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Environmental assisted cracking of pipeline steels in CO2 containing environment

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EAC phenomena on buried pipelines

- Carbonate-Bicarbonate Stress Corrosion Cracking (CB-SCC or TG-SCC)
- Near Neutral – SCC
- Hydrogen Embrittlement (HE) due to cathodic protection or over-protection:
  - On base material
  - On altered microstructure:
    - Effect of welding
    - Effect of mechanical damaged
    - Hard-Spot

CB-SCC (high pH SCC; IG-SCC)

- First case in 1965, widely studied by R.N.Parkins
- Intergranular cracks
- Highly concentrated carbonate-bicarbonate solution (pH ≈ 9-10)
- Specific temperature range 50-70°C
- Specific potential range
- Easily controlled by cooling the gas after compression

NN- SCC (low pH- SCC, TG-SCC)

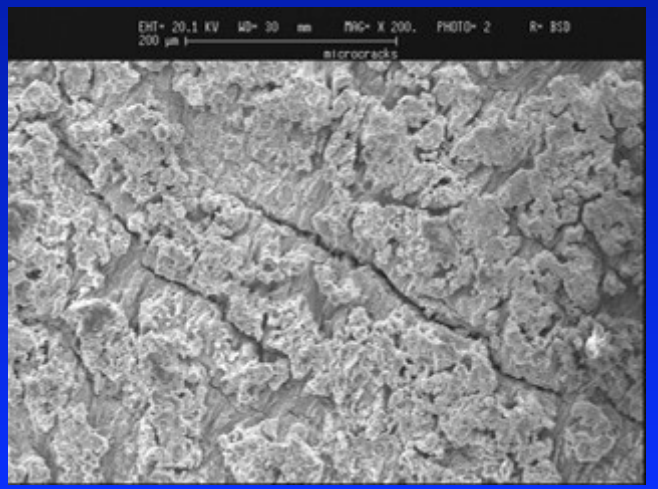
- First cases published by TransCanada Pipeline in 1985-86 but several cases were also detected in other countries, included Italy
- Transgranular cracks
- Low temperature
- pH 5.5 ÷ 6.5
- No cathodic protection
- pCO_2 0.05 bar (HCO_3^-)
- Particular loading conditions
- Effect of localized attacks on cracks initiation

Example of NN-SCC circumferential crack observed on buried flow-line

- Circumferential cracks were due to the soil landsliding
- NN-SCC cracks are under disbonded but not fully removed coatings

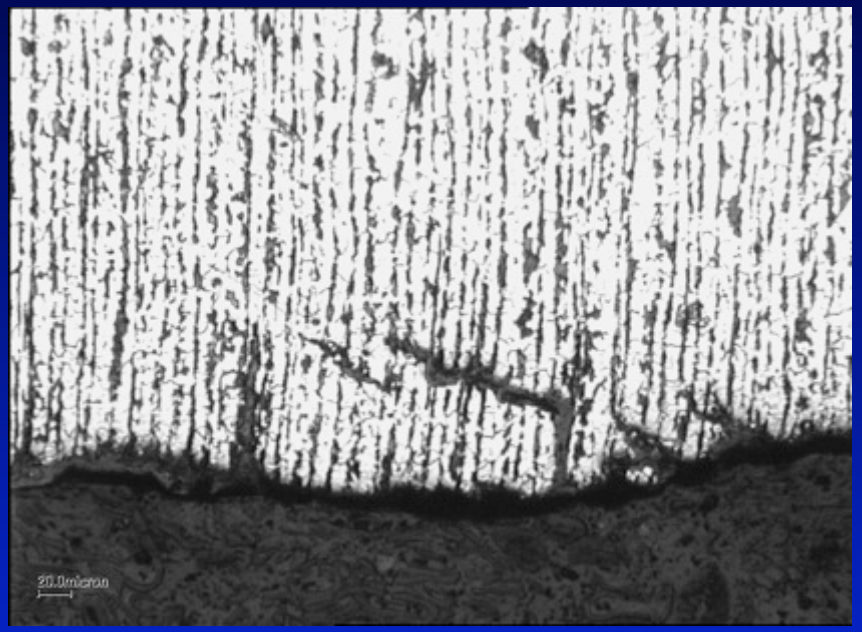
Role of localised attacks

- In these zone the pipe shows an intense generalised corrosion attack with presence of corrosion products.
- Cracks are initiated by localised attacks
- many closely localised attacks in the correspondence of cracks giving a generalised corrosion morphology



Cracks growth morphology

- The cracks were closed in colonies, coalescence between near cracks was observed
- The cracks have a **transgranular path**, with an enlarged tip owing to plastic strain and generalised corrosion

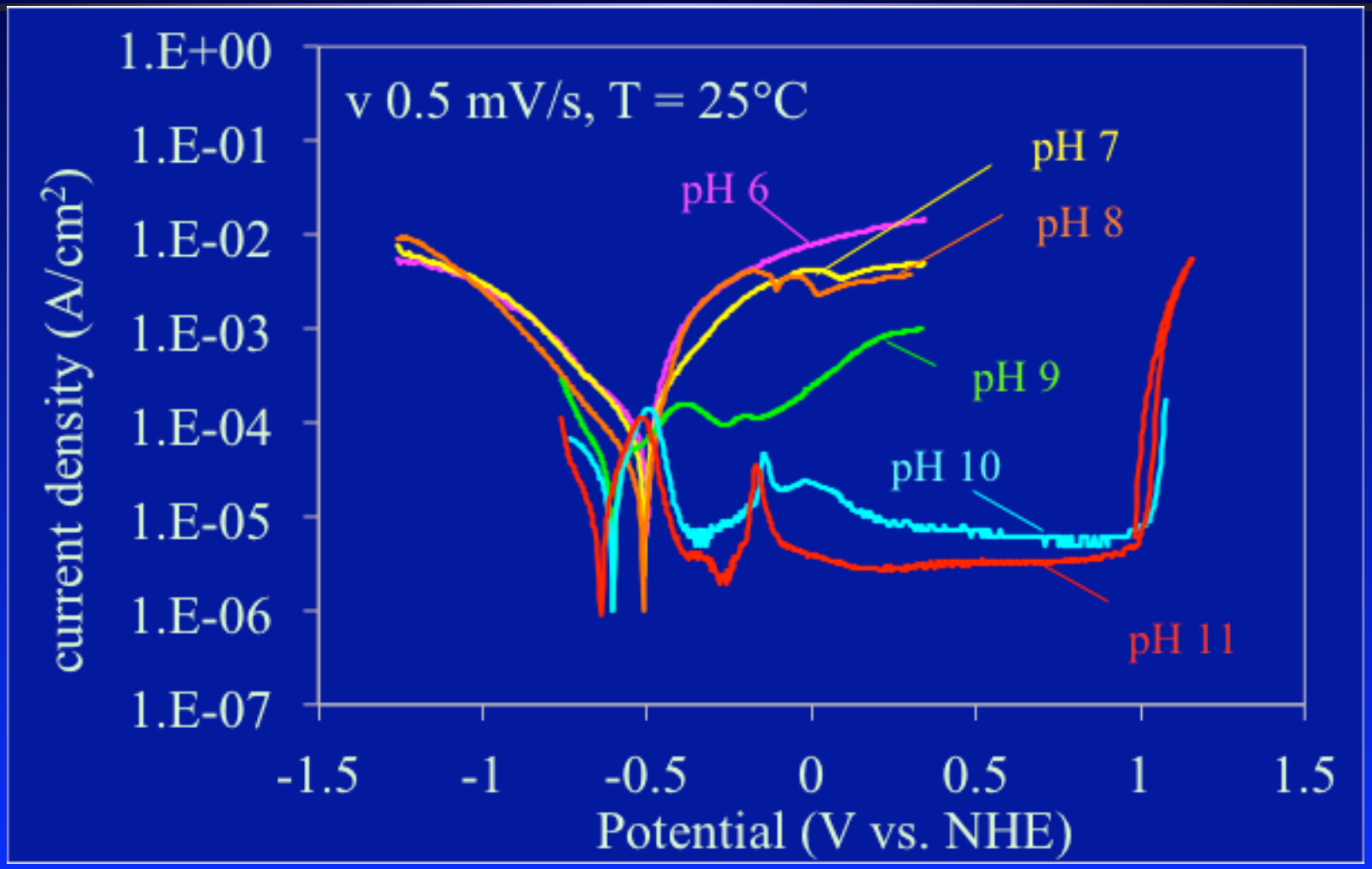


- In the presence of MnS inclusion cracks change their propagation direction

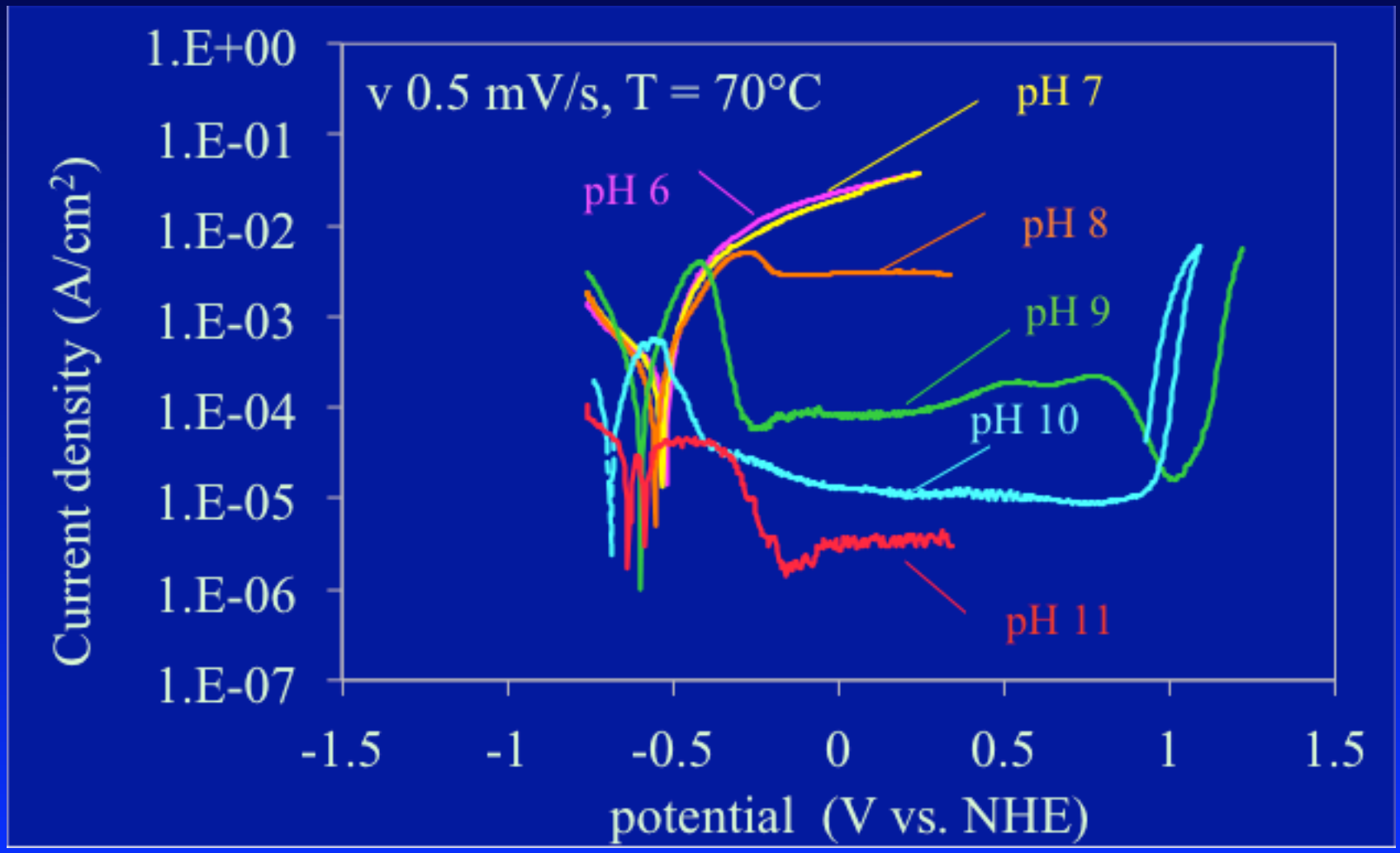
Laboratory studies on NN-SCC

- Electrochemical characterization and evaluation of the condition of localized attacks initiation
- Study of the NN-SCC affecting parameters (pH, T, Strain Rate, Environment, steel) by means of the traditional slow strain rate (SSR) tests
- Study of the effect of the surface condition (as received, electrochemically pre-corroded specimens) by means of traditional SSR tests and Slow Bending and Ripple Loading tests
- Evaluation of the NN-SCC cracks propagation by means of da/dN vs ΔK curves

