ENVIRONMENT INSIDE BREACHED CONTAINERS
Approaches to Issue Resolution

Presented by

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Contributors to Ideas

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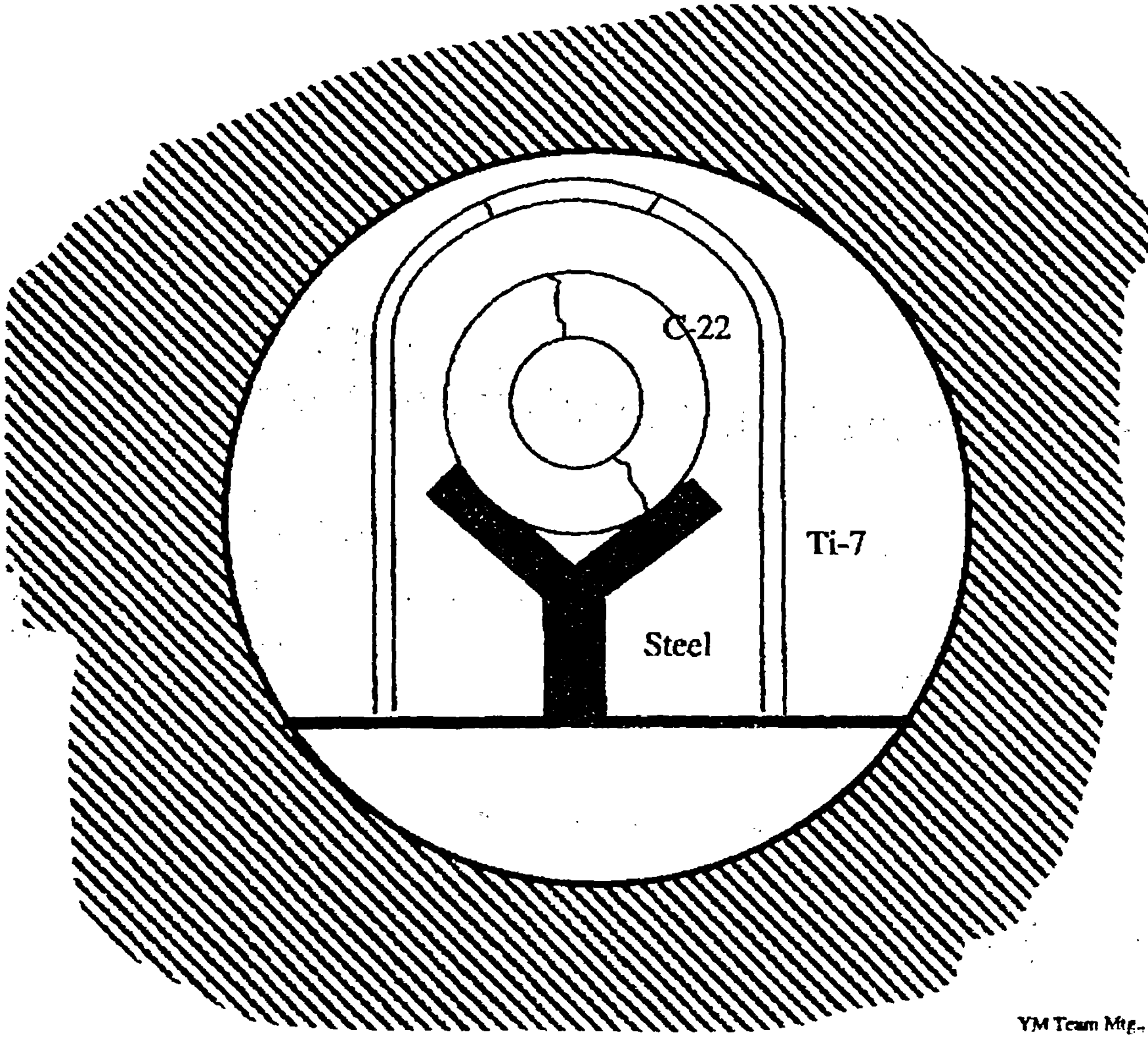
YM Team Meeting

Main/Legacy-XU

OBJECTIVES

- ❑ Identify the range of environmental conditions relevant for waste form dissolution and radionuclide solubility (ENFE subissue #3)
- ❑ Review FEP's
- ❑ Determine acceptance criteria/review methodology for issue resolution/LA review
- ❑ Provide input to TPA 4.0

