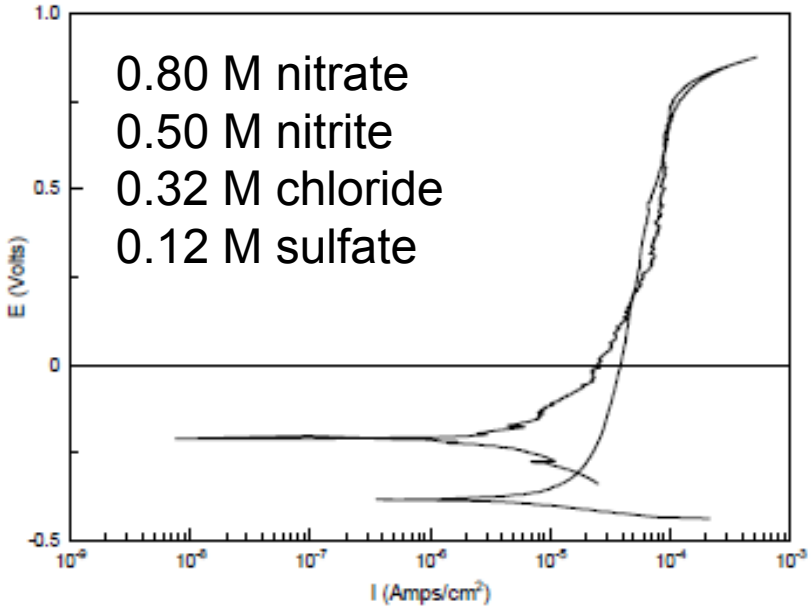
NO_2^- = 0.15 M

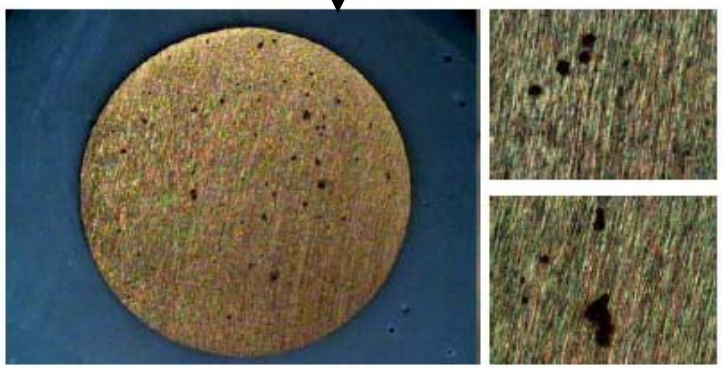
Carbon Steel Microstructure

- A537 carbon steel was chosen to evaluate the tank walls of Type III.
- Developed for use as pressure vessel plate.
- Microstructure of A537 Carbon steel a) longitudinal b) transverse c) short directions. Scale bar equals 30 microns.