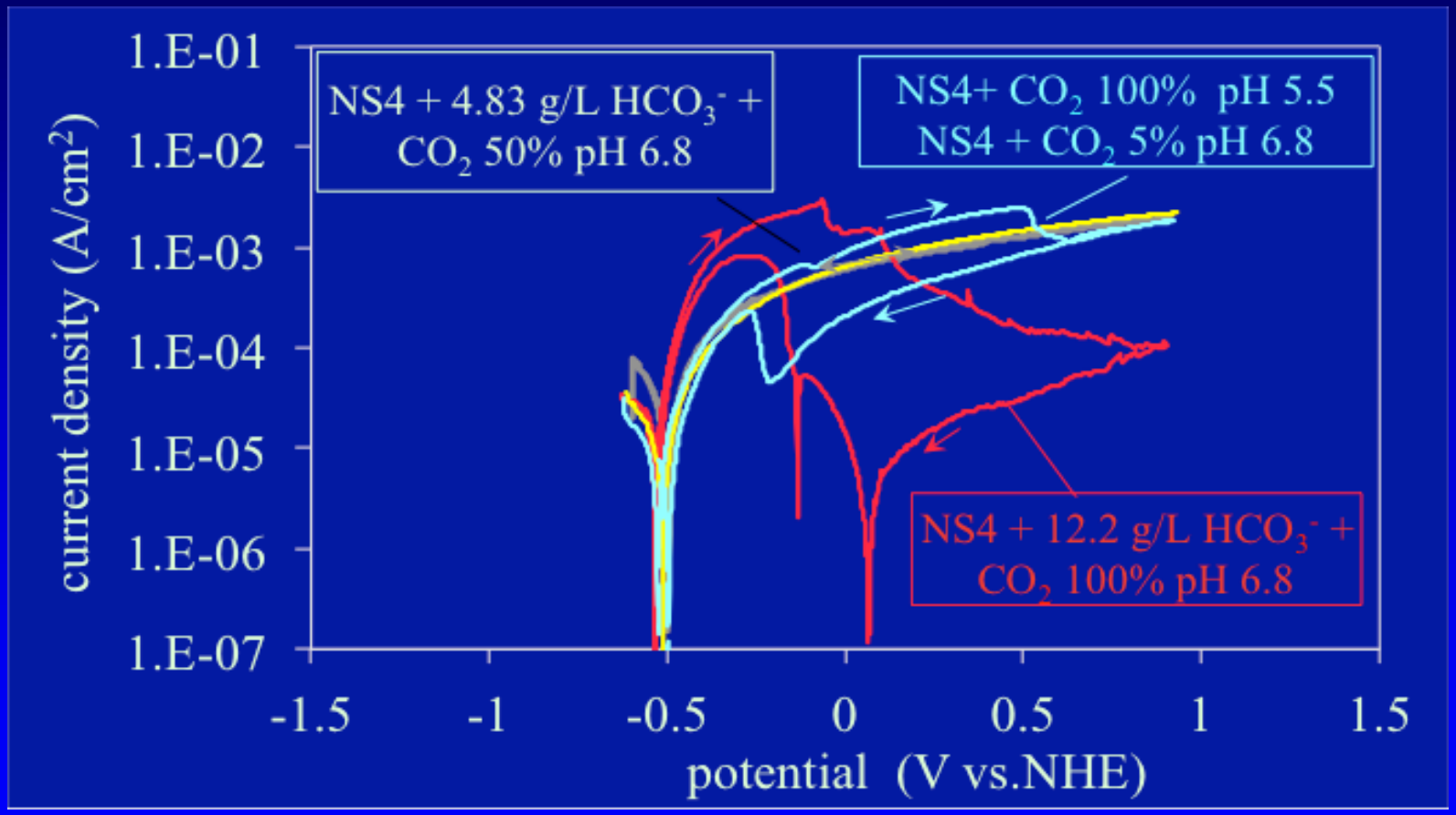
Potentiodynamic curves in Na_2SO_4 + CO_2 + NaOH at different pH and 25°C



Potentiodynamic curves in Na_2SO_4 + CO_2 + NaOH at different pH and 70°C

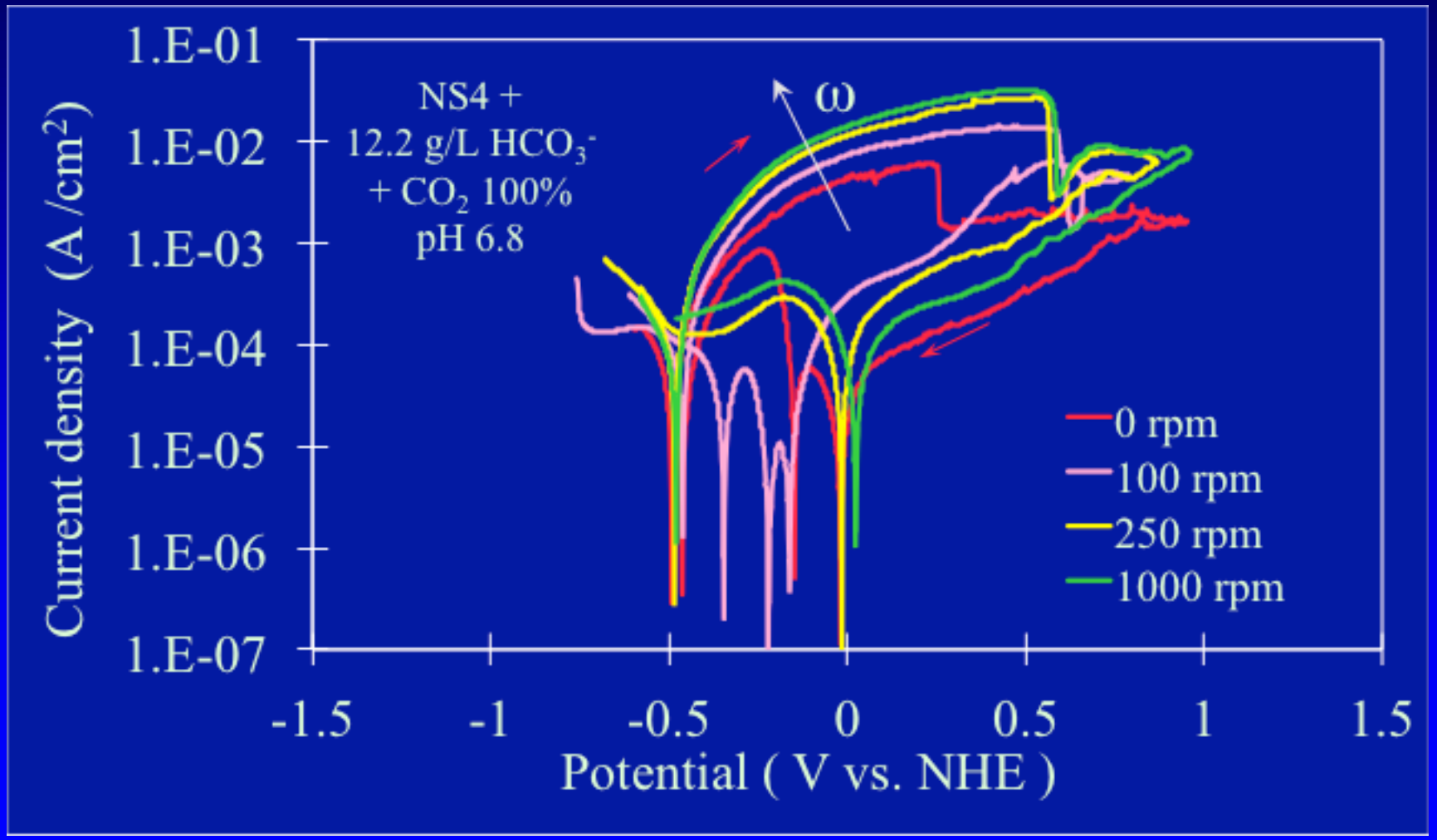


Effect of bicarbonate ions concentration on cyclic potentiodynamic curves

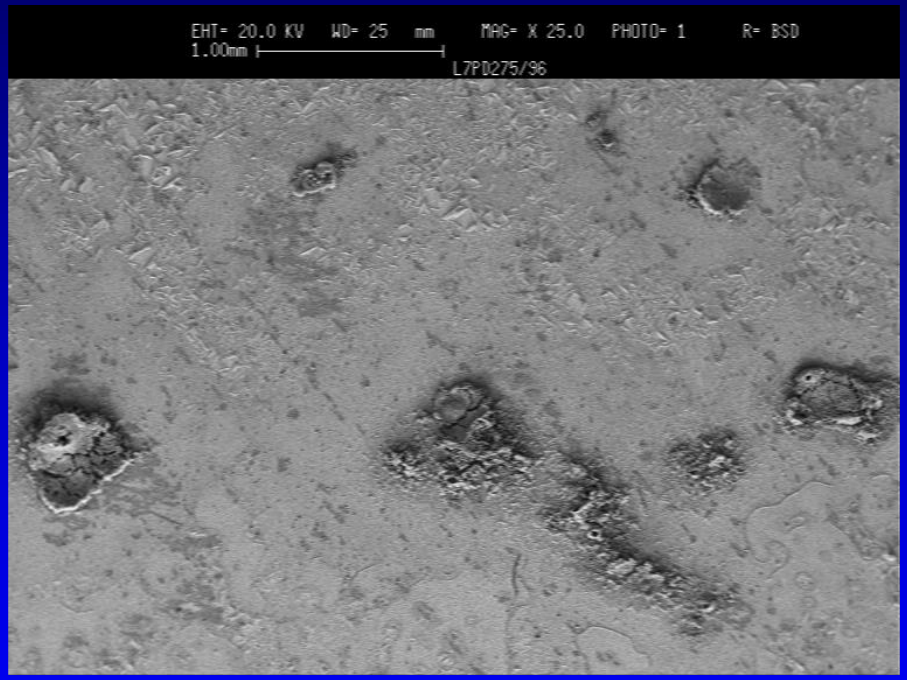


NS4 solution 0.483 g/L $NaHCO_3$, 0.122 g/L KCl, 0.18 g/L $CaCl_2$, 0.1 g/L $MgSO_4$;

Effect of diffusion on cyclic potentiodynamic curves

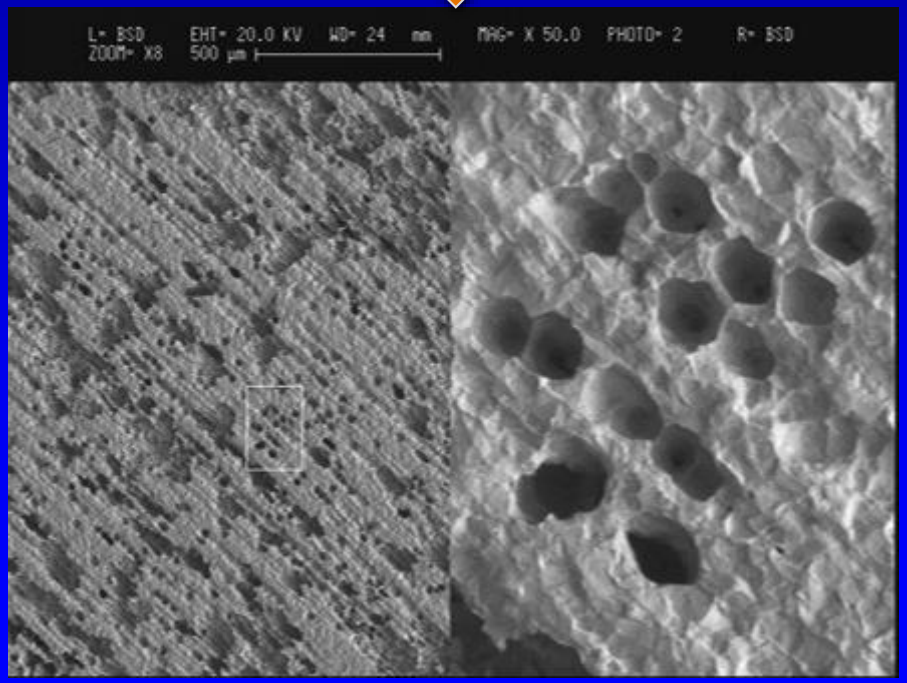


Effect of diffusion on the corrosion morphology



0 rpm

100 rpm



Study of corrosion of steels in CO_2 environments by means of cyclic voltammetry

- Iron dissolution in neutral solution takes place througth an intermediate of hydroxide

