EFFECT OF RADIOLYSIS ON LONG-TERM CORROSION PRODUCTS FORMED ON LOW-ALLOY STEELS

Hugues Badet[1,2], Delphine Neff[1], Gérard Baldacchino[2], Jean-Paul Gallien[1], Jean-Philippe Renault[2], Philippe Dillmann[1].
[1]Laboratoire Archéomatériaux et Prévision de l'Altération (LAPA)
[2]Laboratoire de Radiolyse (LRad)
CNRS UMR 3299
CEA Saclay/ DSM/IRAMIS/SIS2M
Hugues.badet@cea.fr

OUTLINE

1

- INTRODUCTION:
  - Context
  - Approach and Methodology

2

- RESULTS
  - Irradiation Experiment
  - Simulation

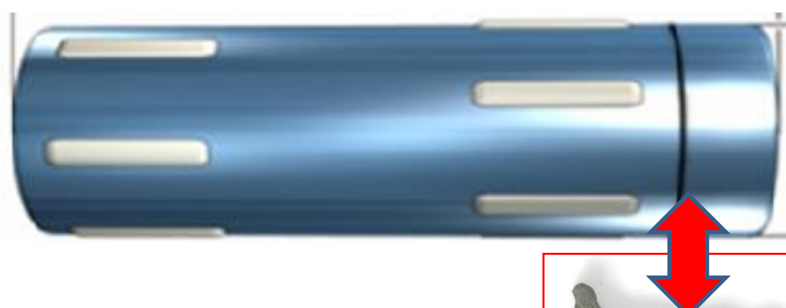
3

- CONCLUSION
- PERSPECTIVES

CONTEXT

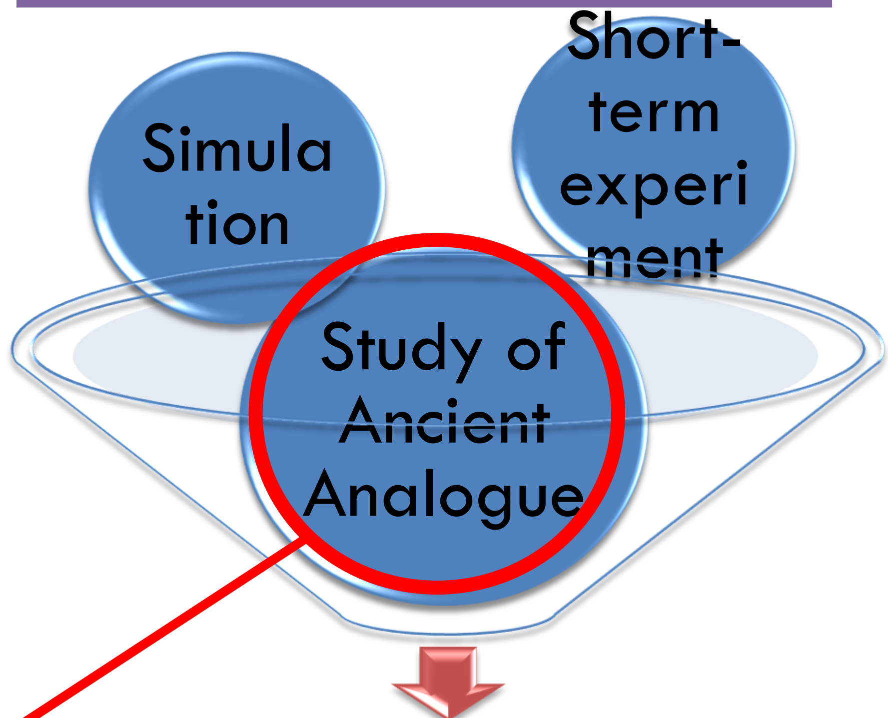
FRENCH NUCLEAR WASTE DISPOSAL

- Multibarrier system: steel pack and overpack for geological storage



Similar Materials

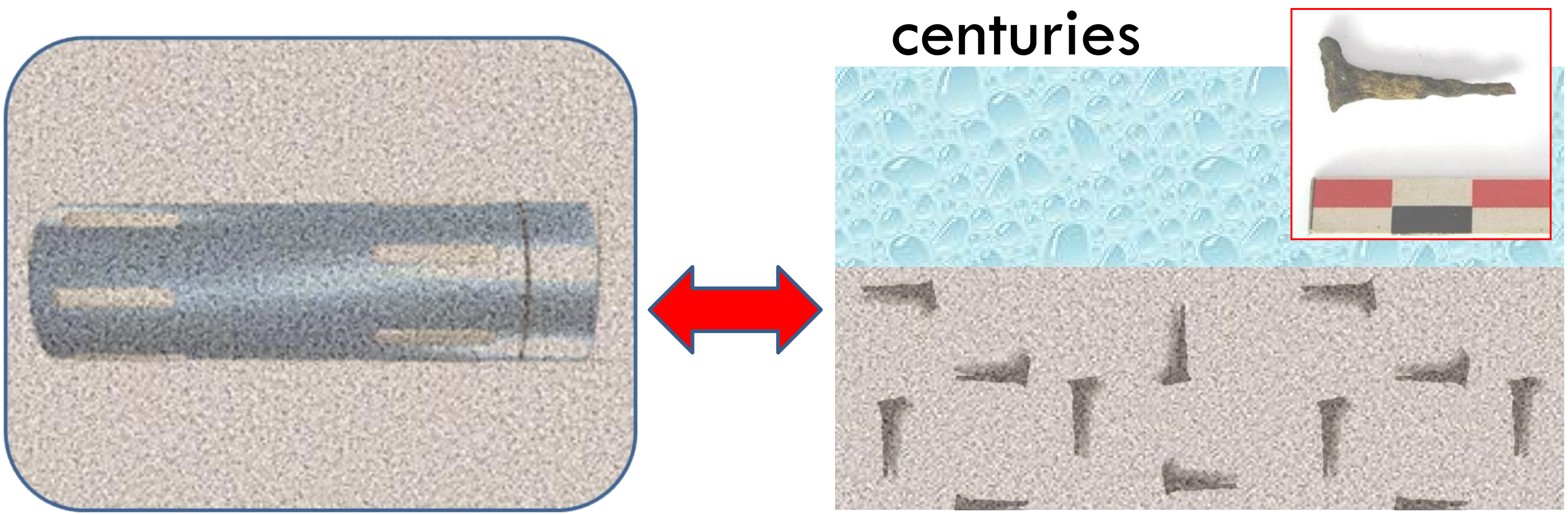
LONG-TERM PREDICTION MODEL



LONG-TERM BEHAVIOUR PREDICTION

ANCIENT ANALOGUE APPROACH

DISPOSAL MEDIA	ANALOGUE
Clay: Anoxic conditions in presence of various ions	Buried in a water saturated anoxic media during several centuries