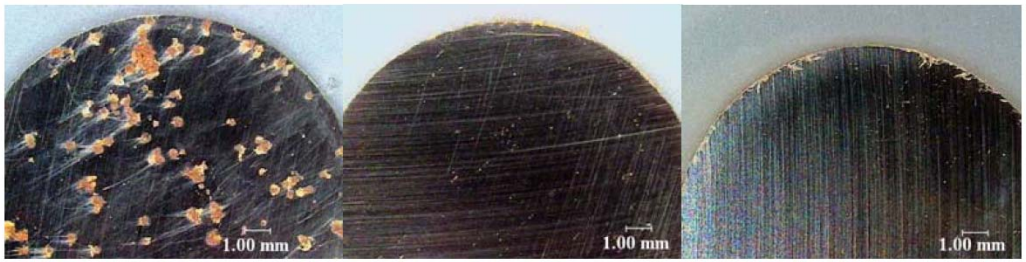


Electrochemical Results - Example





Categories of Visual Pitting Performance



Significant *Moderate* *None*

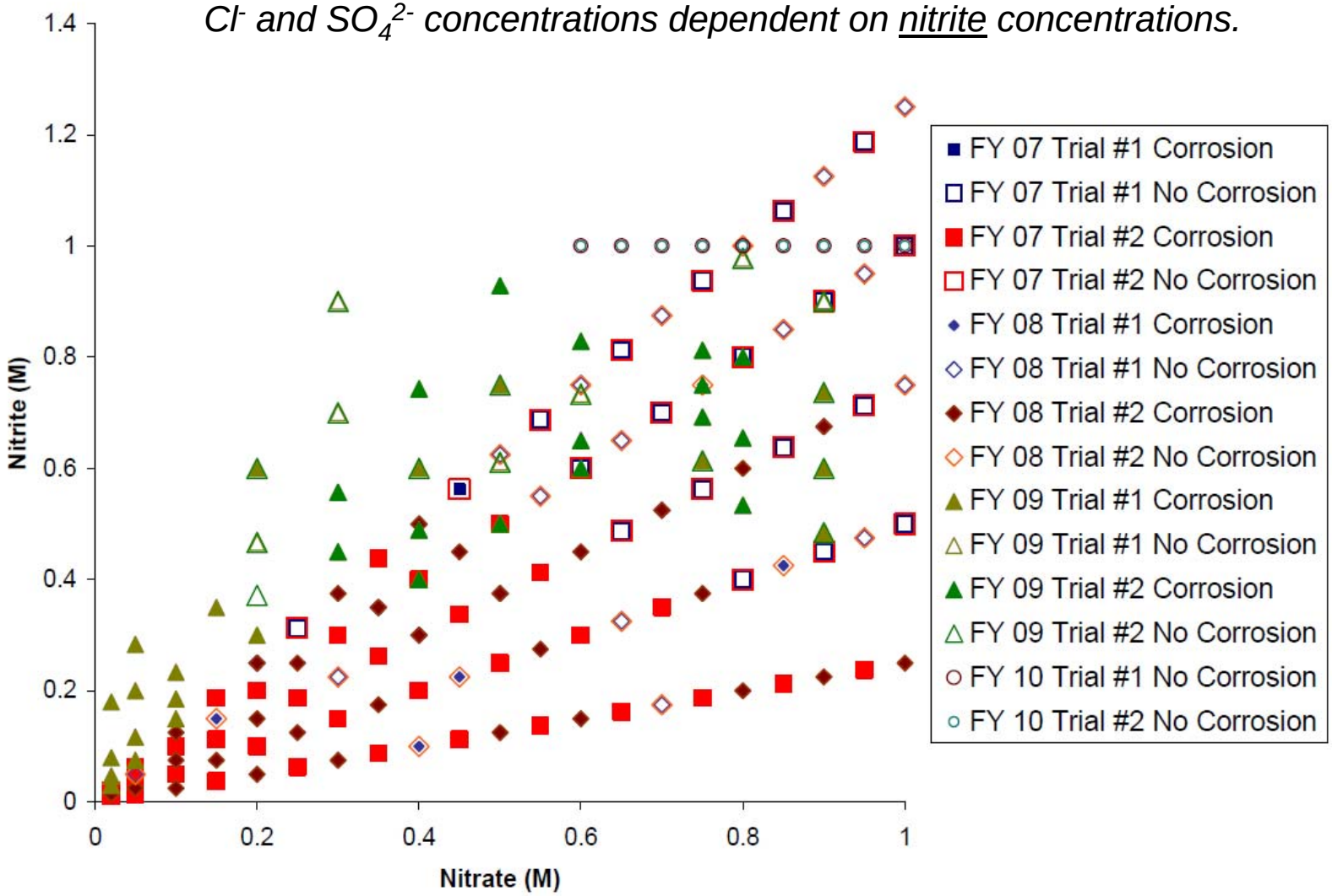
To create a binary outcome, any degree of pitting, moderate to significant, was considered a pitting response.

CPP curves and optical images were evaluated for each solution tested.