$$Fe \rightarrow Fe(OH)_{2(met)} + 2e^- \rightarrow Fe^{2+}_{(sol)} + 2OH^-$$

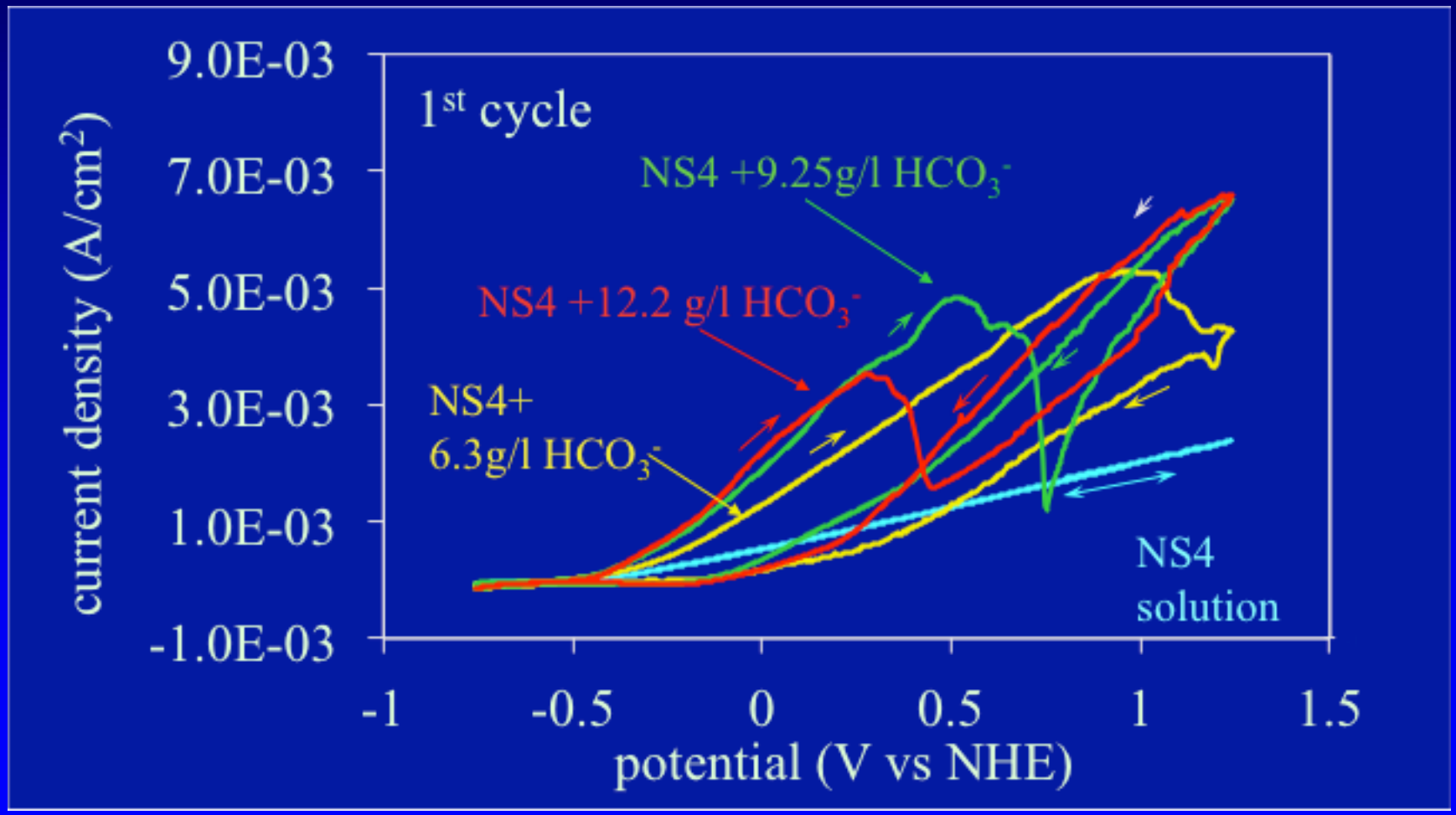
- The presence of bicarbonate ions avoid this intermediate and on the cyclic voltammetry curves are not present peaks

$$Fe + HCO_3^- \rightarrow FeCO_3 + H^+ + 2e^-$$

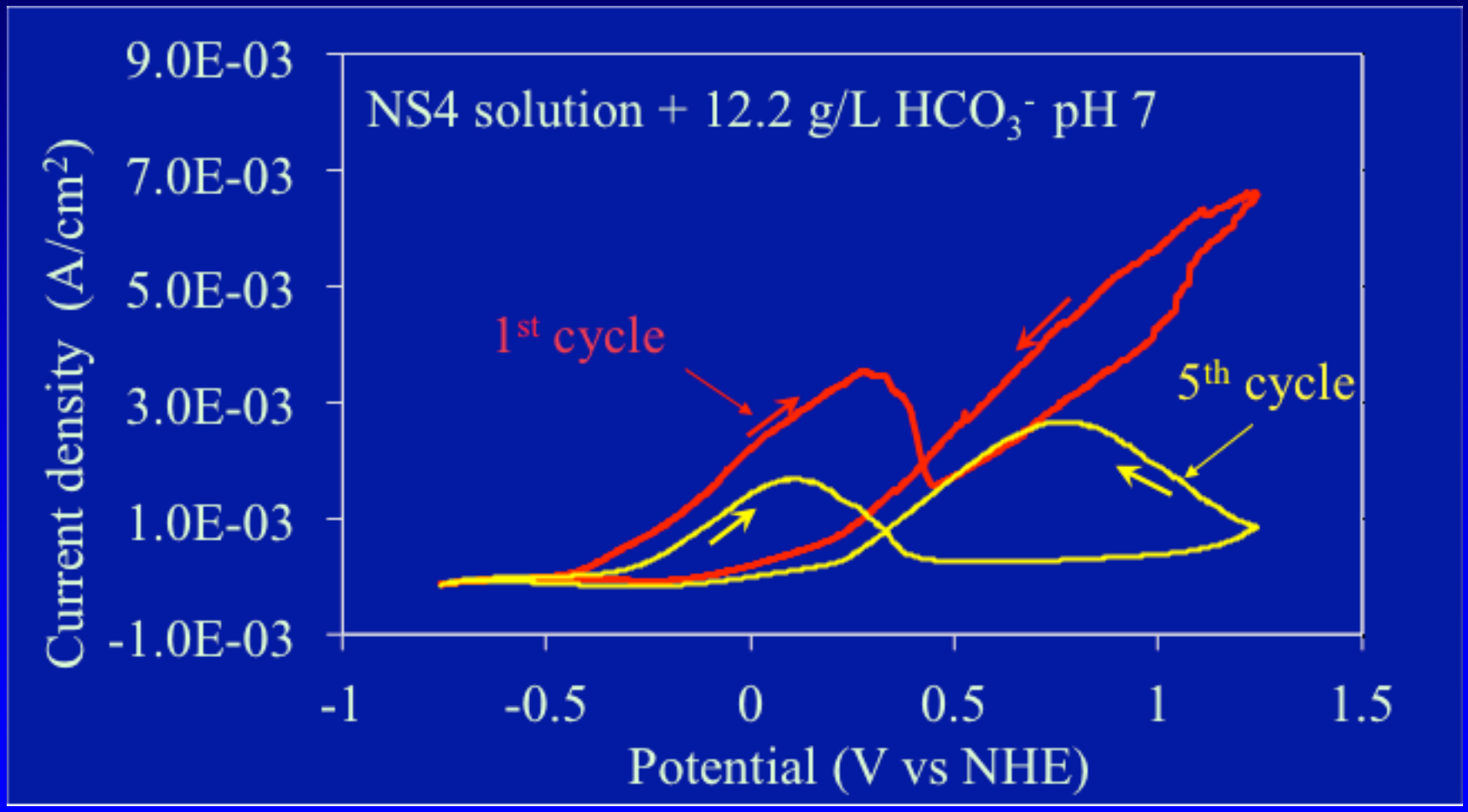
$$Fe + 2HCO_3^- \rightarrow Fe(HCO_3)_2 + 2e^-$$

$$FeCO_3 + HCO_3^- \rightarrow Fe(CO_3)_2^{2-} + H^+$$

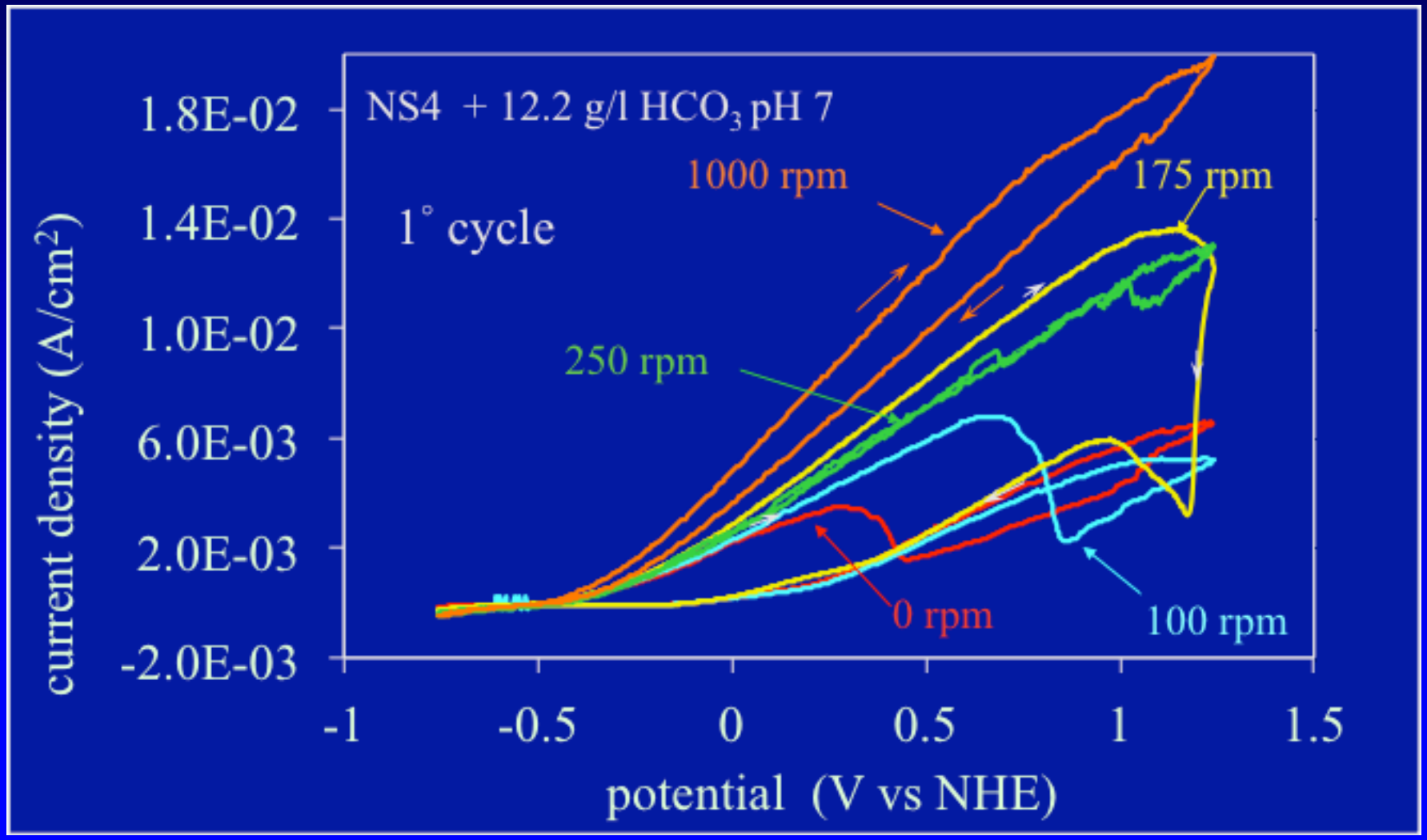
Effect of bicarbonate ions on cyclic voltammetry curves