COMPONENTS DICTATING ENVIRONMENT



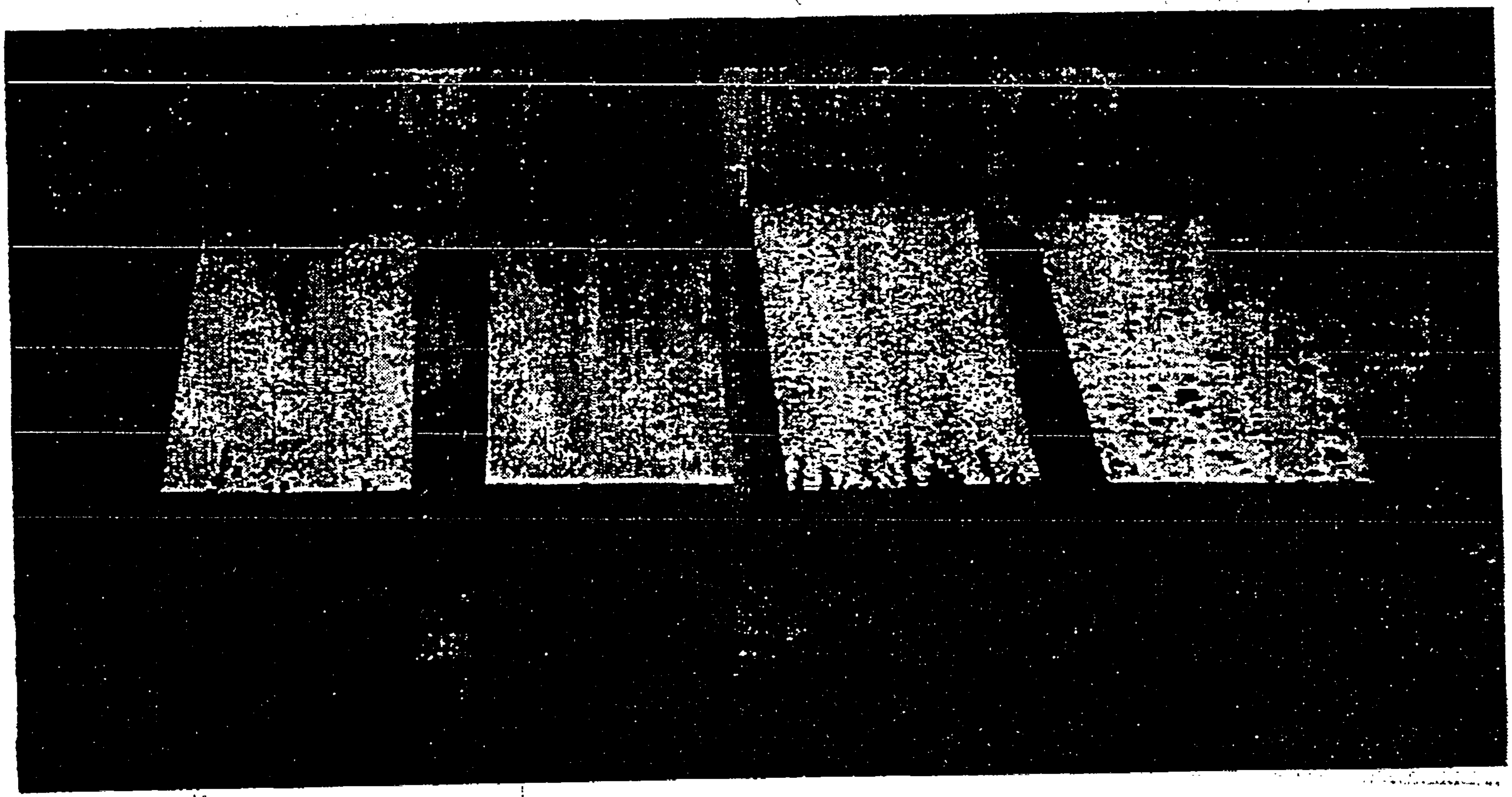
CURRENT STATUS OF TPA 3.2 EBSREL

- ❑ Information on WP temperature, volumetric flow rate, and WP failures from other modules
- ❑ Decay chains, half lives, inventories etc obtained from EXEC
- ❑ Solubilities, dissolution rate parameters, amount of water in WP are specified in input file

CONCEPTUAL MODELS FOR RELEASE

- In TPA 3.2
  - Bathtub model assumes water accumulation through a single pit up to a height, h (specified by user)
  - Flow through model is invoked by user through input file, but exit hole height is used to specify SF wetted fraction
- In reality
  - Numerous entry pits may exist around closure weld
  - More pits may occur at lines of contact with pedestal
  - Pits will be gravity driven
  - Pits influenced by interior WP corrosion chemistry
  - Exit holes are most likely to be at the bottom of container

PIT MORPHOLOGY



EFFECTS OF WP INTERNAL ENVIRONMENT

- Cladding performance
- SNF dissolution rate
- Radionuclide solubility within WP
- Criticality within and outside WP
- Radionuclide release pathways (number and location of pits)

WP COMPONENTS

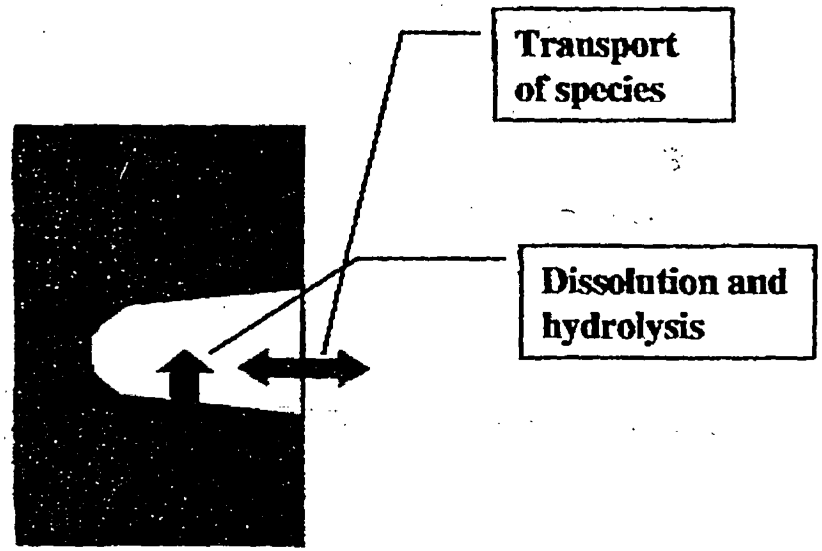
- Alloy 22: Cr and Mo likely to generate very low pH - bounding values
  - Type 316L/NG SS will generate low pH, but not as low as alloy 22
  - Steel corrosion will not generate pH as low as SS
  - Zr will generate low pH, but hard to predict because of polynuclear complexes. Probably not a bounding case