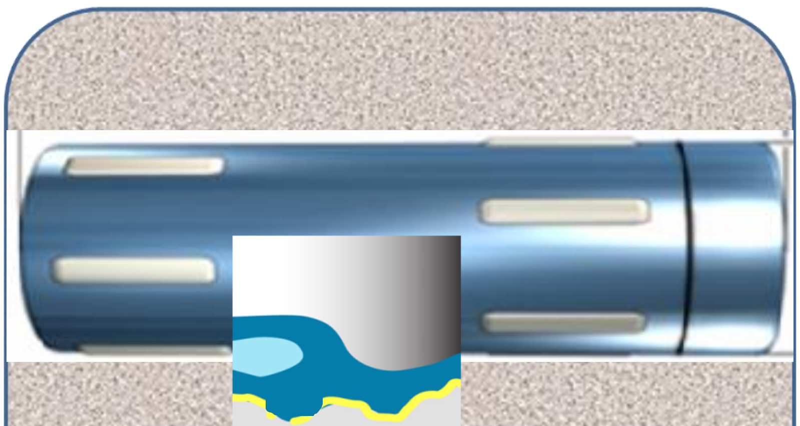


ANCIENT ANALOGUE APPROACH

LONG-TERM BEHAVIOUR PREDICTION

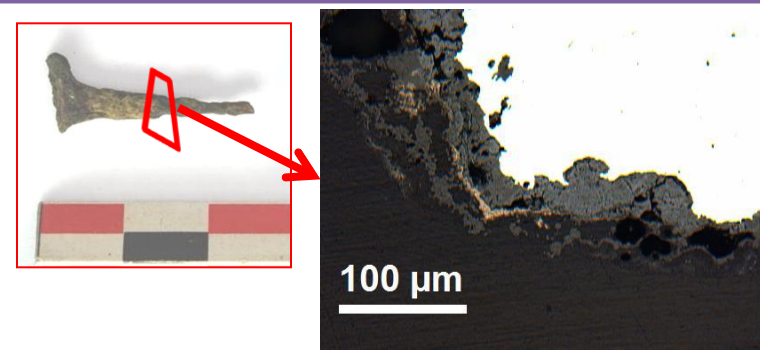
- Slow corrosion rate:

$\leq 1\,\mu m.year^{-1}$*

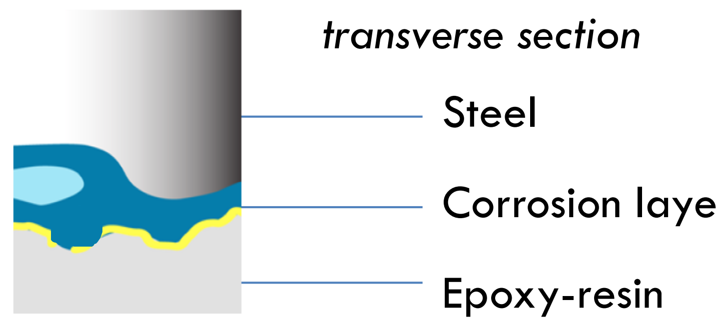


PROTECTIVE AND STABLE CORROSION LAYER COMPOSED BY FERROUS CARBONATE SPECIES AND OTHER OXIDES*

CHARACTERISATION OF THE CORROSION LAYER



Optical Micrography of transverse section



*Saheb et al. (2010). CEST**45(5): 381-387**

SCENARIO OF RADIOLYSIS

RADIOLYSIS OF WATER PHENOMENA

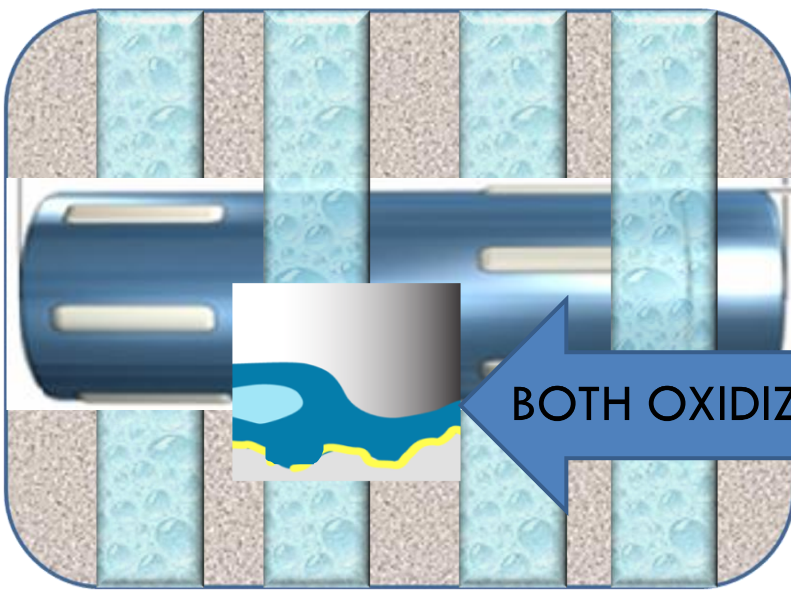
- Ionizing Radiation + Water Saturation

EFFECTS ON THE CORROSION SYSTEM?

- Water radiolysis:

$$H_2O \xrightarrow{\alpha,\ \beta,\ \gamma} \begin{array}{l} H_2O_2,\ H_2 \\ H^\circ,\ {}^\circ OH,\ HO_2^\circ \\ H_3O^+,\ OH^- \end{array}$$

ABOUT 1Gy.h^{-1}*



BOTH OXIDIZING AND REDUCTIVE SPECIES

IMPACT ON SYSTEMS WITH THICK CORROSION LAYERS?

*ANDRA (2001). Référentiel Matériaux Tome 4 La corrosion des matériaux métalliques, ANDRA.