Effect of the number of cycles on voltammetric curves

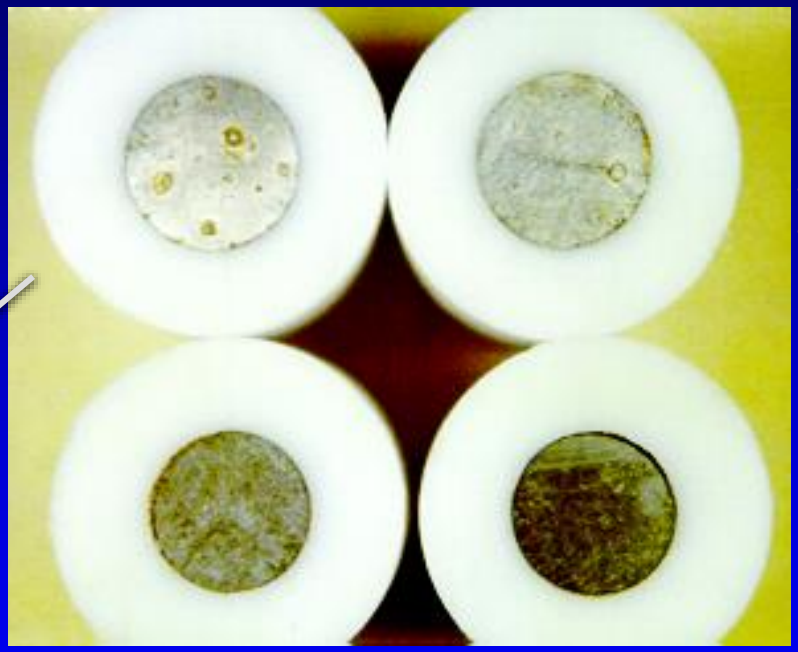


Effect of diffusion



Effect of diffusion on specimen's attacks after cyclic voltammetry

0 rpm

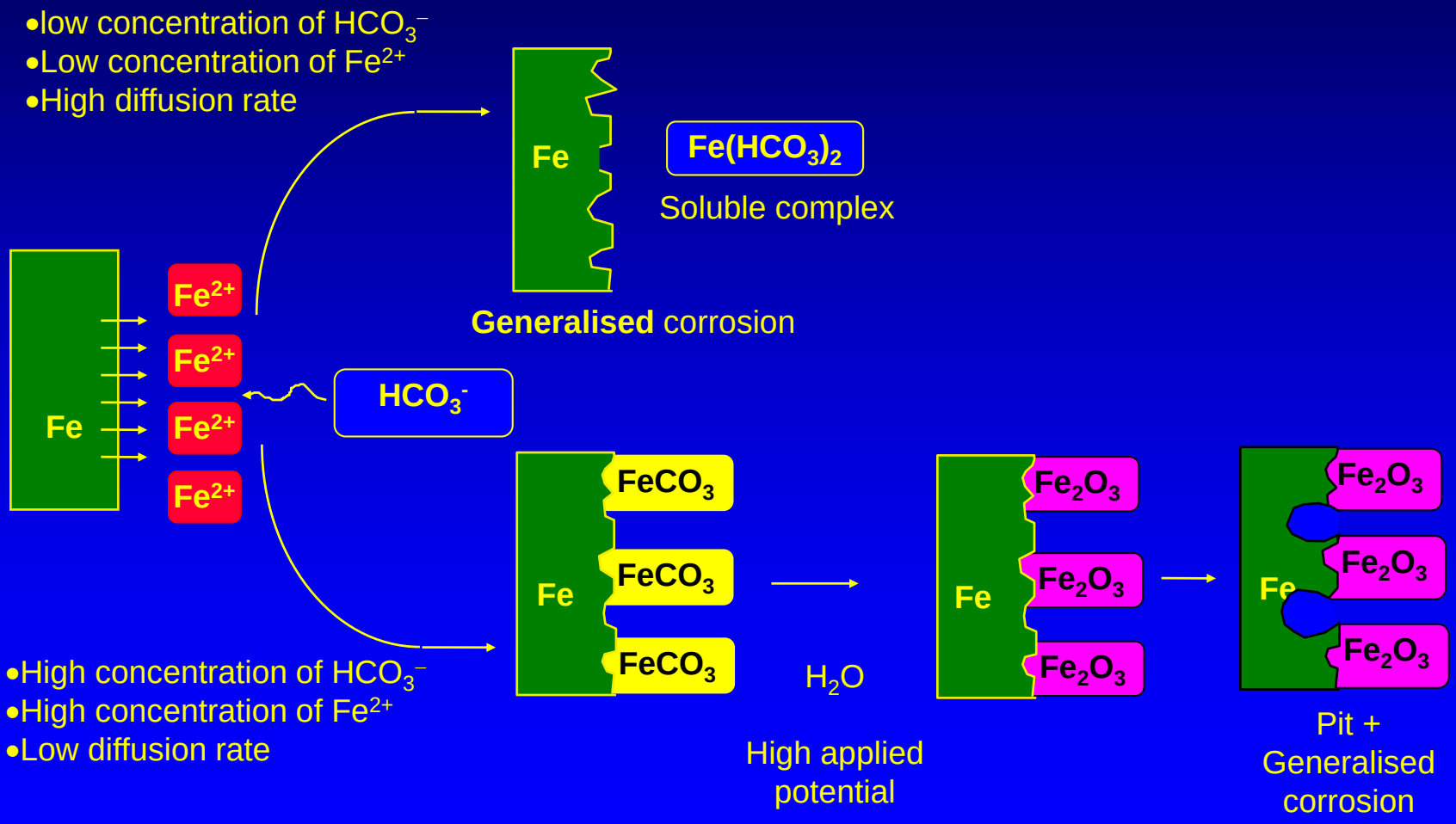


100 rpm

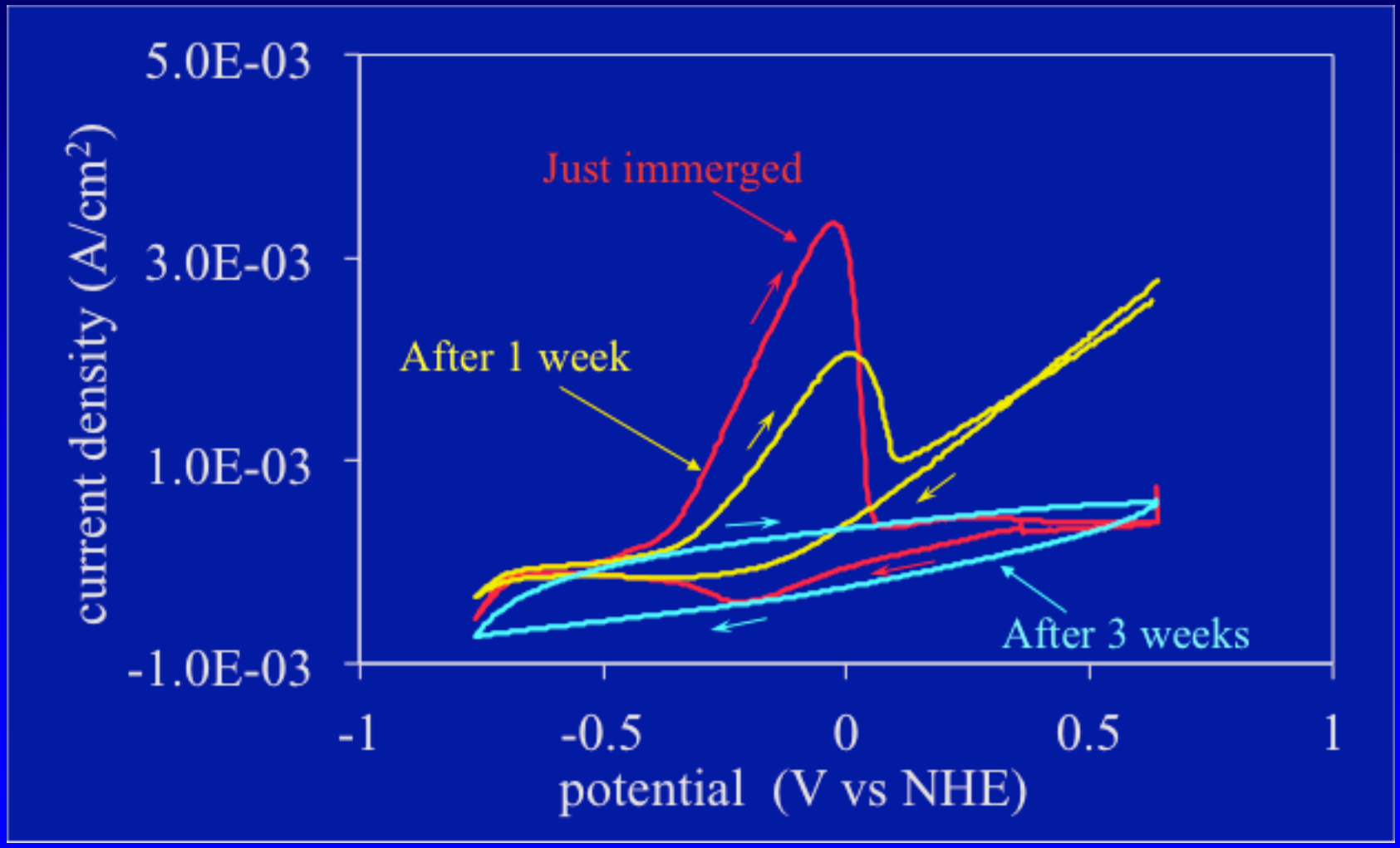
250 rpm

1000 rpm

Proposed mechanism for pit initiation



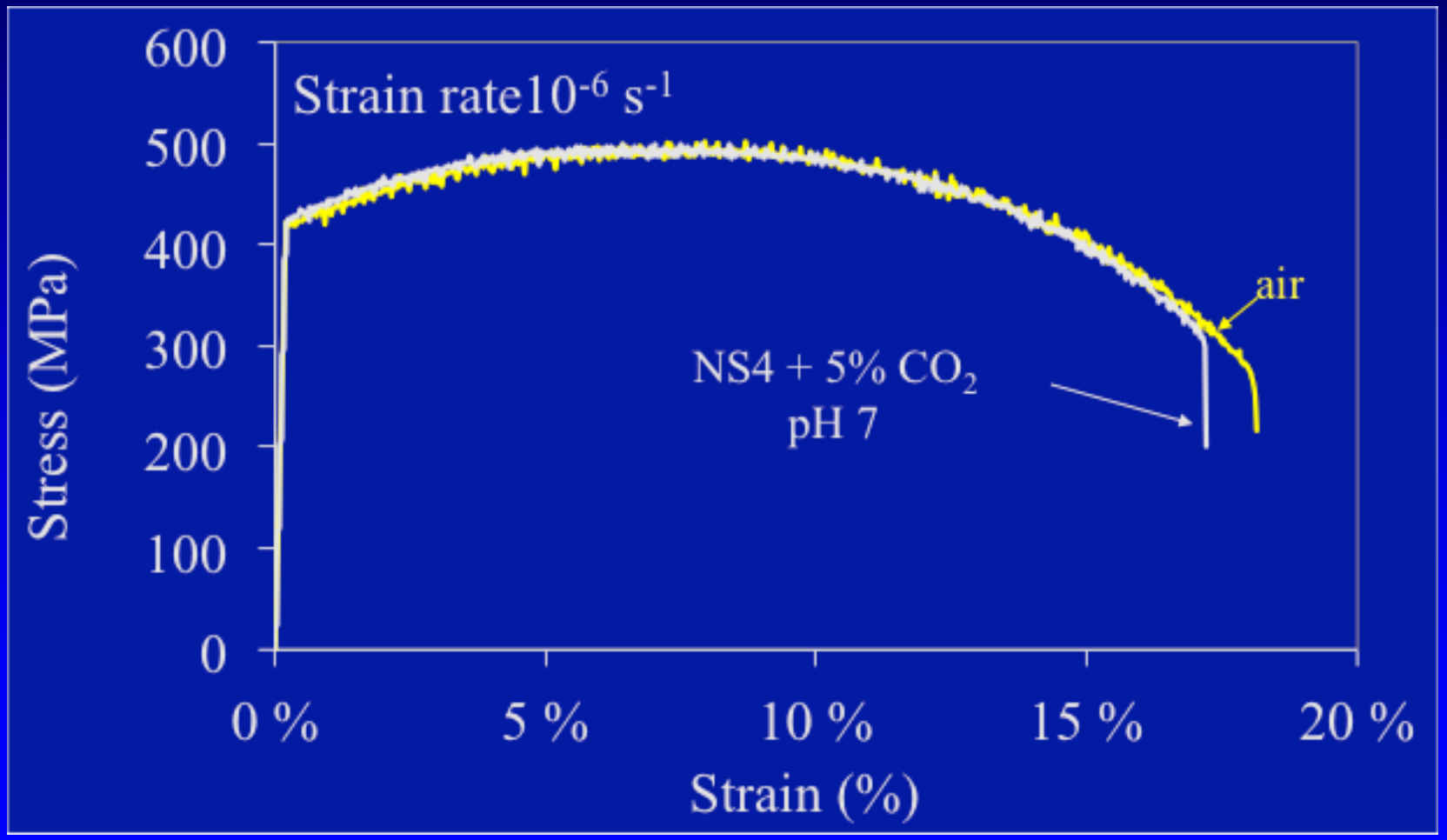
Effect of pre-immersion time on cycli voltammetry curves