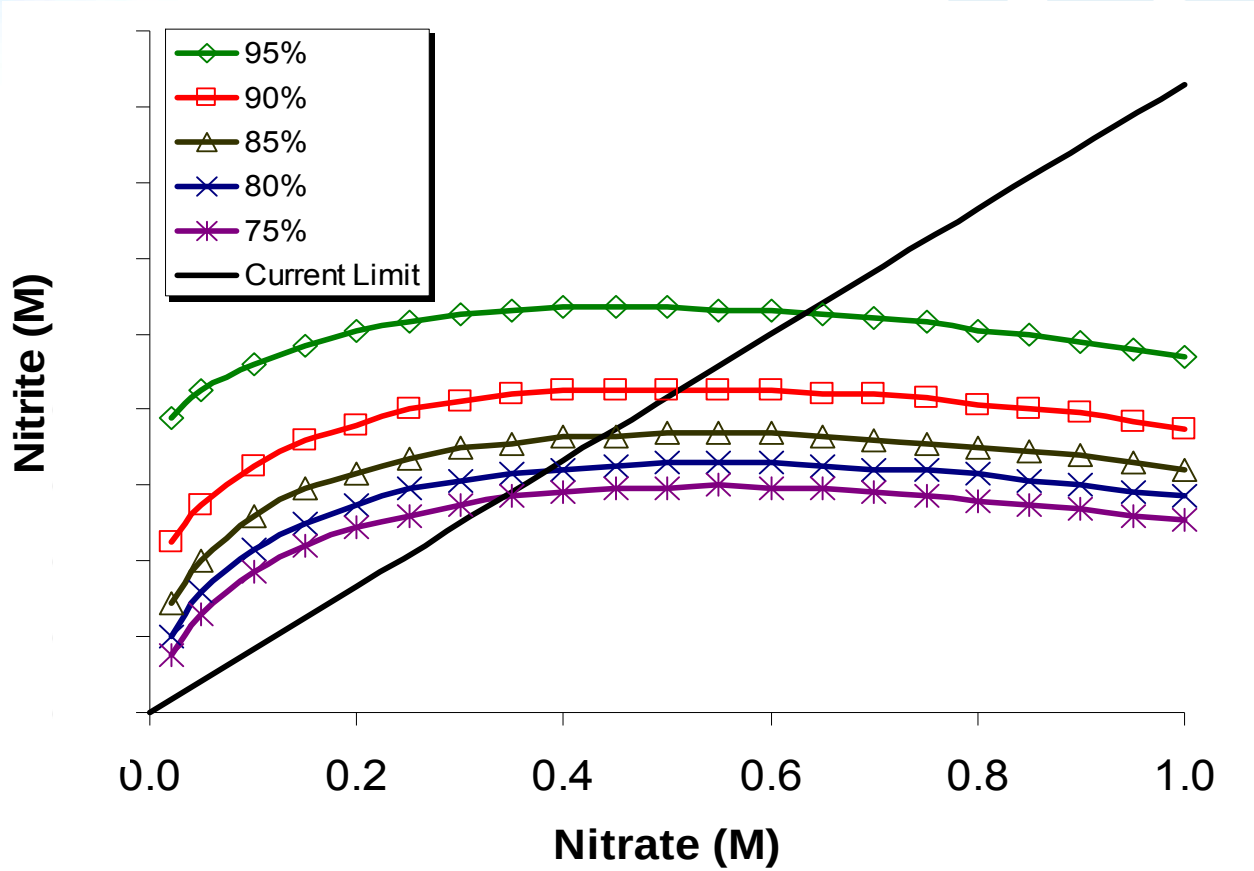
Visual results yielded a more straightforward categorization of pitting responses, therefore, modeling efforts are based on optical micrographs.

Experimental Results to Date

Cl^- and SO_4^{2-} concentrations dependent on nitrite concentrations.