METHODOLOGY

EXPERIMENTS

- Short-term data:
  - Irradiation of synthetized powders of pure phases
  - Steel coupon
- Irradiation of Archaeological ferrous objects
- Modelling

FACILITIES

- Gamma-ray irradiator (kGy range)
- Pulsed electron accelerator (LINAC type, up to 1 MGy)

FOCUS ON FERROUS CARBONATE PHASES WHICH ARE THE MAJOR SPECIES OF THE ANOXIC CORROSION PROFILE OF STEEL

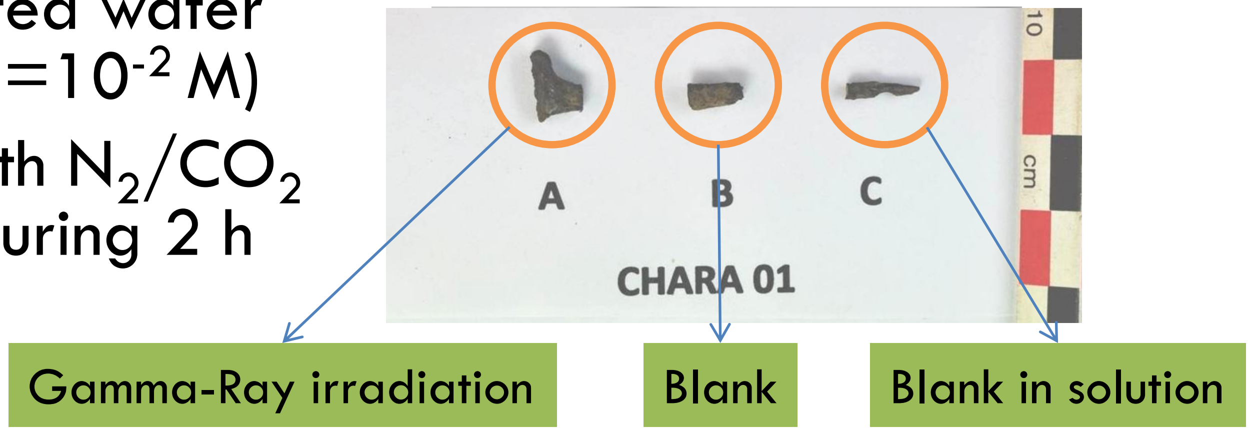
ARCHAEOLOGICAL OBJECT IRRADIATION

PROTOCOL

- Gamma-ray irradiation for 6 days
- Cumulated dose: 34 kGy
- Anoxic stainless steel cell containing 60 ml of carbonated water ($[HCO3^{-}]=10^{-2}$ M)
- Purge with N_2/CO_2 (95/5) during 2 h

OBJECT

- Medieval Nail (Charavines, FRANCE ca 1000AD)
- Buried in a water-satured anoxic media

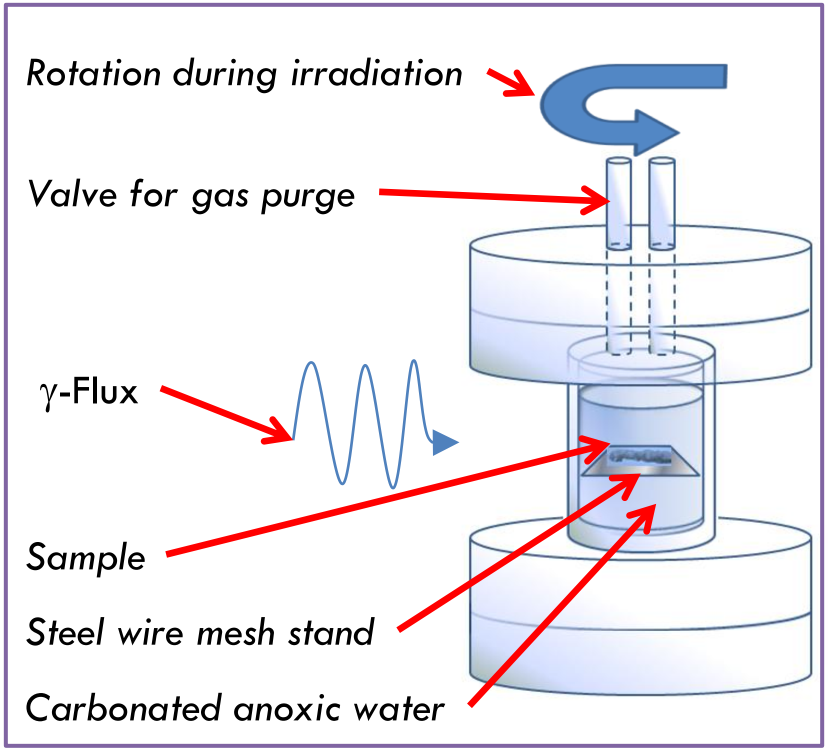


ARCHAEOLOGICAL OBJECT IRRADIATION

ON PURPOSE IRRADIATION CELL

Stainless steel cell components for γ-Irradiation

IRRADIATION WITHOUT:
-ORGANIC COMPONENT
-OXYGEN



ARCHAEOLOGICAL OBJECT IRRADIATION

ANALYSIS AT ALL STAGES OF THE EXPERIMENT

- Optical Microscopy (OM) (in an anoxic cell after irradiation)
- µRAMAN Spectroscopy (in an anoxic cell after irradiation)
- EDX-SEM

STAGES OF THE EXPERIMENT

Before irradiation

1
- Cutting with a diamond saw into 3 parts
- Polishing (Reference Analysis)

After irradiation

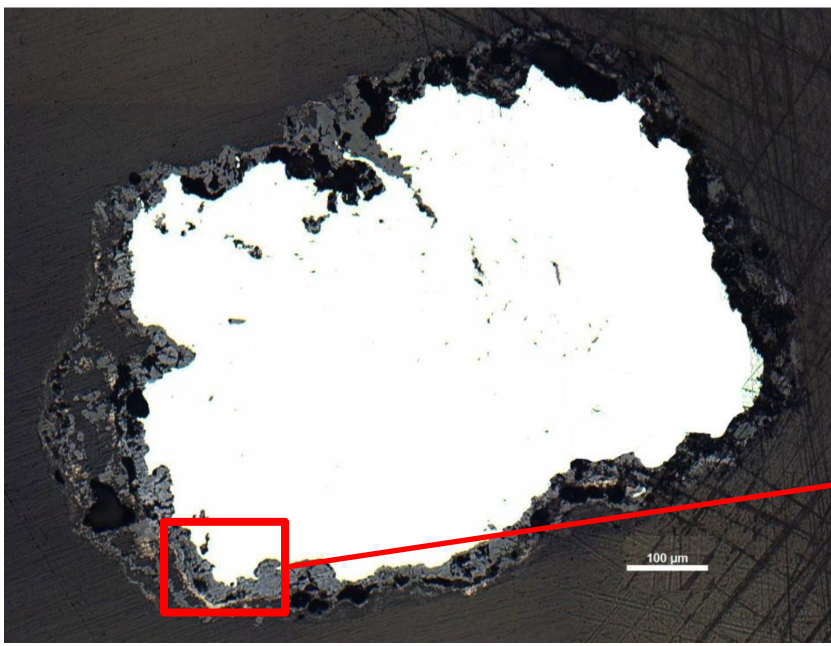
2
- Glovebox (N_2 atmosphere)
- No polishing (Surface analysis)