Stress corrosion tests

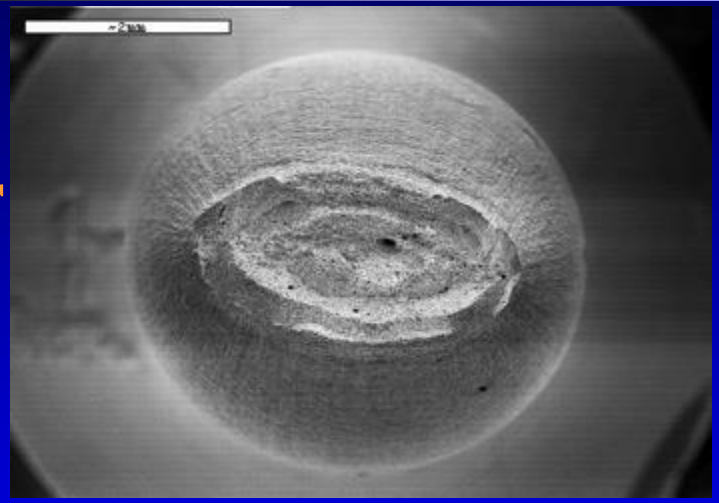
- No NN-SCC in static loading conditions
- NN-SCC was detected in:
  - Slow strain rate tests
  - Ripple-loading tests
  - Corrosion fatigue tests
- NN-SCC take place in the presence of CO_2
- Localized attacks enhance the SCC phenomena