Transient ElectroChemical TRANsport CODE

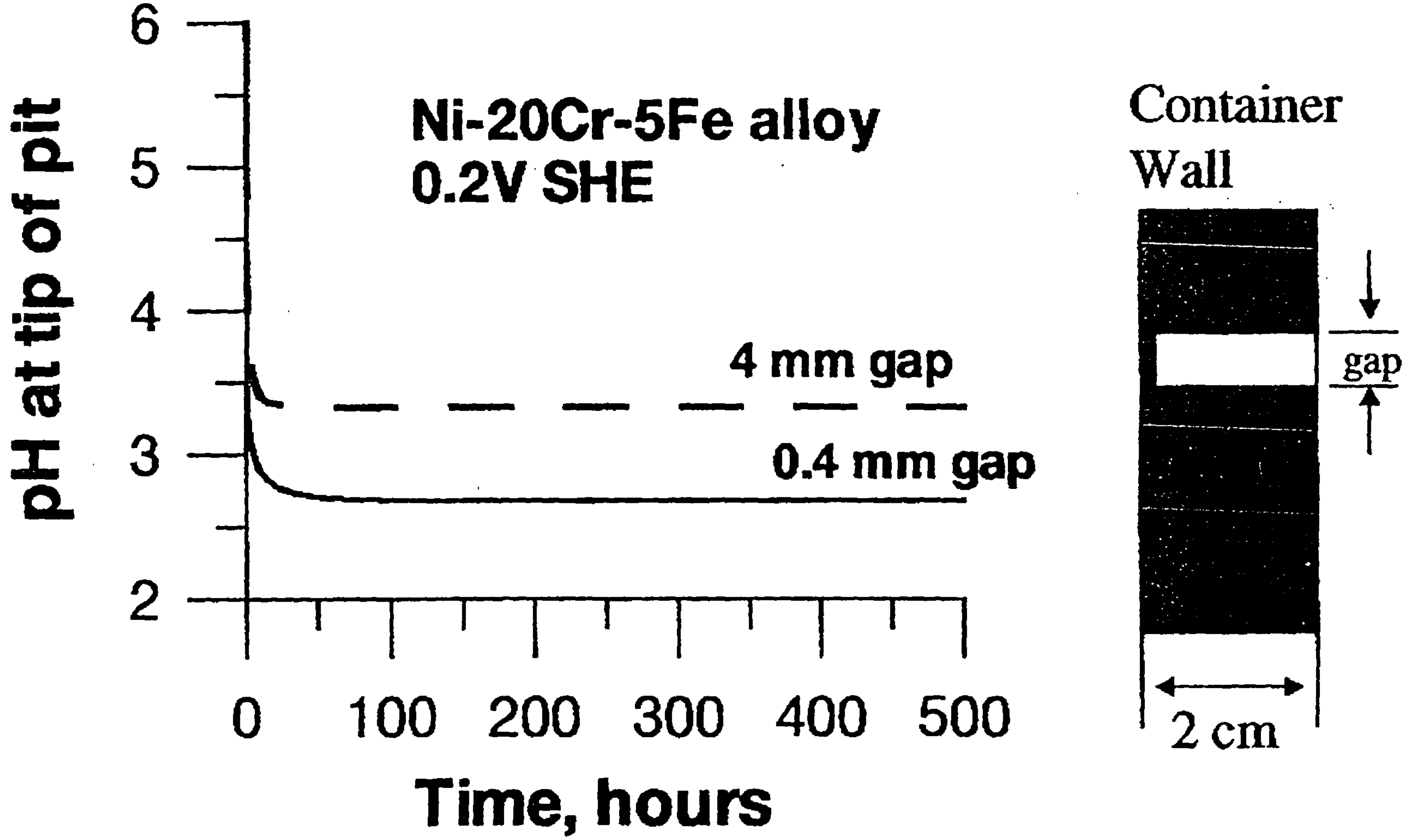
- Developed for GRI
- Similar to GEM, but includes electrochemical reactions
- Option for equilibrium speciation
  - EQ3/6: data0.com.v8.r6
  - OLI ESP/CSP, v.6.2
- Fully implicit, 3-D formulation