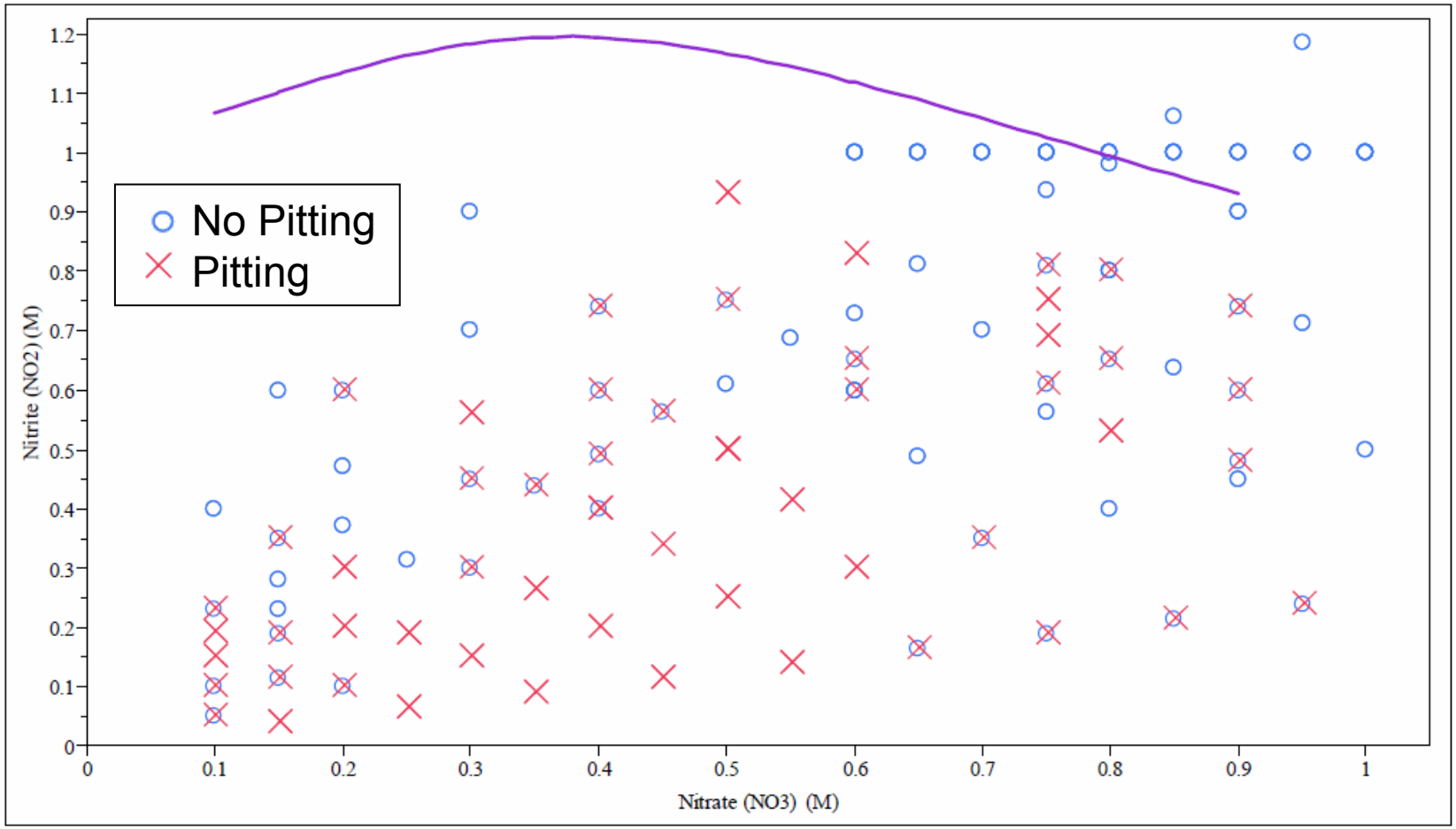


Mixture/Amount Model – Concept



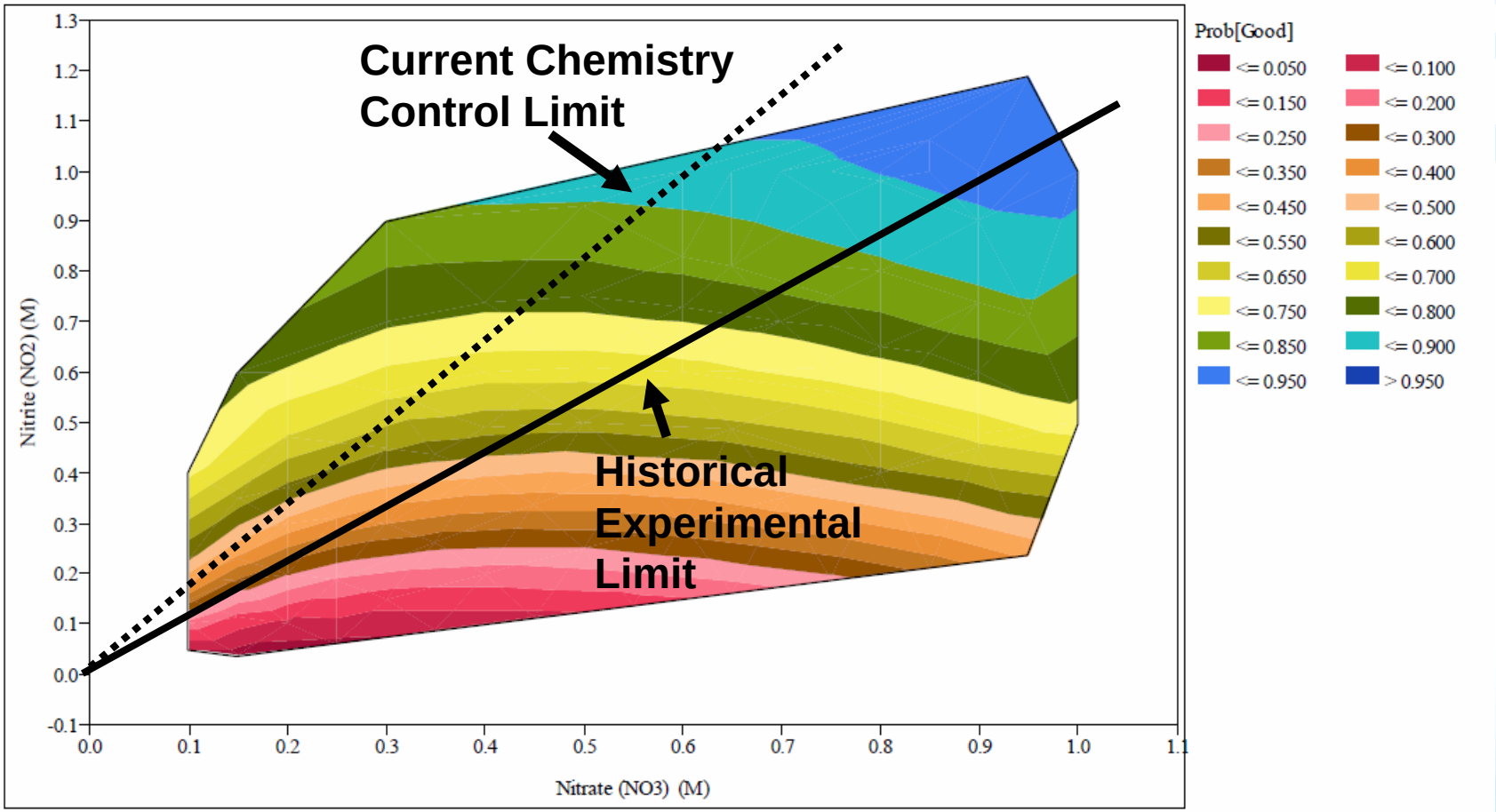
- *Mixture/Amount Model* based on ratio of inhibitive to aggressive species (mixture) **and** concentration of species (amount).
- Model allows for limits to be drawn based on varying levels of risk.