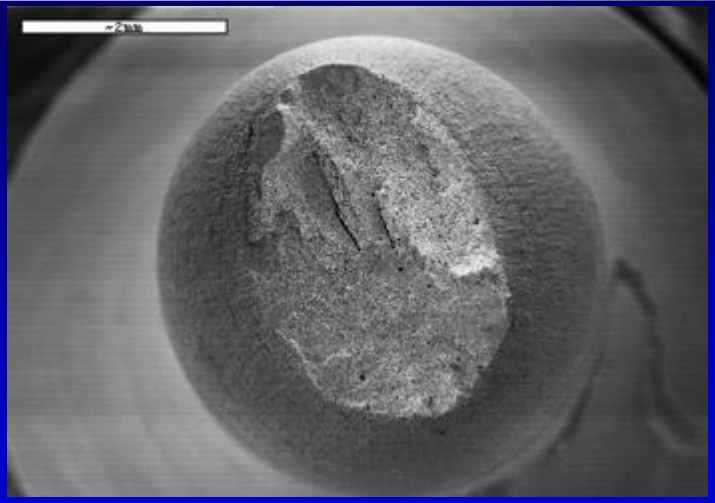
Stress vs strain curves in SSR tests

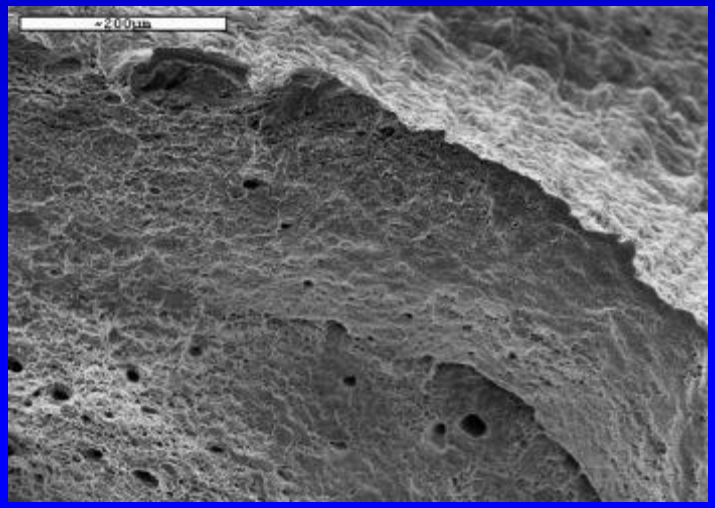


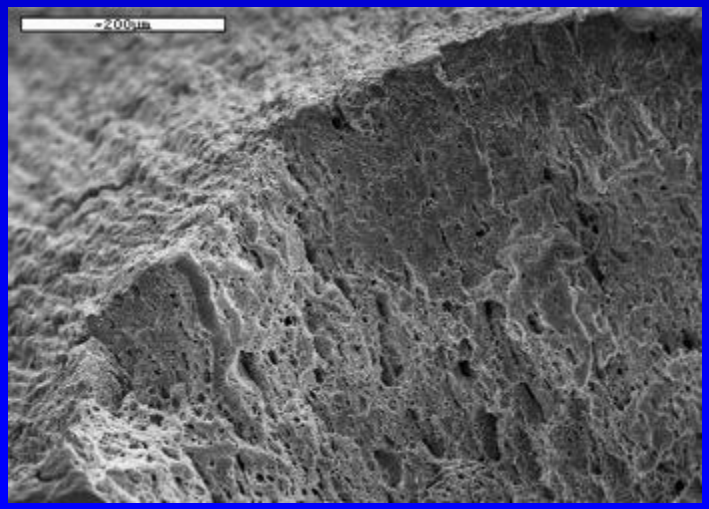
Fracture surface

air



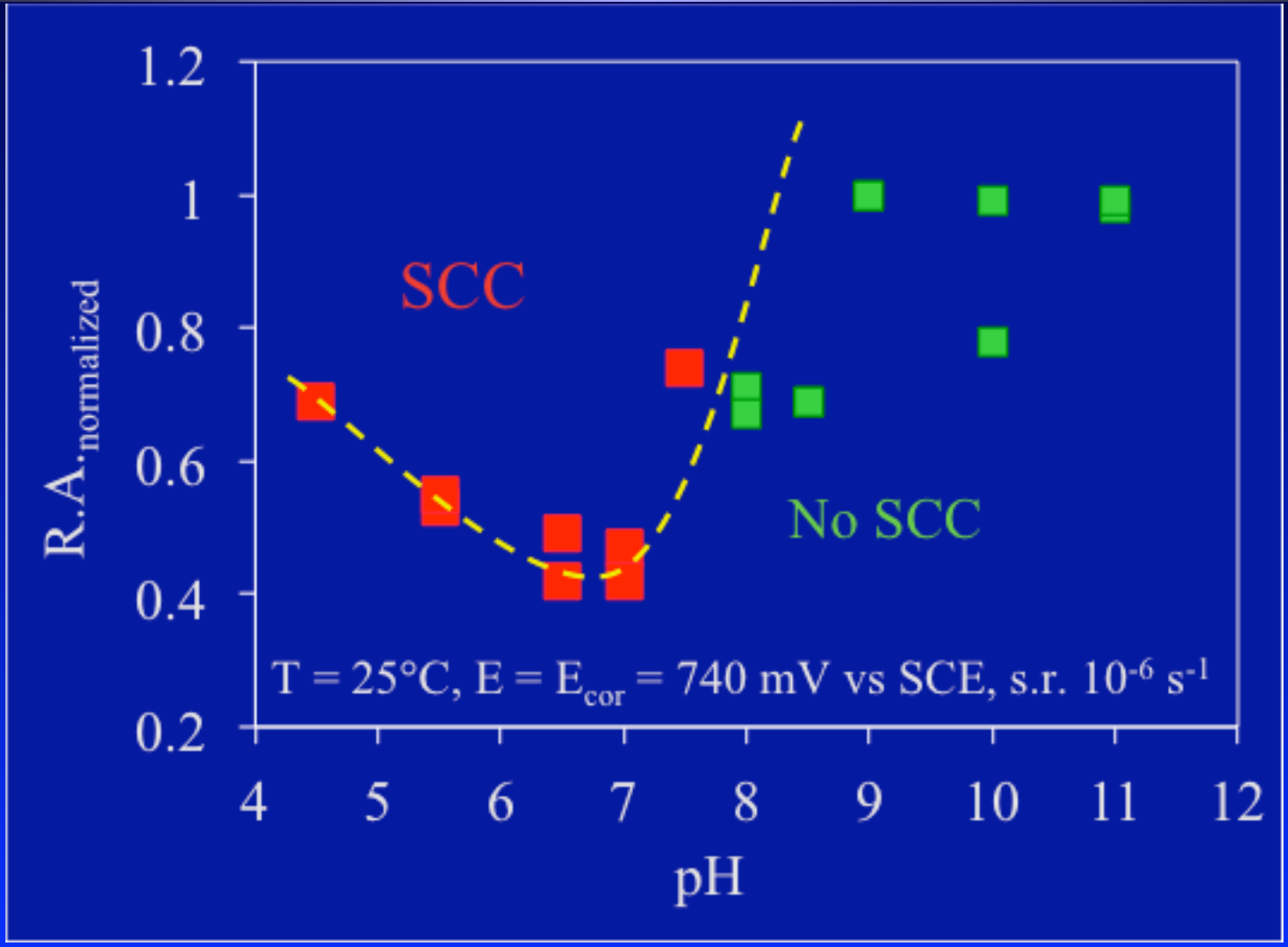




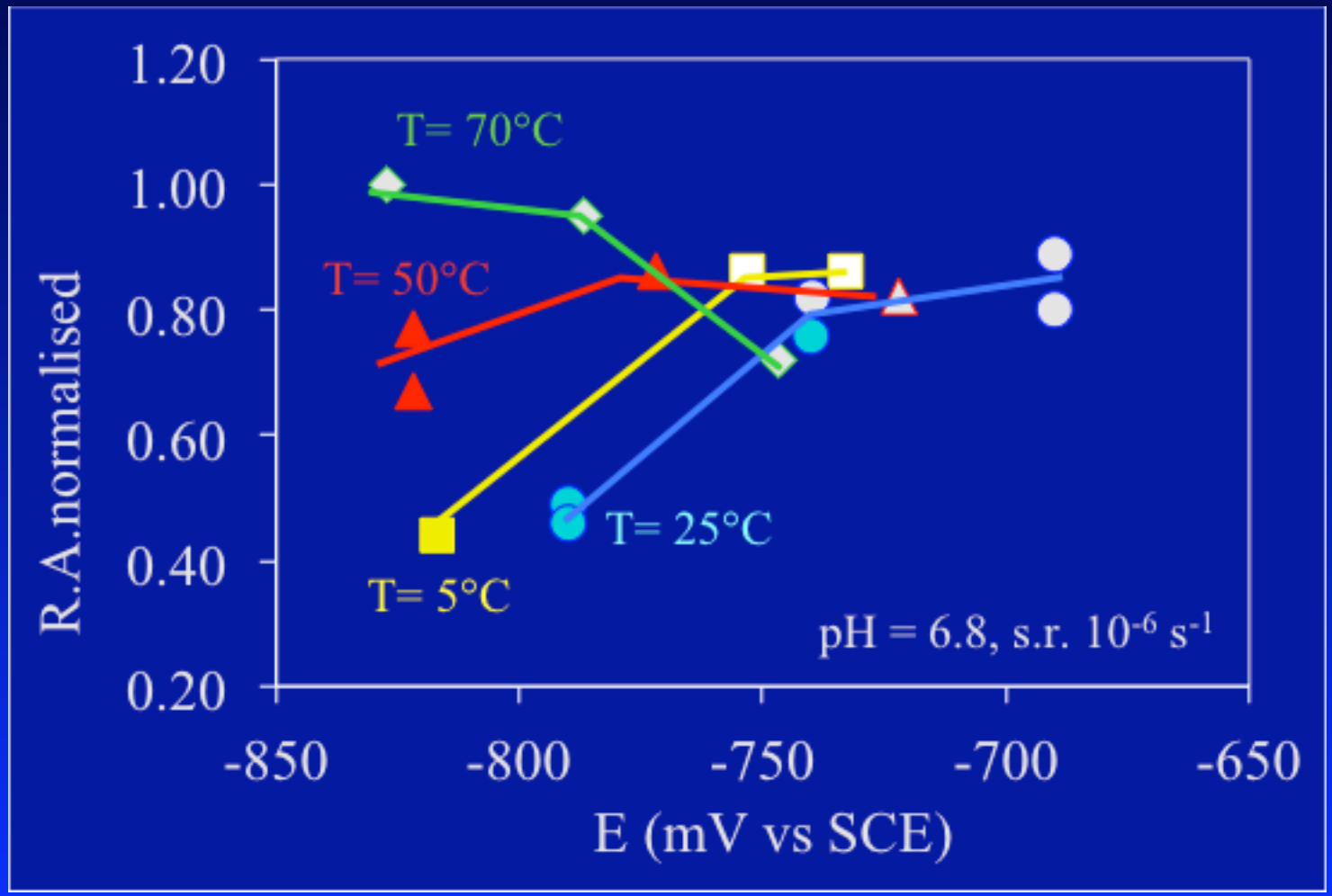


NS4
+
5%CO_2
pH 7

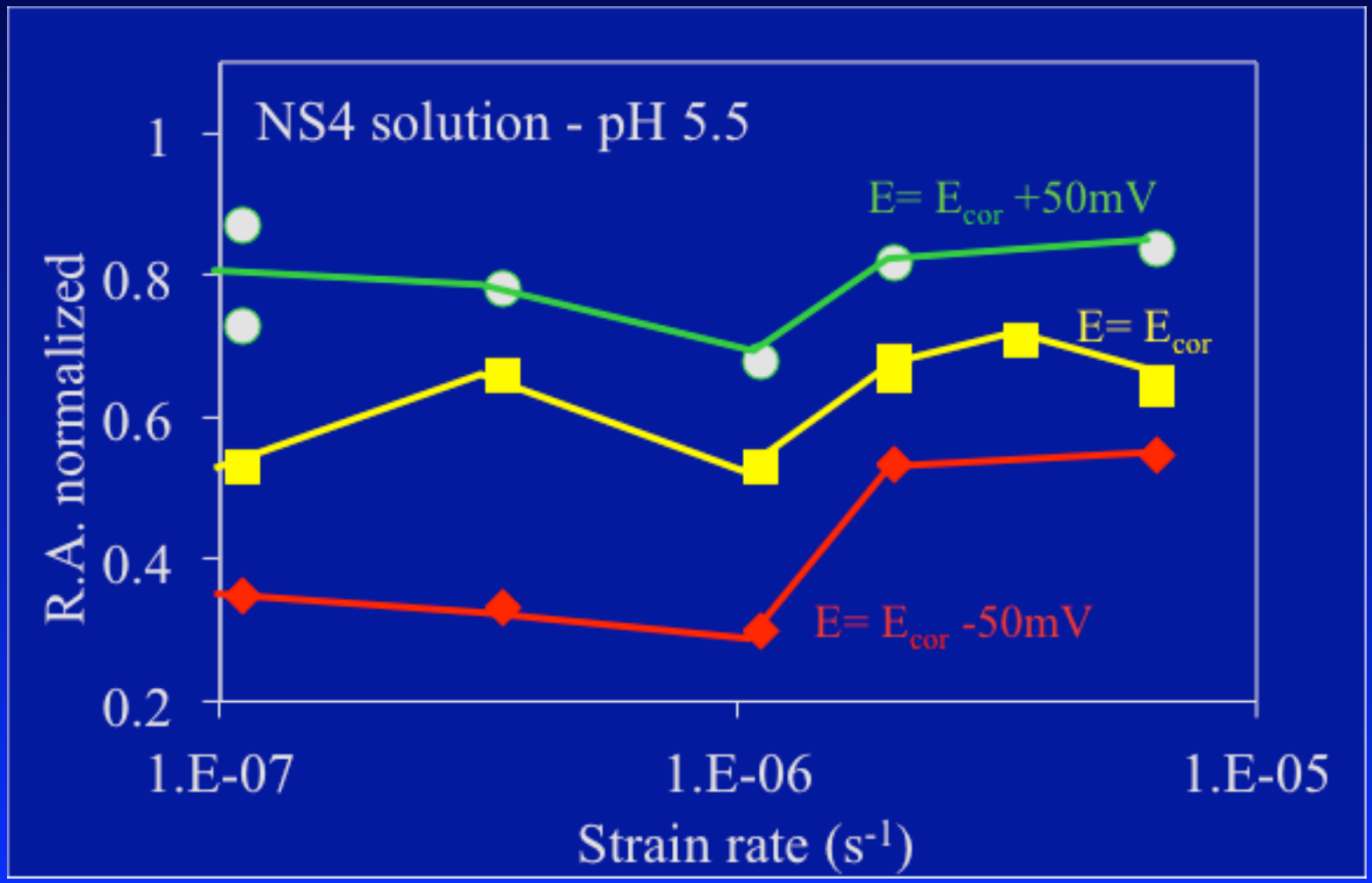
Effect of pH on SSR results



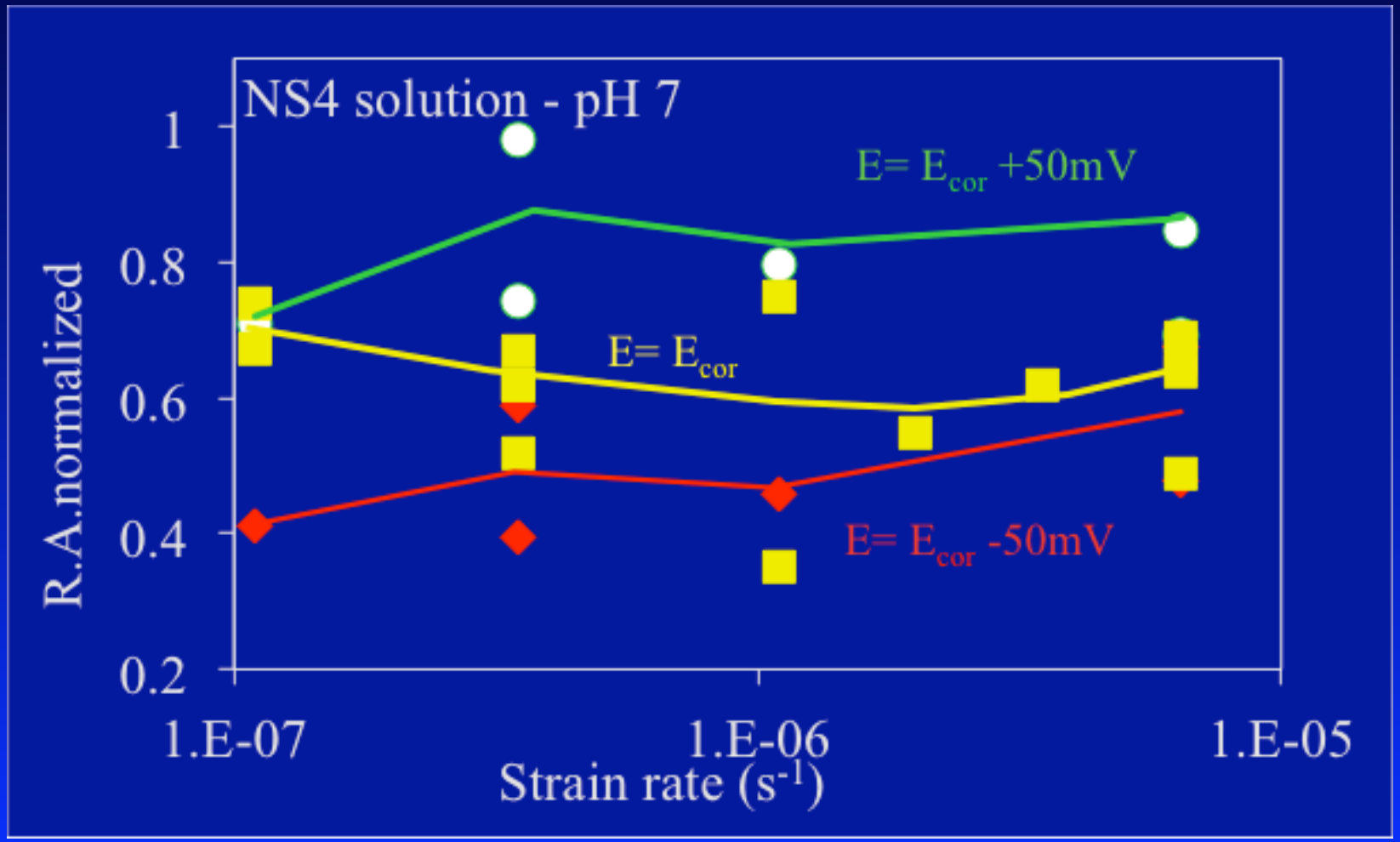
Effect of temperature and potential on SSR results