3
- Glovebox
- Epoxy-resin embedding
- Polishing (Section analysis)

BLANK SAMPLE (NON-IRRADIATED)

CHARACTERISATION ON TRANSVERSE SECTION BY OM

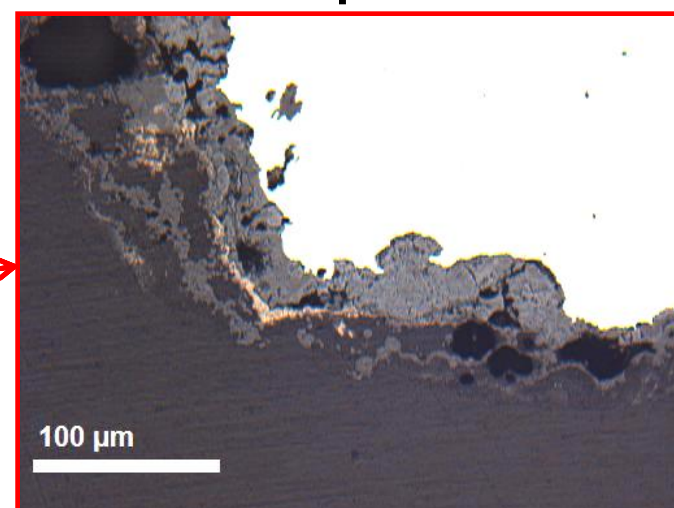
- OM



Optical Micrography of non irradiated- sample

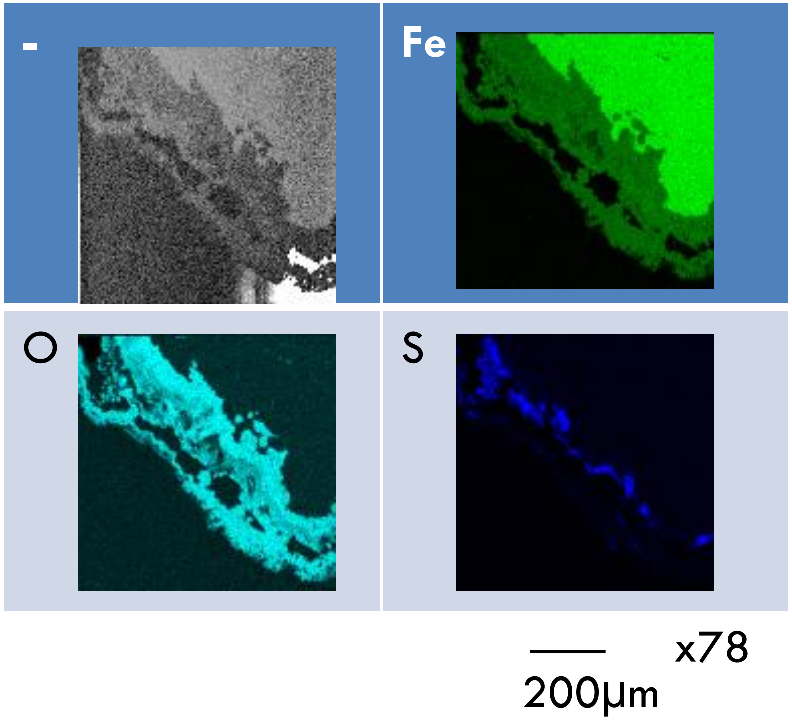
- Thickness of the corrosion layer:

  20 – 200 µm



BLANK SAMPLE (NON-IRRADIATED)

CHARACTERISATION ON TRANSVERSE SECTION BY EDX-SEM



Cartography by EDX-SEM of non-irradiated sample

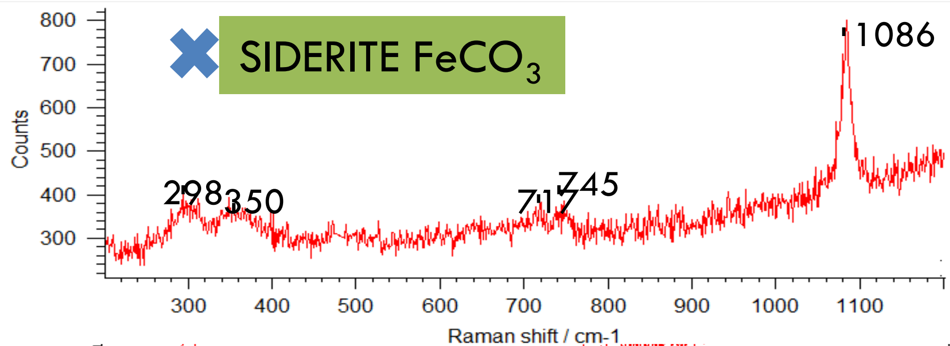
- Grey Layer:

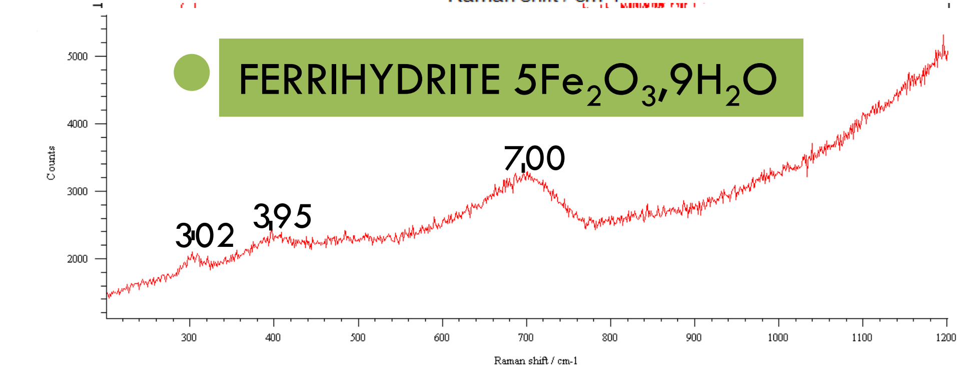
  Atomic ratio Fe/O= 0.25 to 0.42
- Islets of Fe_xS_y
- Calcium-iron substitution: Atomic ratio Ca/Fe= 0 to 0.10