$$M = M^{z+} + ze^-$$
$$O_2 + 2H_2O + 4e^- = 4OH^-$$
$$2H^+ + 2e^- = H_2$$

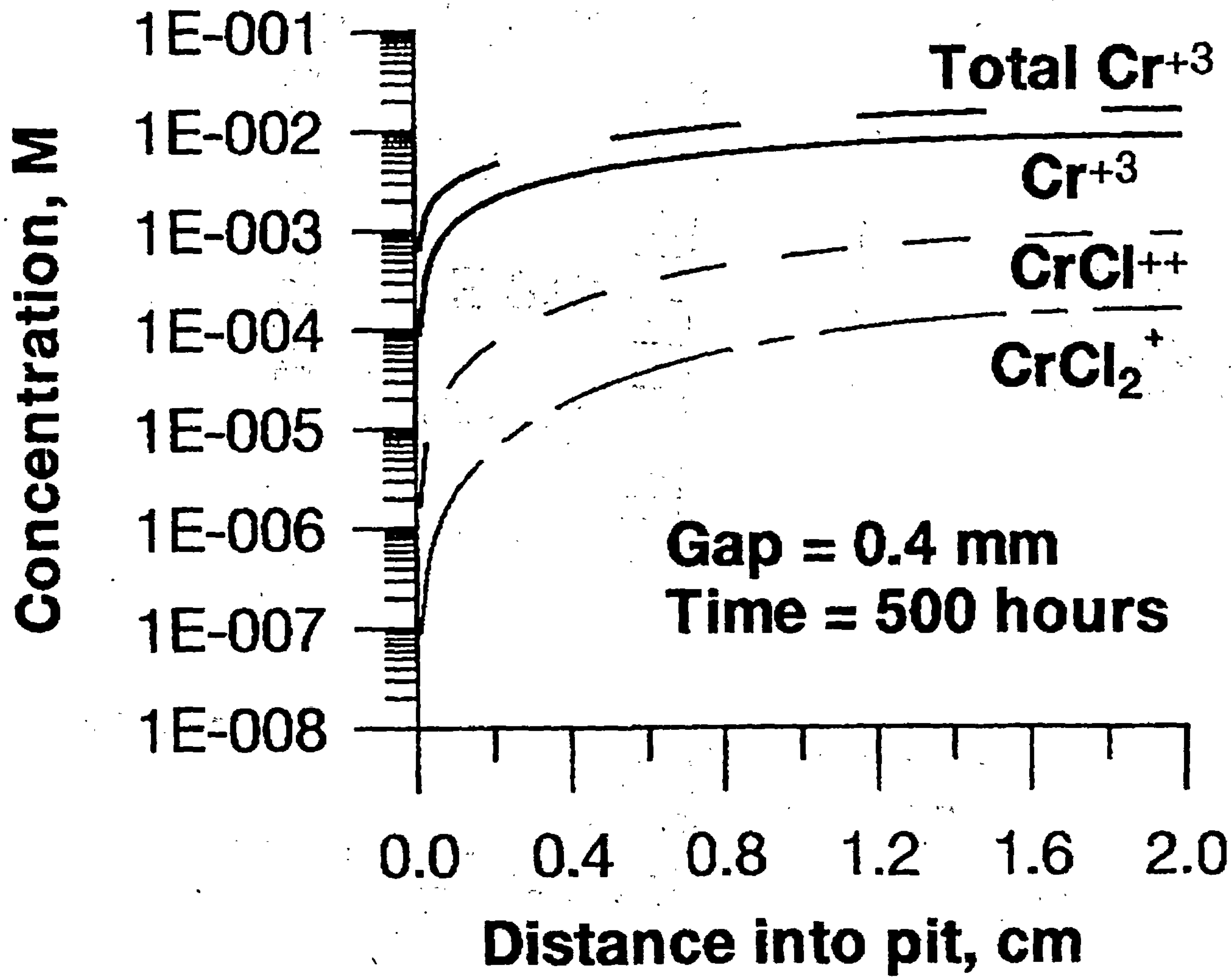
$$M^{z+} + H_2O = M(OH)_x^{(z-x)+} + xH^+$$