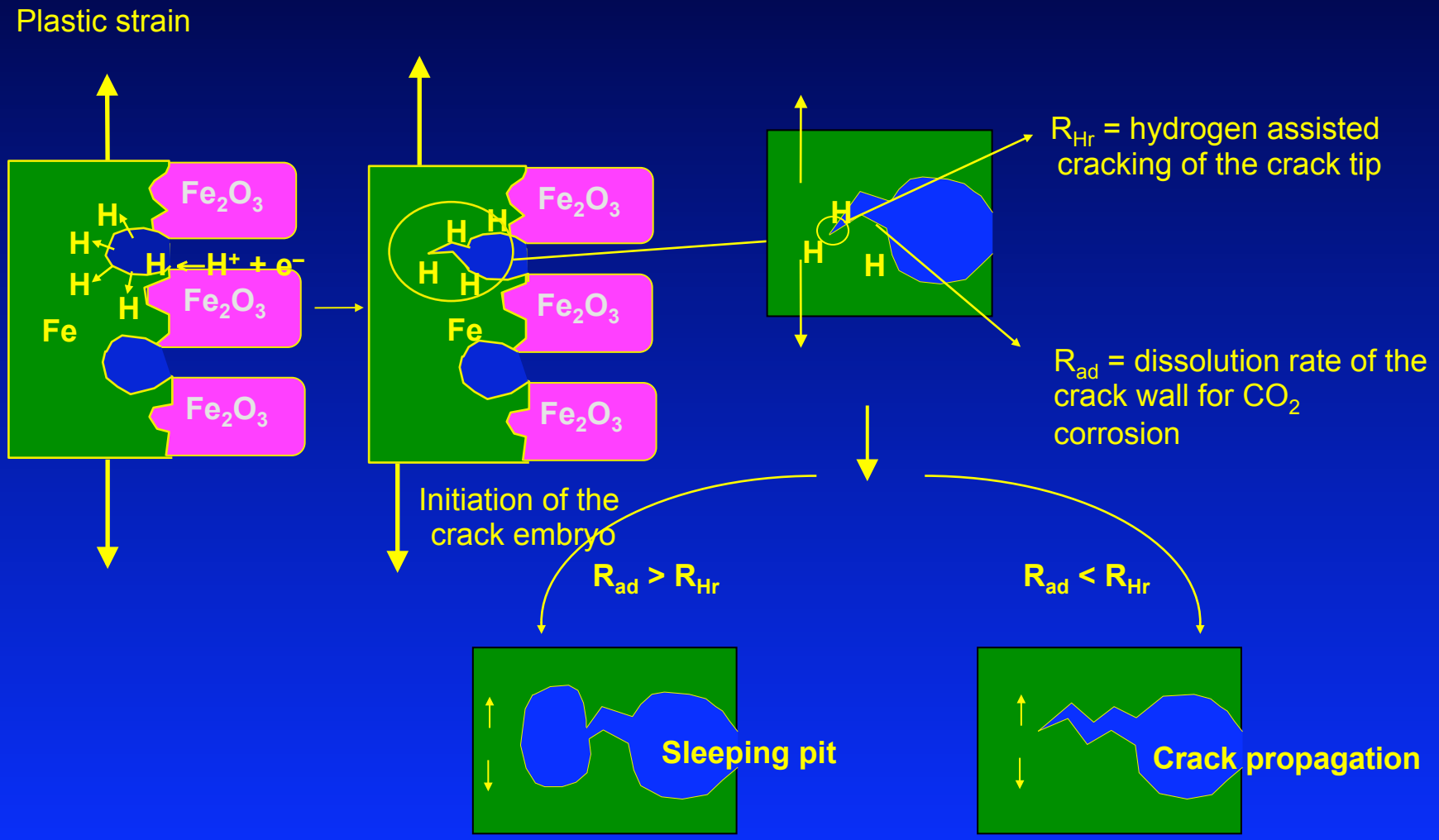
Effect of the strain rate at pH 5



Effect of the strain rate at pH 7

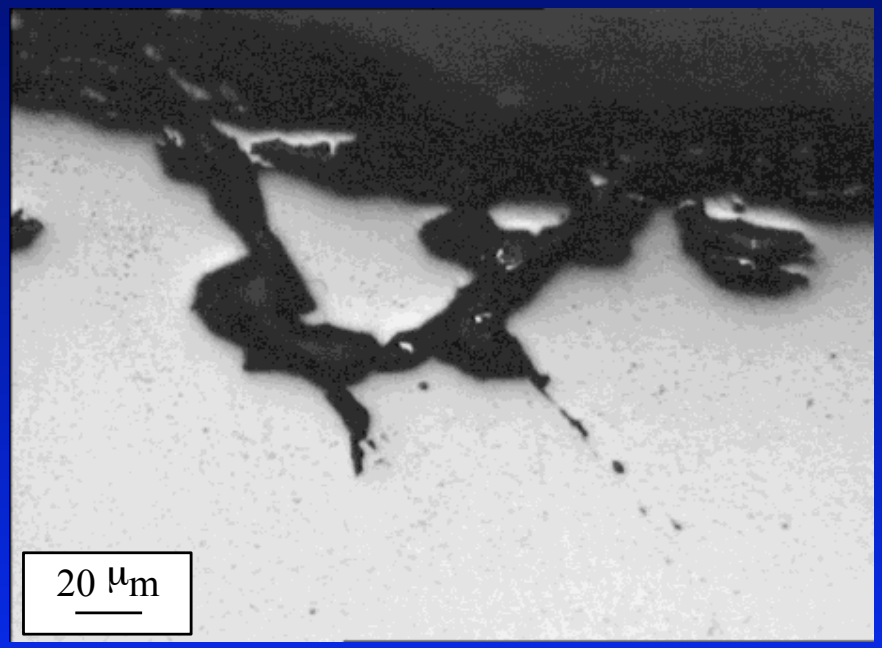


Proposed mechanism for cracks initiation and propagation

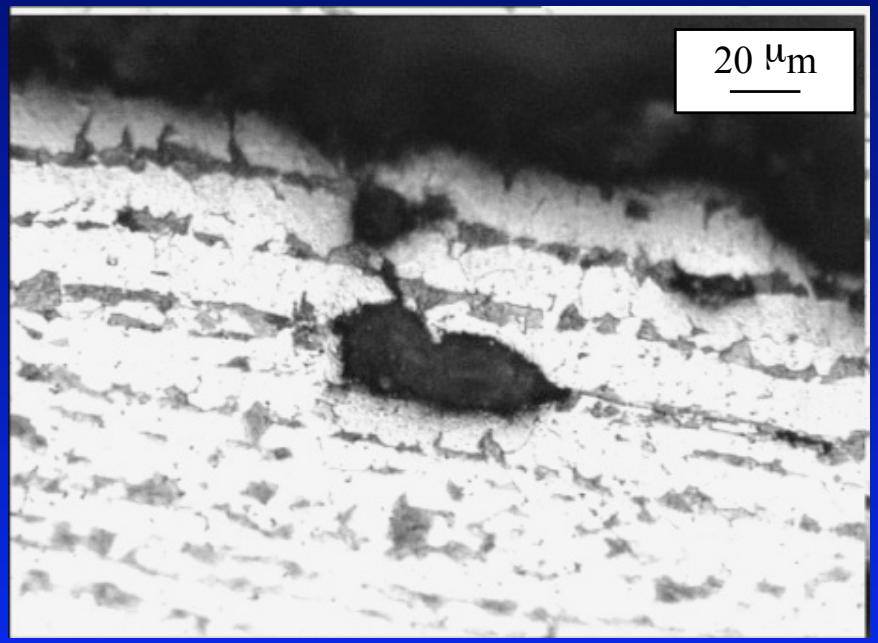


Experimental results

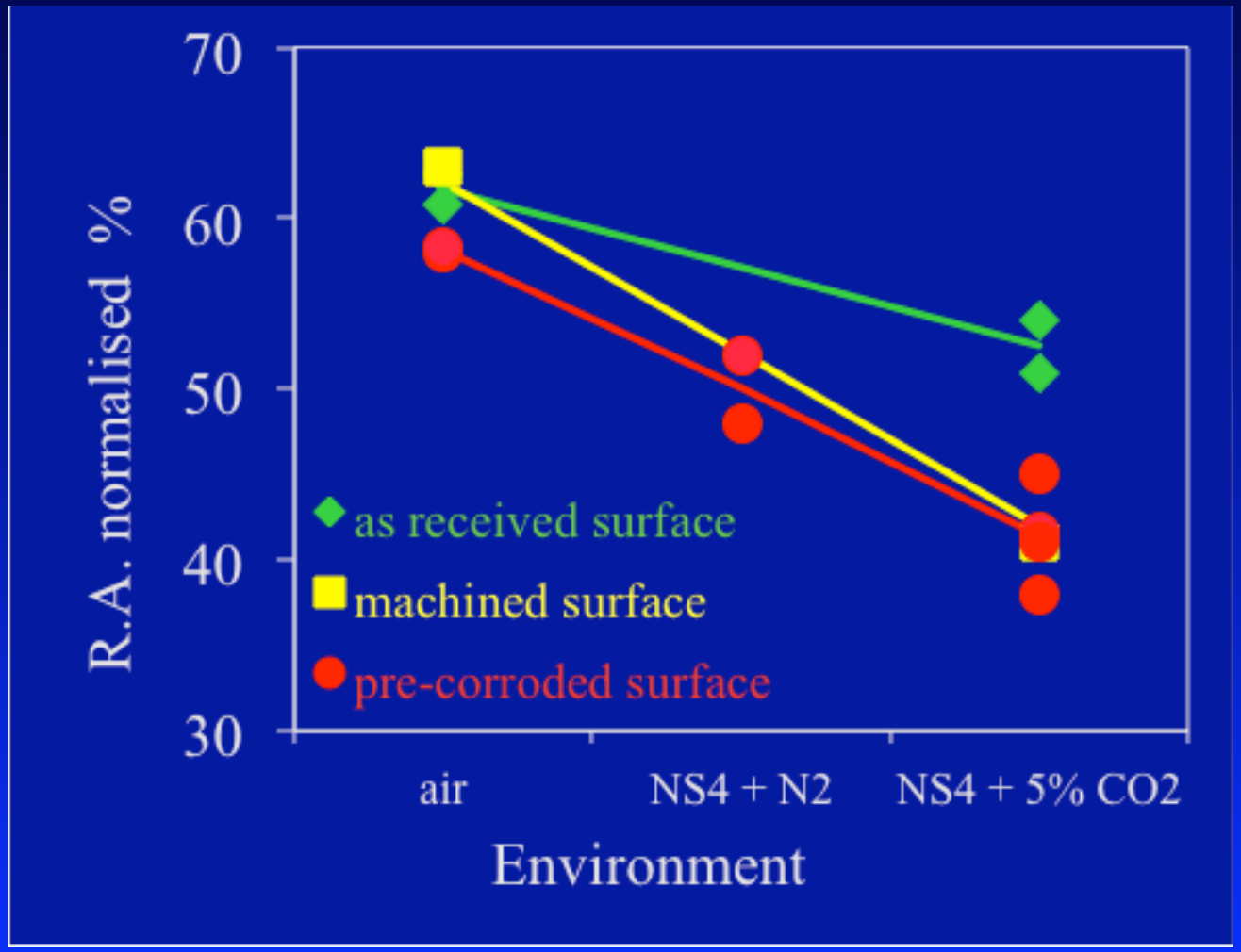
NN-SCC Crack



Sleeping pit

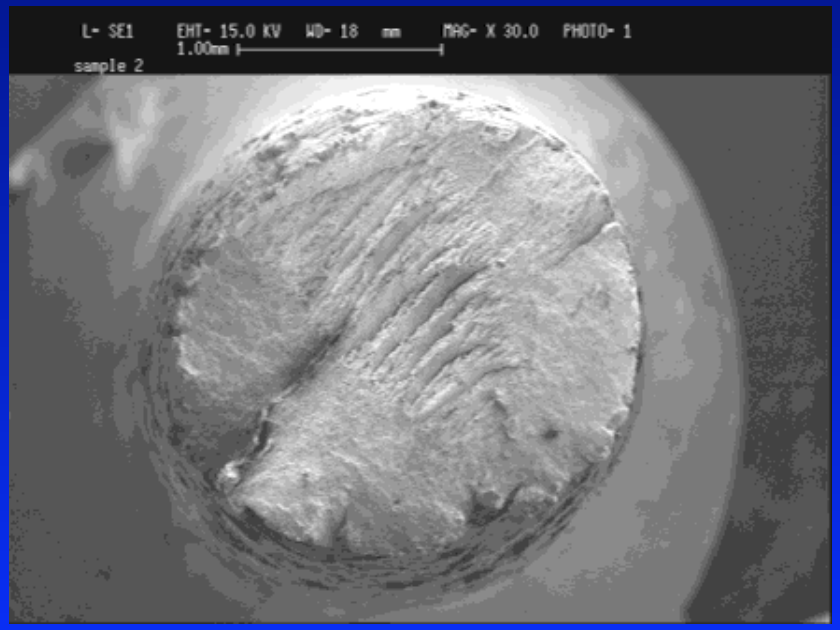


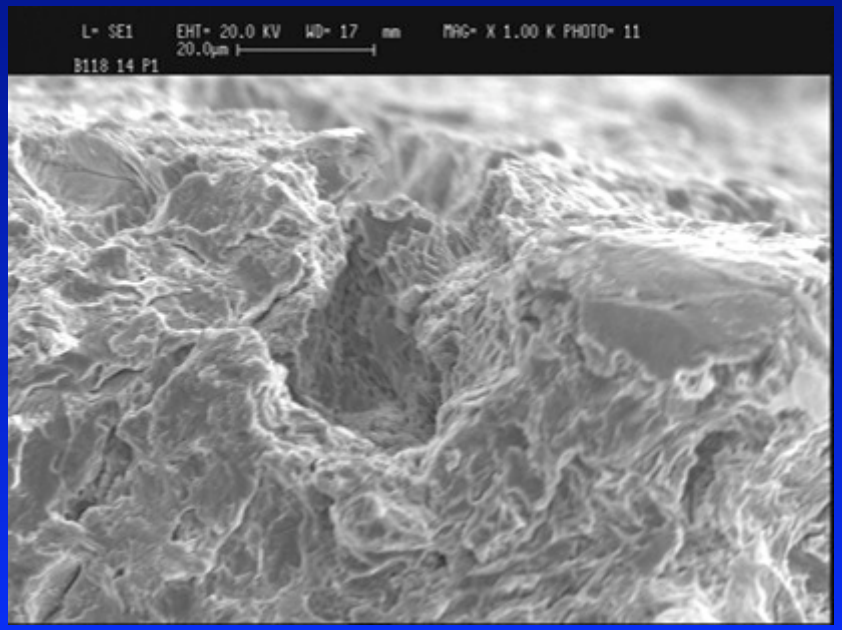
Effect of localized attacks: SSR tests on specimens with pre-corroded surface