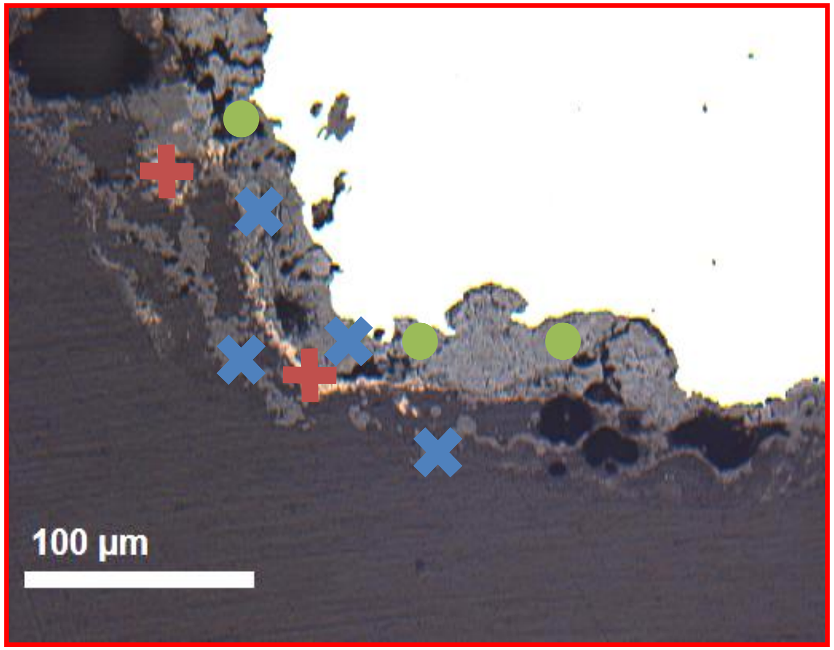
BLANK SAMPLE (NON-IRRADIATED)

CHARACTERISATION ON TRANSVERSE SECTION BY µRAMAN-S

- Spectrum:
  - Grey Layer:







SIDERITE $FeCO_3$

FERRIHYDRITE $5Fe_2O_3,9H_2O$

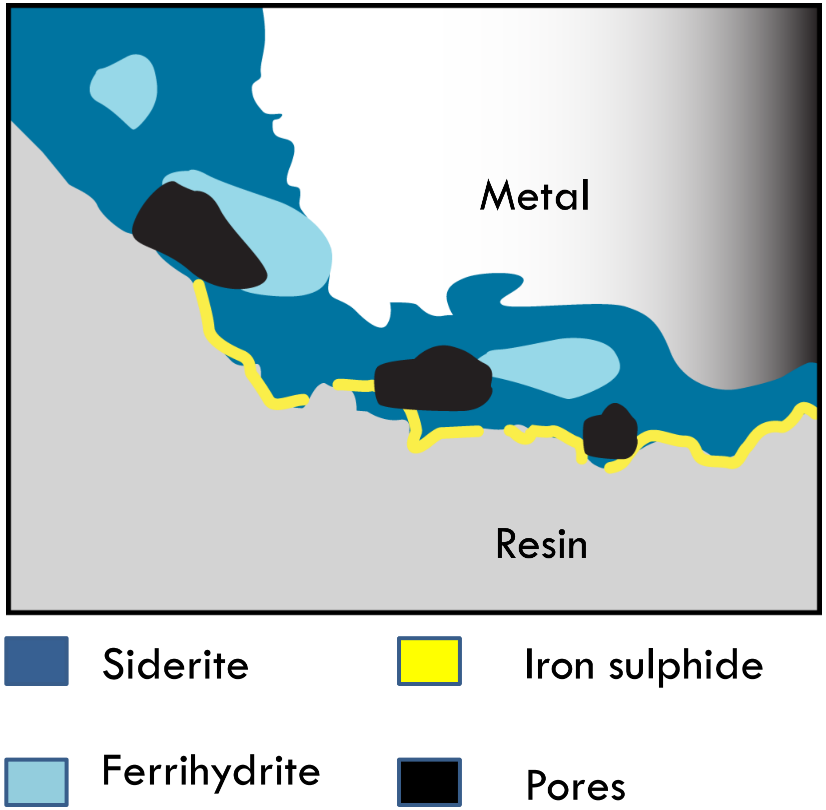
IRON SULFIDE n.i. Fe_xS_y

BLANK SAMPLE (NON IRRADIATED)

CHARACTERISATION ON TRANSVERSE SECTION

- Layer of Siderite and Ferrihydrite
- Discontinuous Fe_xS_y islets
- Micro pores
- Thickness of the corrosion layer: 20-200µm