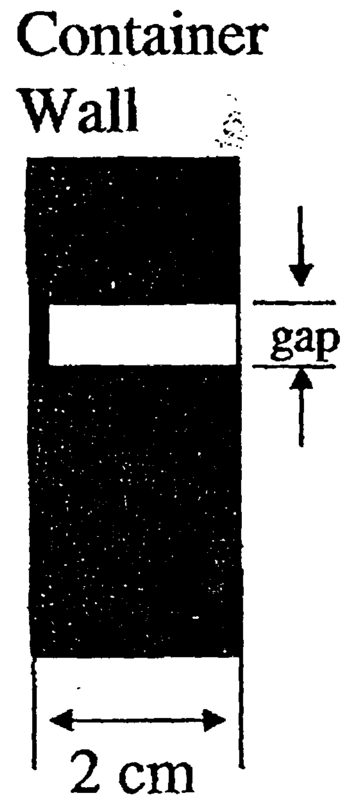


TECTRAN CALCULATION
Evolution of pH within pits/cracks

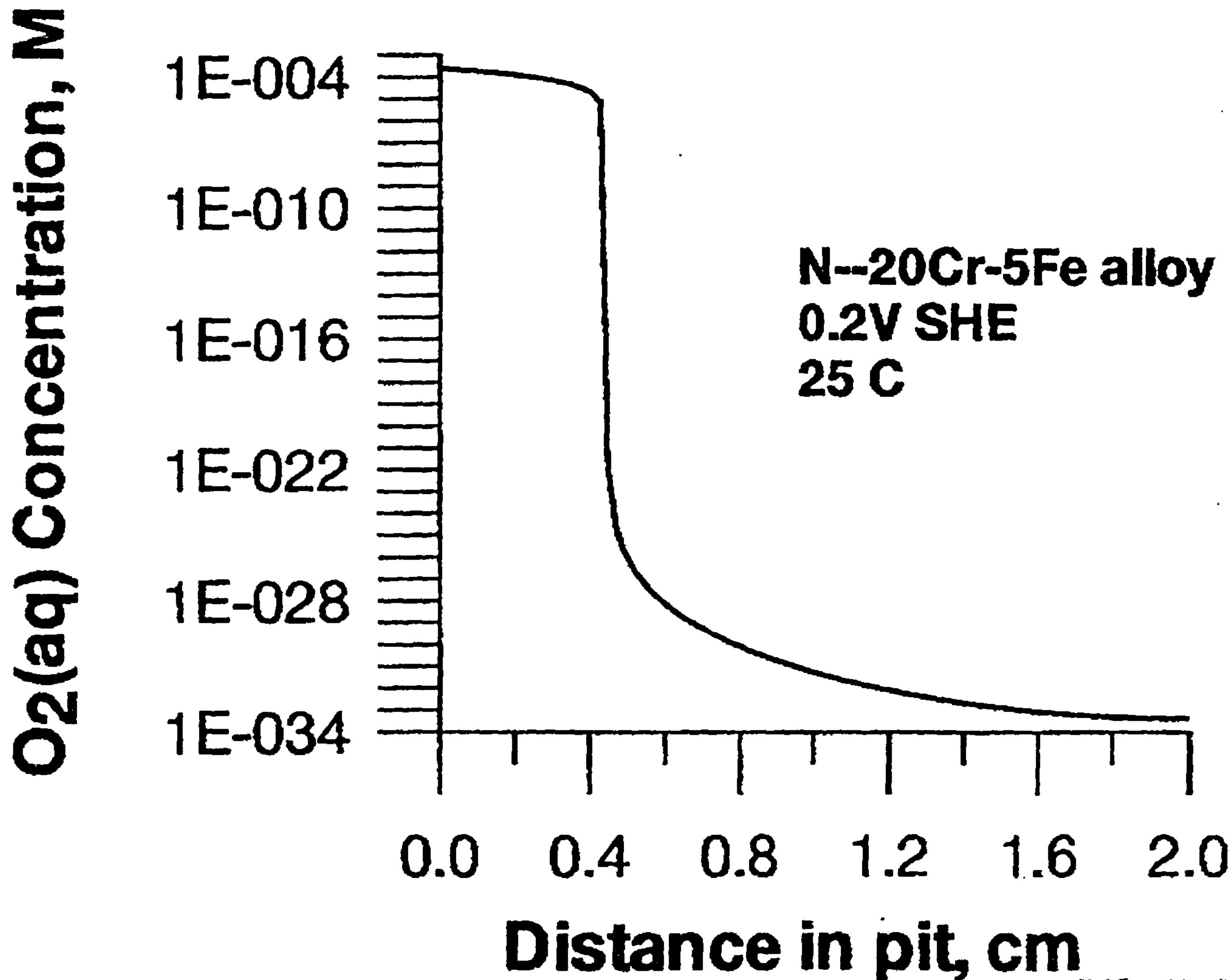


SPECIATION WITHIN PIT (TECTRAN)





OXYGEN CONCENTRATION WITHIN CORRODING PITS (TECTRAN)

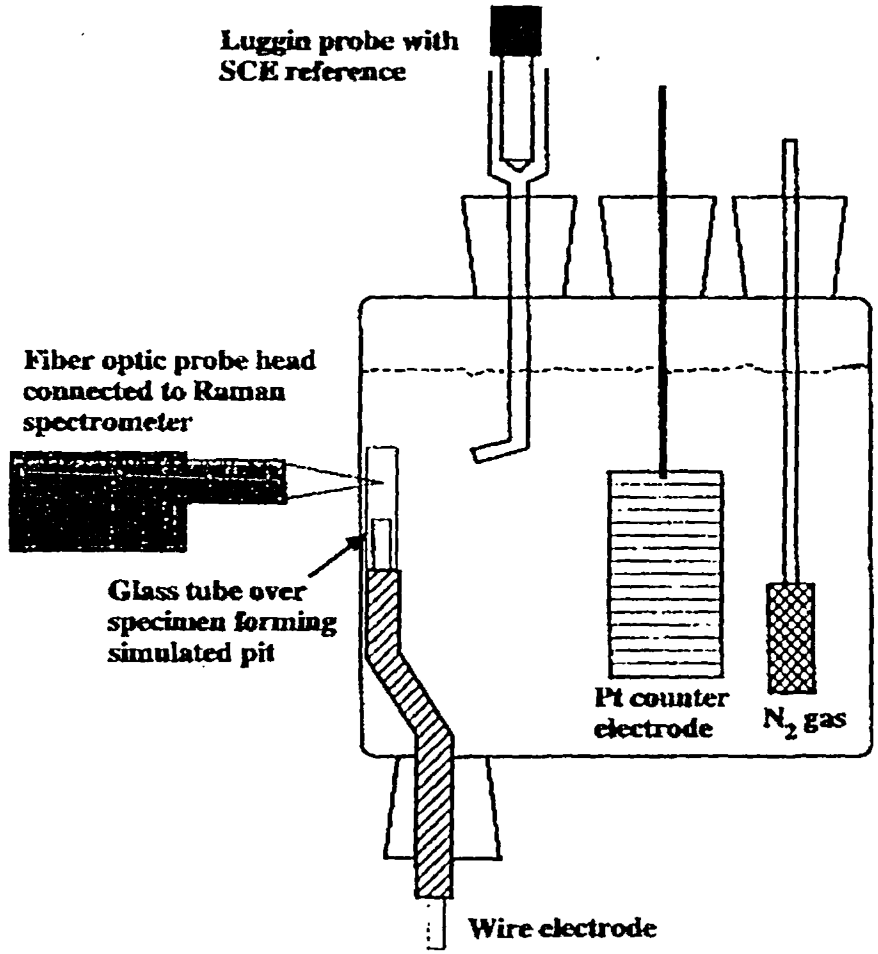


EXPERIMENTS ON ALLOY C-276
(Cavanaugh et al., 1983)

- Reported pH values ranging from 2 to 0 in artificial pits
- pH correlated with dissolved Mo and Cr concentrations