Mixture/Amount Model Applied to Results

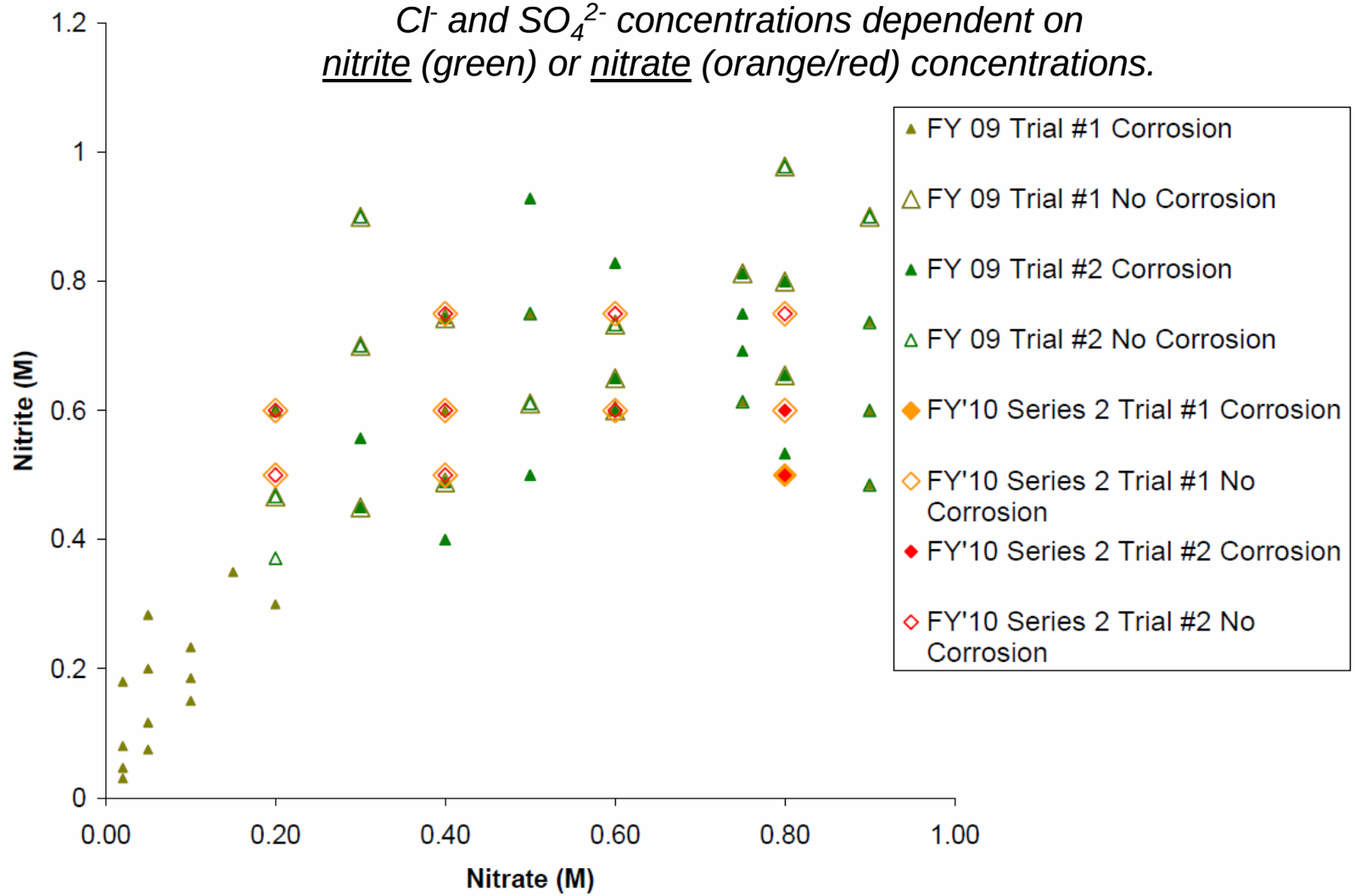


Mixture/amount model curve evaluated for a 90% probability of no pitting.

Varying Probability using Mixture/Amount Model



Dependence of Cl^- and SO_4^{2-} Concentrations



Conclusions

- A statistically designed experimental study has been undertaken to improve the effectiveness of the minimum nitrite concentrations to inhibit pitting corrosion.
- Mixture/amount model supports that pitting depends on the ratio of aggressive to inhibitive anions, as well as the concentration of each species.
- Secondary aggressive species, Cl^- and SO_4^{2-}, significantly effect the corrosion response.
- Results support the reduction of the chemistry control nitrite inhibitor concentrations in the regime of 0.8-1.0 M nitrate.

Questions

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