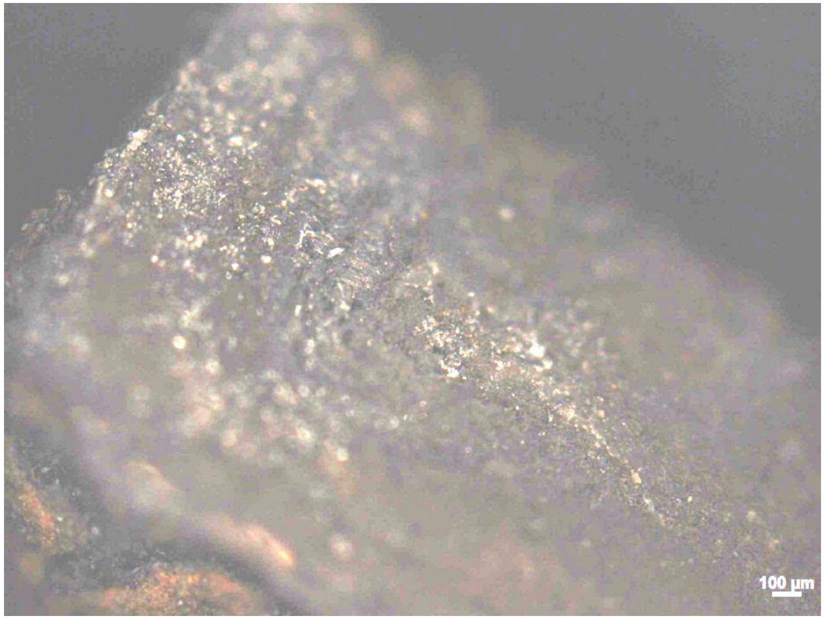
CORROSION LAYER PROFILE



IRRADIATED SAMPLE

CHARACTERISATION BY OM

- Before polishing:
  - Uniform dark layer grew up on the cut metallic surface

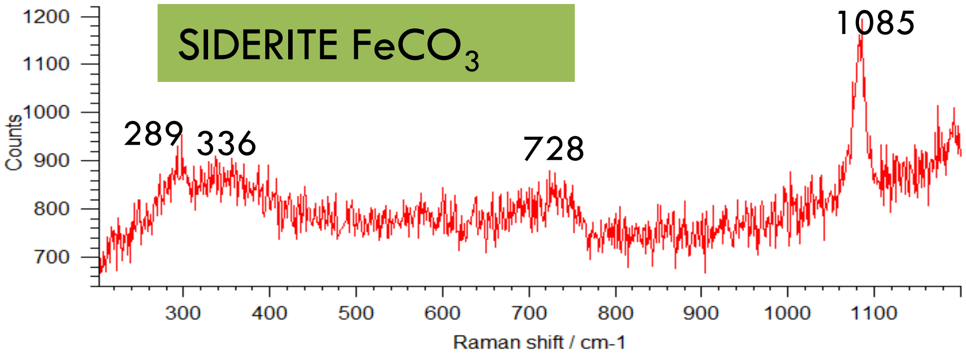


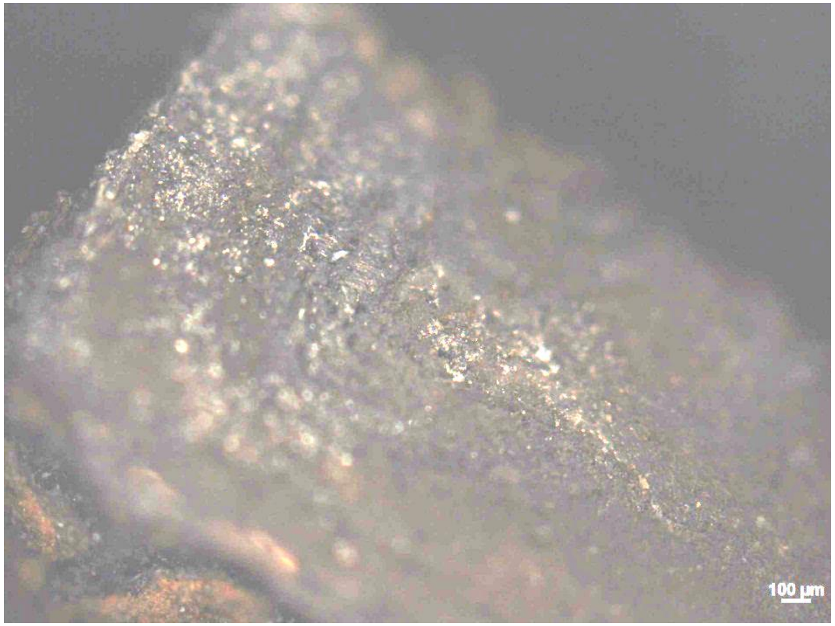
Optical Micrography of irradiated sample without polishing

IRRADIATED SAMPLE

CHARACTERISATION BY µRAMAN-S

- Unpolished stage:
  - Siderite grew up on the metallic surface



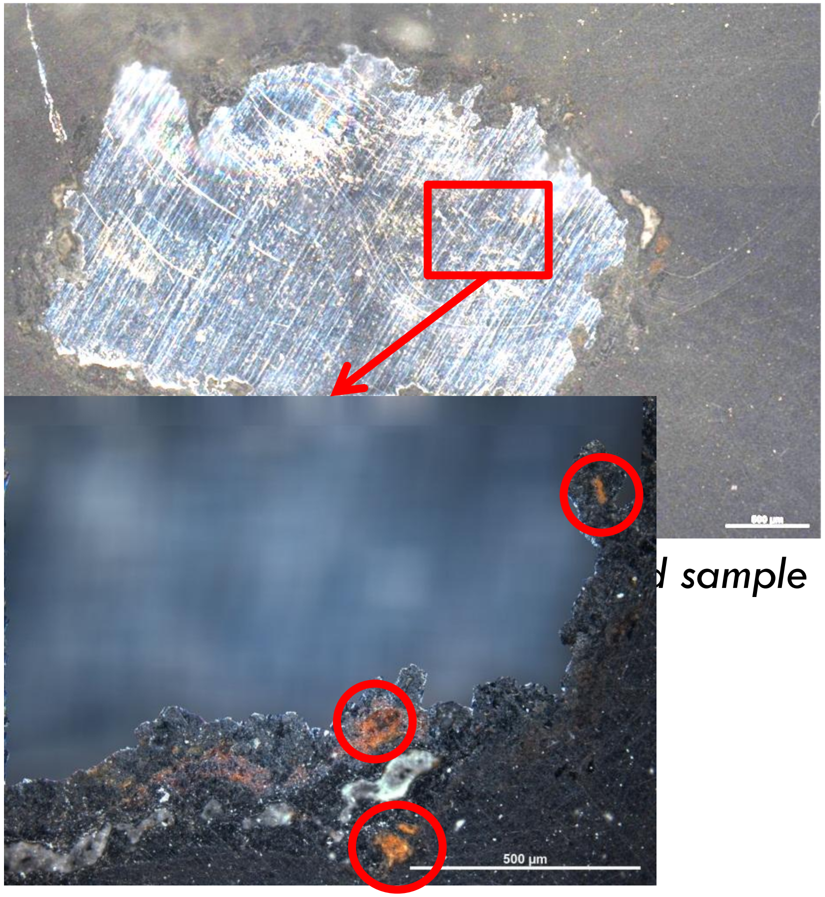


Optical Micrography of irradiated sample without polishing

IRRADIATED SAMPLE

CHARACTERISATION BY OM

- After polishing:
  - few orange species appear inside the corrosion layer
  - Same Thickness: 20-200µm