ENVIRONMENT INSIDE PITS - CNWRA STUDIES

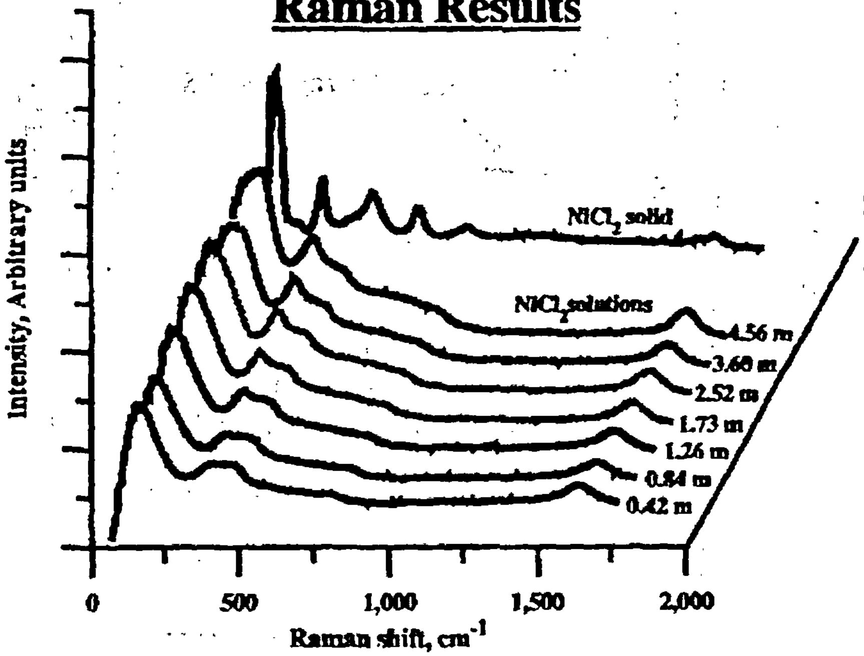
- Raman Spectroscopy: salt film and pit solution composition
- DC Electrochemistry: electrochemical kinetics
- AC Electrochemistry: salt film properties (limited)
- Thermodynamic Speciation: solution chemistry and precipitation (OLI ESP v. 6.0)



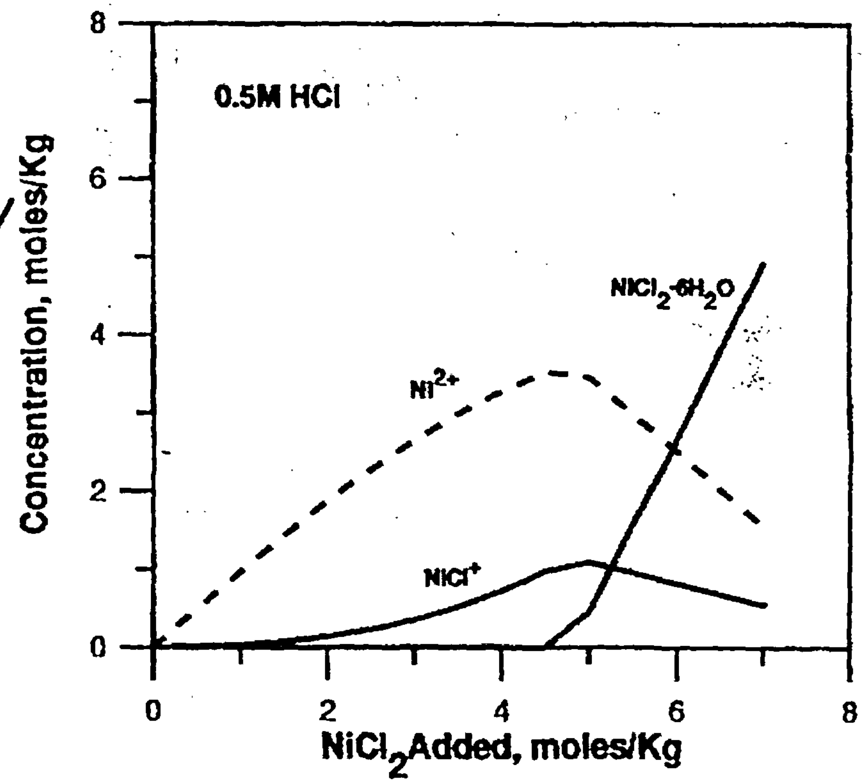
SPECIATION OF NICKEL CHLORIDE SOLUTION

- Salt film composed of $NiCl_2 \cdot 6H_2O$
- Dominant dissolved Ni species in pit solution $Ni(H_2O)_6^{2+}$, but $NiCl^+$ also present