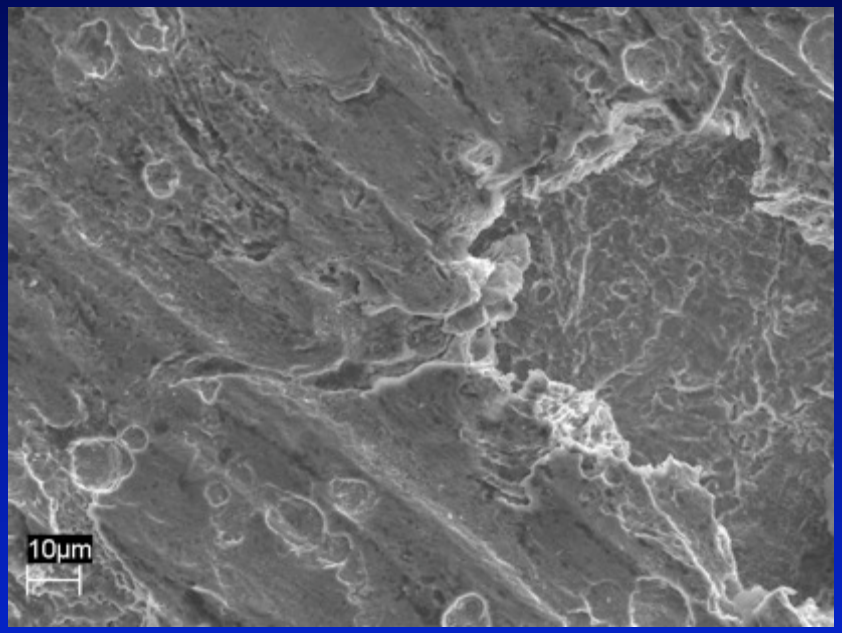
Example of NN-SCC crack initiated from localized attacks

Specimen of X65 steel with surface electrochemically pre–corroded surface after the SSR tests NS4 solution + 12.2 g/L of $NaHCO_3$



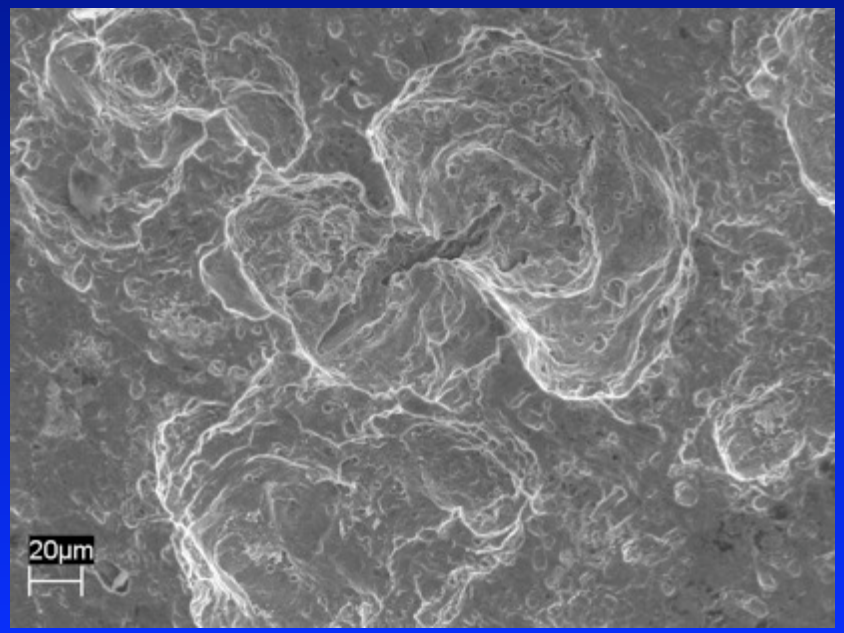


Slow bending tests

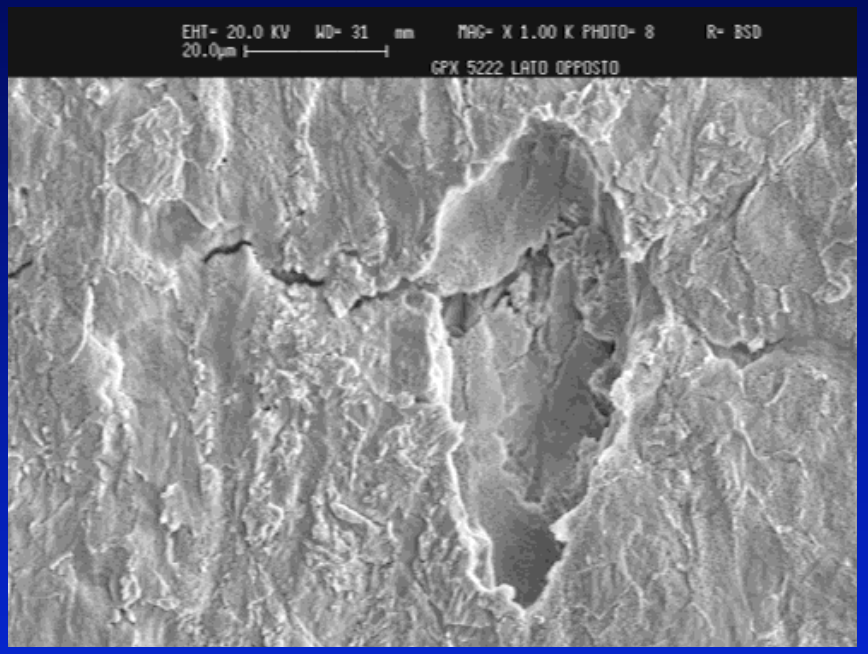


As received surface

Pre-corroded surface



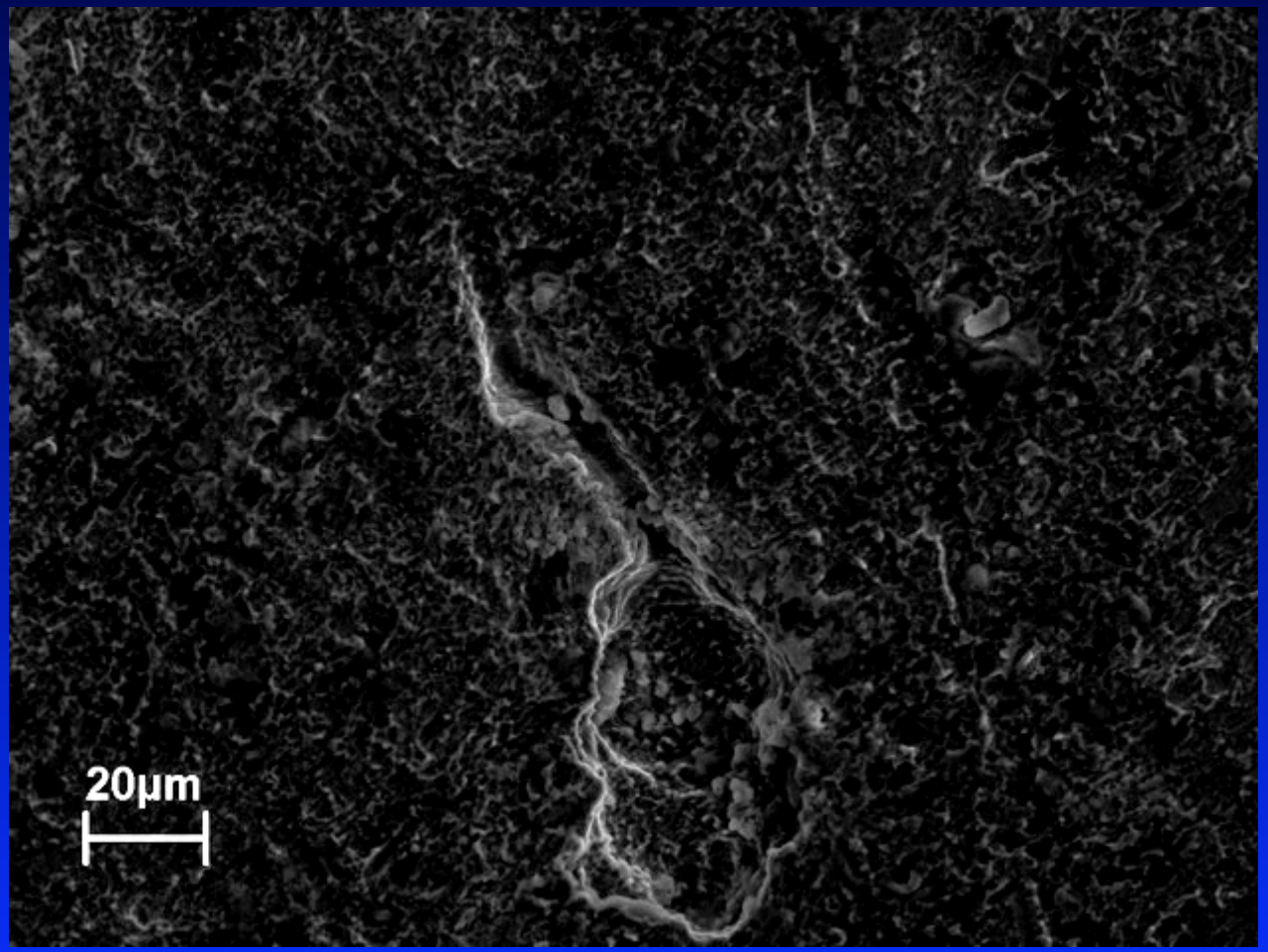
Comparison between the crack obtained in the ISSR tests on electrochemically pre-corroded specimens and the field NN-SCC cracks



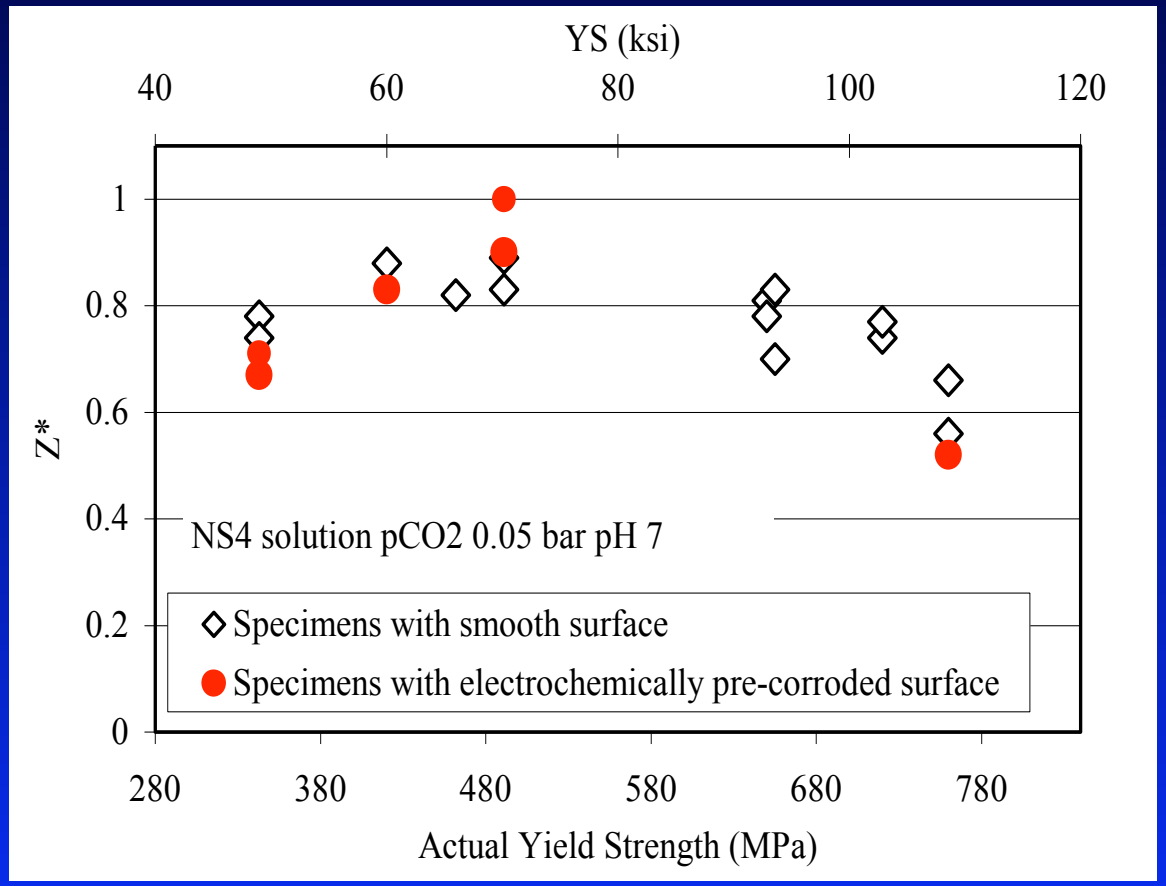
Field NN-SCC

ISSR specimen

Ripple loading tests on X100 specimen with electrochemically pre-corroded surface



Effect of steel on NN-SCC



Main conclusions

- Localized attacks can take place on pipeline steels in solution with high bicarbonate ions concentration
- The localized attacks acts as preferential sites for NN-SCC nucleation
- The NN-SCC cracks propagation is due to hydrogen embrittlement
- Hydrogen atomic inside the metal lattice is generated by the active corrosion of the steel