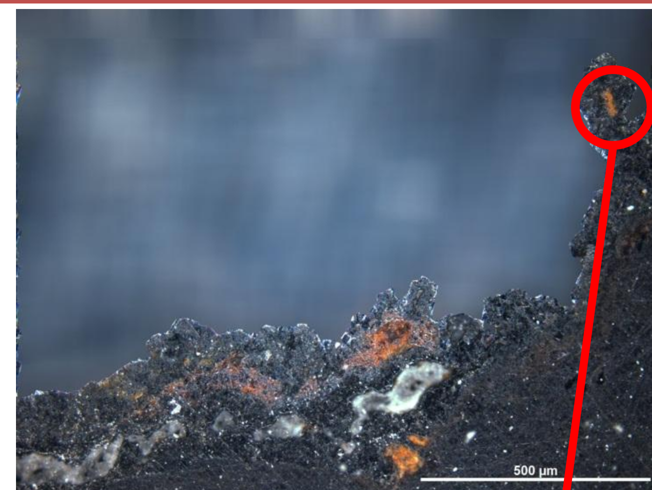


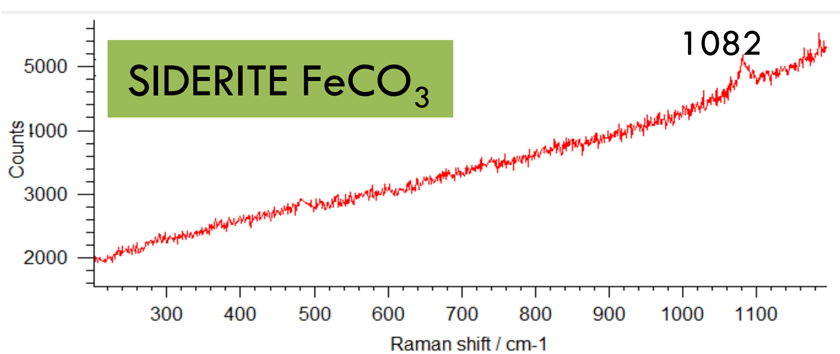
sample

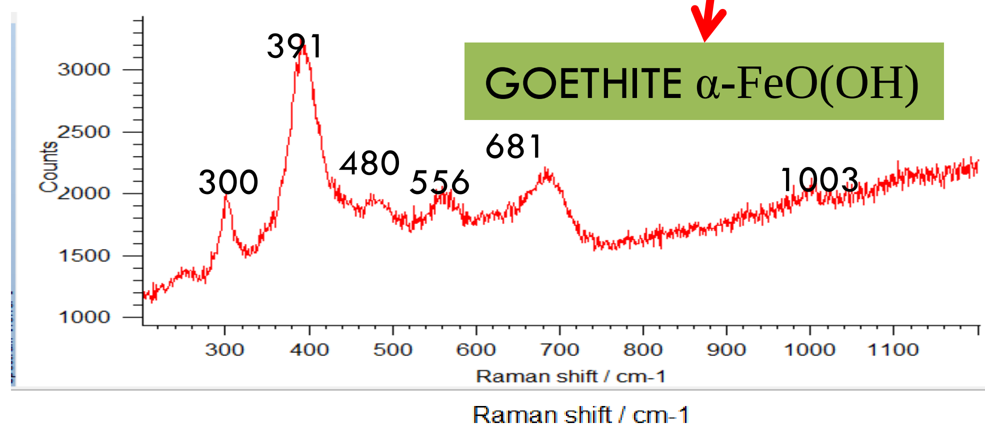
IRRADIATED SAMPLE

CHARACTERISATION ON TRANSVERSE SECTION BY µRAMAN-S

- Layer composition similar to blank sample
- Goethite spectra is detected once inside the corrosion layer





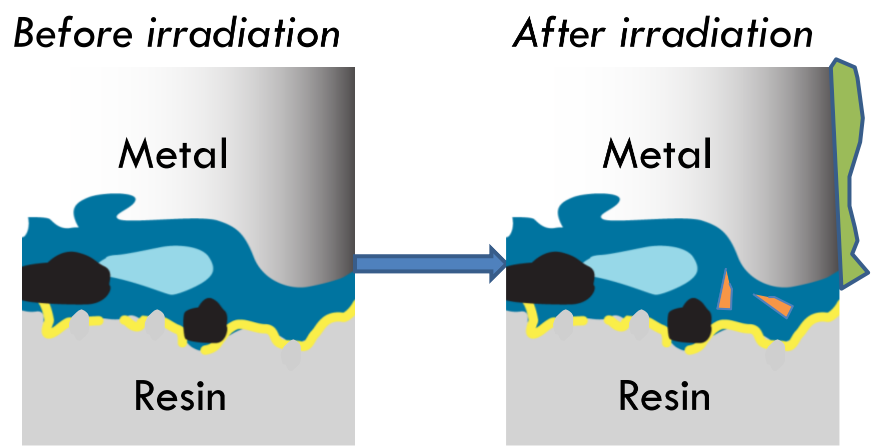


CONCLUSION

RESULTS

- Similar matrix composition
- Thickness of the corrosion layer: 20 – 200 µm
- Siderite layer grew up on the metallic surface
- Goethite detected

CORROSION PROFILE CHANGE



Siderite
Iron sulphide
Ferrihydrite
Pores
Goethite
New-formed Siderite

MODELING KINETICS DURING IRRADIATION

SOFTWARE

- Chemsimul Software
- Simulation of Kinetics of chemical systems with and without irradiation
- Solve differential equation system

SYSTEM OF INTEREST

- Water with carbonate ($[HCO_3^-]=10^{-2}$ M)
- pH=7
- T=25°C
- Time=136 h
- Total Dose=34 kGy
- Gamma-ray
- More than 100 reactions*

*NIST Database

MODELING KINETICS

GUIDELINE REACTIONS

- Water cleavage and recombining reaction:

(1) $H_2O \dashrightarrow H_2O_2, H_2$; H°, $^\circ OH$, HO_2°; H_3O^+, OH^-; e^-_{aq}

- Dioxygen production:

(2) $2H_2O_2 \dashrightarrow O_2 + 2H_2O$ ↔ (1)
$2O_2^{\circ -} \dashrightarrow O_2 + O_2^{2-}$