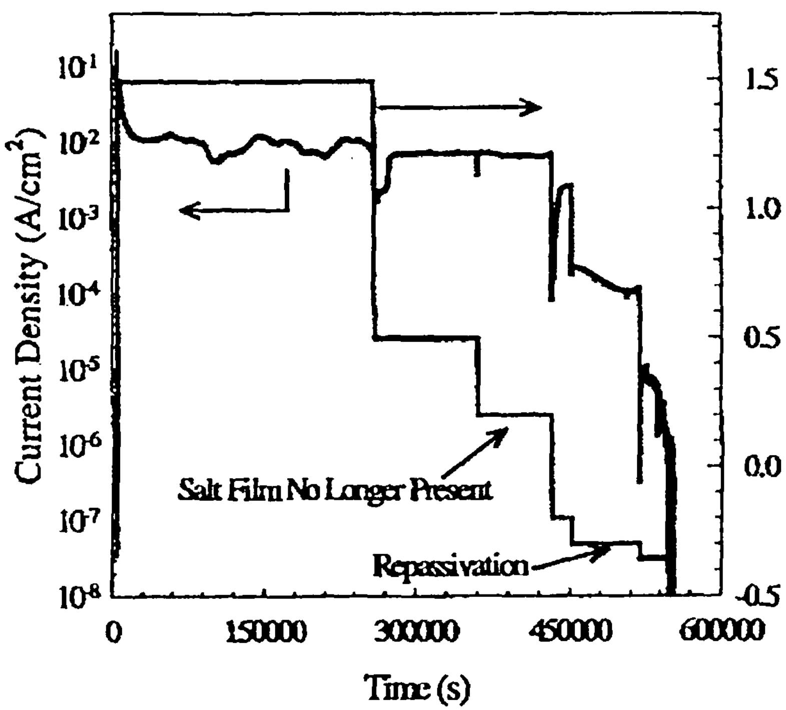
Raman Results

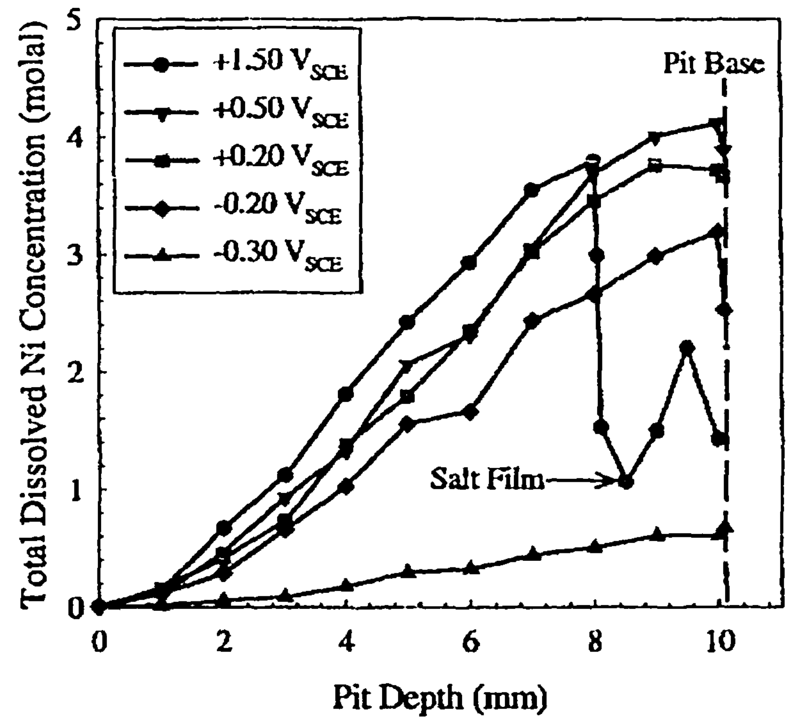


OLI Speciation Calculation



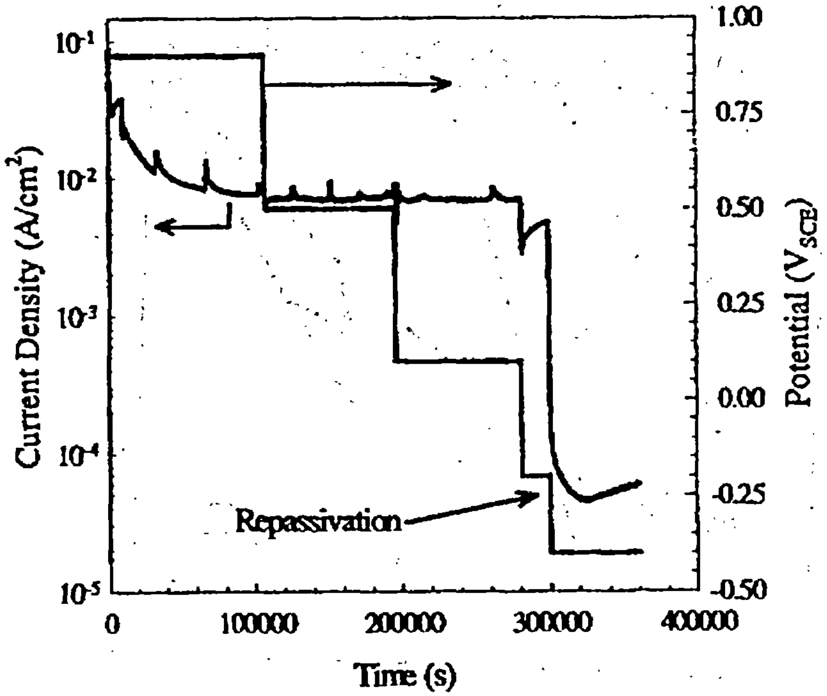
EXPERIMENTAL RESULTS - NI

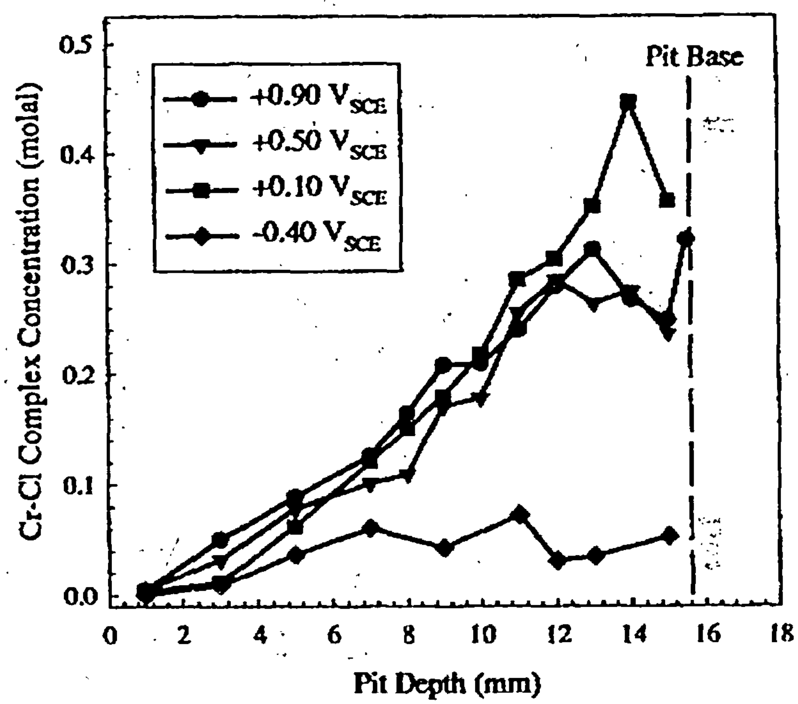




- High chloride concentrations are necessary for pit growth
- Pit ceases to grow if chloride concentration decreases below about 15% saturation with respect to nickel chloride