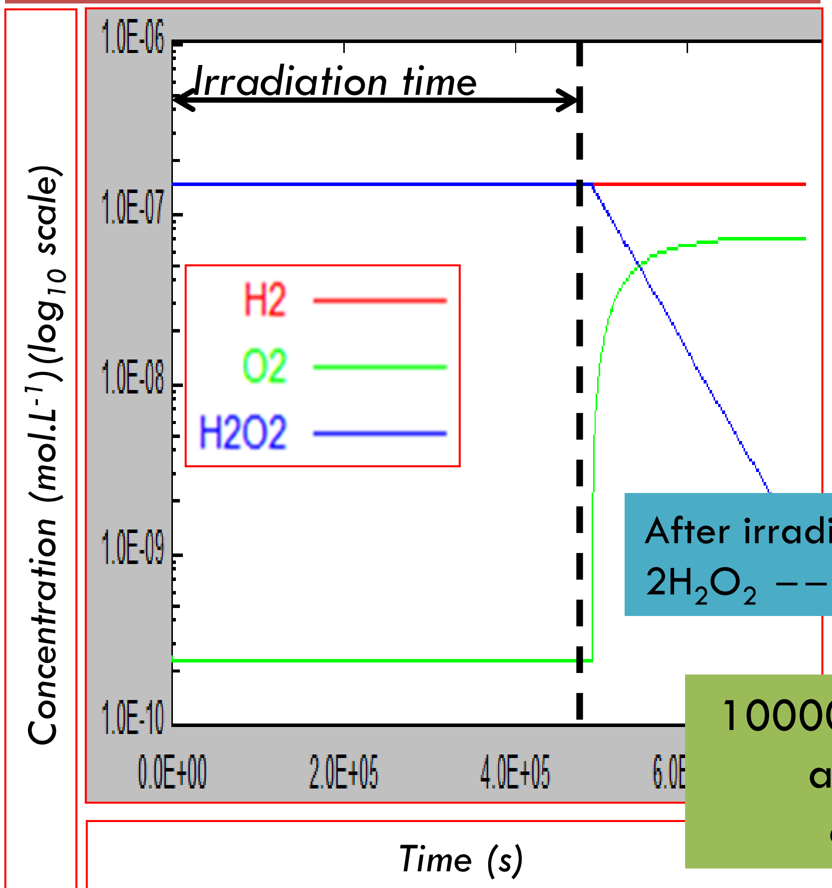
- Hydrogen carbonate cleavage reaction:

(3) $HCO_3^- + e^-_{aq} \dashrightarrow HCO_2^- + O^{-\circ} + H_2O$ ↔ (1)

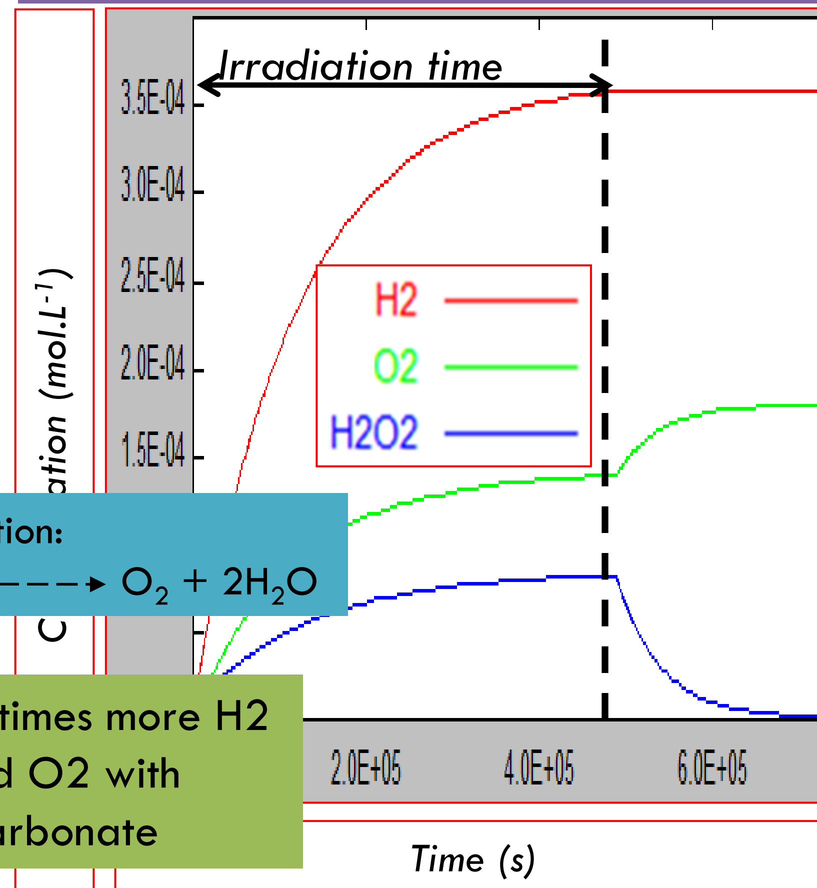
- Iron species will be included later (+80 reactions)

MODELING KINETICS: H_2, O_2 and H_2O_2

IRRADIATED PURE WATER



IRRADIATED CARBONATED WATER



After irradiation:
$2H_2O_2 \dashrightarrow O_2 + 2H_2O$

10000 times more H2 and O2 with carbonate

SIMULATION CONCLUSION

- Both oxidizing and reductive species appear during the irradiation
  - 10^3 times more molecular species accumulate with 10^{-2} M [HCO_3^-] than with pure water
- [H_2]=about 2[O_2] → Balance verified.
- pH increases up to 8 with carbonate media
- Iron species will react with these species
- Potentiel of solution have to be modelled and measured

CONCLUSION

- Experimental setup is validated by this first set of results
- Solution composition will be measured in further experiments
- Simulation reveals a complex modification of the solution – to be continued
- Effect of radiolysis of water on ancient ferrous system could have a potentiel impact on the corrosion layer.

WHAT WE PLAN NEXT

SHORT-TERM LAB EXPERIMENT	LONG-TERM STUDIES	MODELLING
• Estimation of first stage corrosion rate with Electric Impedance Spectroscopy and micro-Gas Chromatography • Irradiation of wet synthetized powder and steel coupon	• Study of unirradiated system in water • Pulsed electron experiment (High-dose) • Reproductibility of first results • Electrochemical solution measurment (pH, Eh)	• Addition of Iron species system in CHEMSIMUL • Thermodynamic studies with CHESS software

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- F. Saillant (LEEL)
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