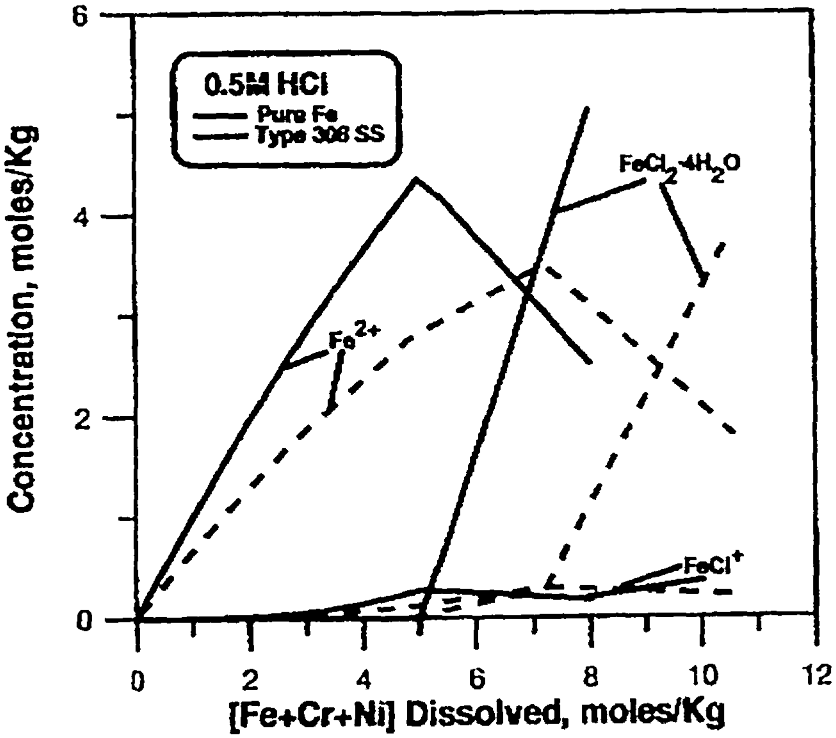
EXPERIMENTAL RESULTS - 308SS

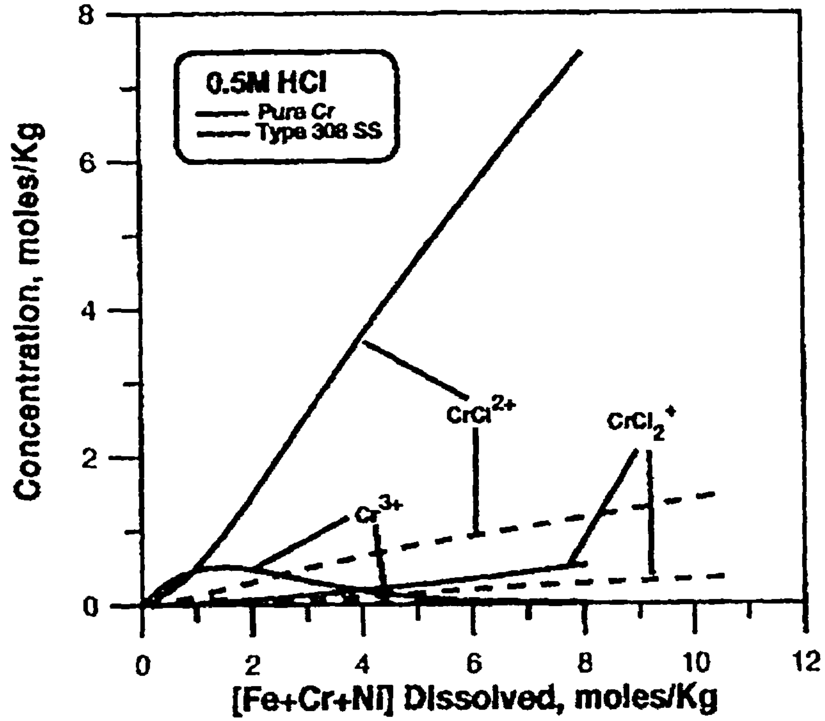




- Dissolution rate still high even at -0.20 V_{SCE}
- Observed relationship between Cr-Cl concentration and dissolution rate -- similar to Ni

CALCULATED SPECIATION - SOLUTION MIXTURE





- Assuming stoichiometric dissolution (Ni:Cr:Fe = 1:2:6.6)
  - Dominant Fe species in 308SS pit solution: $Fe(H_2O)_6^{2+}$
  - Dominant Cr species in 308SS pit solution: $CrCl^{2+}$

DOE APPROACH
(H. Stockman Presentation, 4/20/99)

- ❑ Considered a bathtub and drip models
- ❑ Considered C-22 to be inert and assumed steel, stainless steel, and neutron poisons to dissolve uniformly
- ❑ Calculated pH using EQ6
  - pH decreased to 5.1 after 1000 y and then increased to 7.6
- ❑ Identified the need to consider adding Cr thermodynamic data, “more realistic models”

Discussion

- Detailed calculations of internal environment chemistry are going to be difficult, if not impossible
- Need to resolve differences in conceptual models with DOE
- At this time, a bounding value for pH, chloride concentration is not known. But it can be established
  - Experiments and modeling should focus on alloy 22 or similar material for bounding environment definition
- The oxygen concentration is likely to be very low - radiolytic oxidants, and hydrogen ions likely to be important for calculating corrosion potential
  - Minimum potential for oxidative dissolution of UO2 is not high (about -200 mV vs. SCE)
- Studies of spent fuel dissolution in acid brines may be useful to establish bounding behavior for radionuclide release from WP