Stabilization of corroded lead artefacts in museums:
Insights into the effects of electrolytic reduction as a treatment

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    1. Chemical changes: SR-XRD and XPS
    2. Morphological changes: Neutron Tomography
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Example of ancient lead coin

1a. Corrosion of lead objects in general

Lead metal generally corrodes very slowly

↓

This is due to passivation of the surface

↓

Most lead objects were in a good state when found

↓

Lead objects were placed display cabinets

1b. Corrosion of lead objects in display cases

Materials which built up the display cases can provoke a corrosive environment inside the cabinet

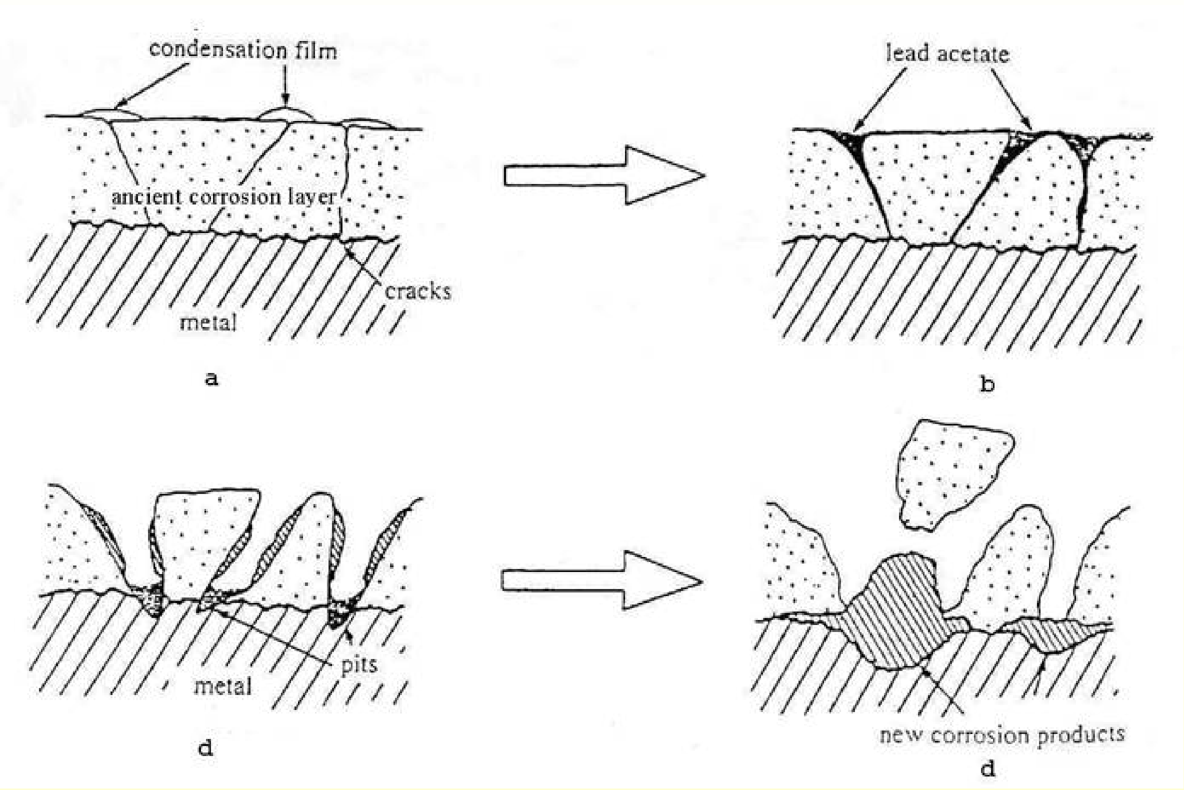
- emission of organic compounds of glues
- degradation of wood

Very aggressive compound towards lead

ACETIC ACID

Example of a display case

2. Active corrosion of lead with acetic acid



$Pb + 2\ CH_3COOH + ½\ O_2 \rightarrow Pb(CH_3COO)_2 + H_2O$

$3\ Pb(CH_3COO)_2 + 2\ CO_2 + 4\ H_2O \rightarrow 2\ PbCO_3.Pb(OH)_2 + 6\ CH_3COOH$

3. Electrolytic reduction treatment

The corroded object is made the working electrode in an electrochemical cell

At a constant potential, a reductive current converts the corrosion products in metallic lead

$PbCO_3 + 2e^- \rightarrow Pb + CO_3^{2-}$

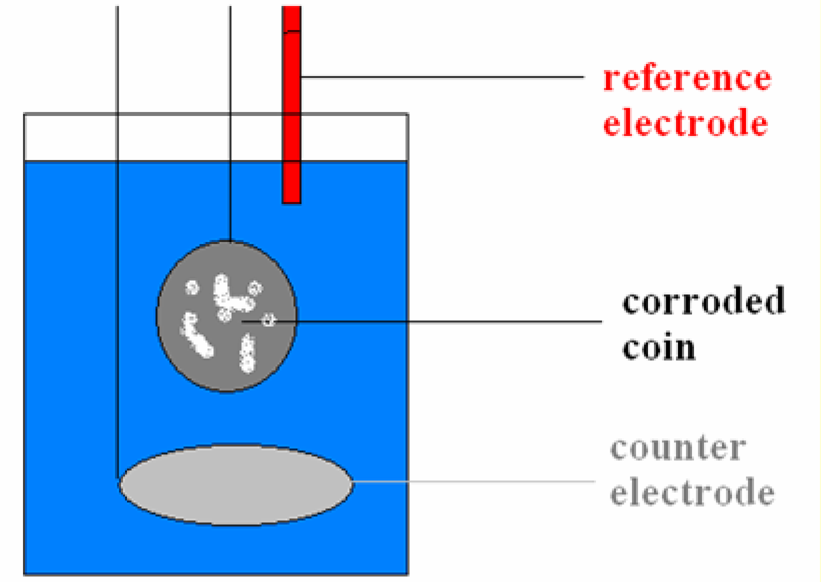
$PbO + + H_2O + 2e^- \rightarrow Pb + 2\ OH^-$

$Pb(OH)_2 + 2\ H^+ + 2e^- \rightarrow Pb + 2\ H_2O$

STABILIZATION

OF THE OBJECT!!!

Electrochemical cell connected to potentiostat



4. Problems concerning this treatment: no full understanding of the electrolytic reduction process

- Morphological changes, chemical changes, surface appearance

- Strategy
  - Real museum objects → not acceptable
  - Less valuable corroded lead objects
    - Coupons from Centre National des Arts et Métiers

Model of a weaving machine to keep tension on the twinning threads

5. Experimental work

A. Corroded lead objects (CNAM)

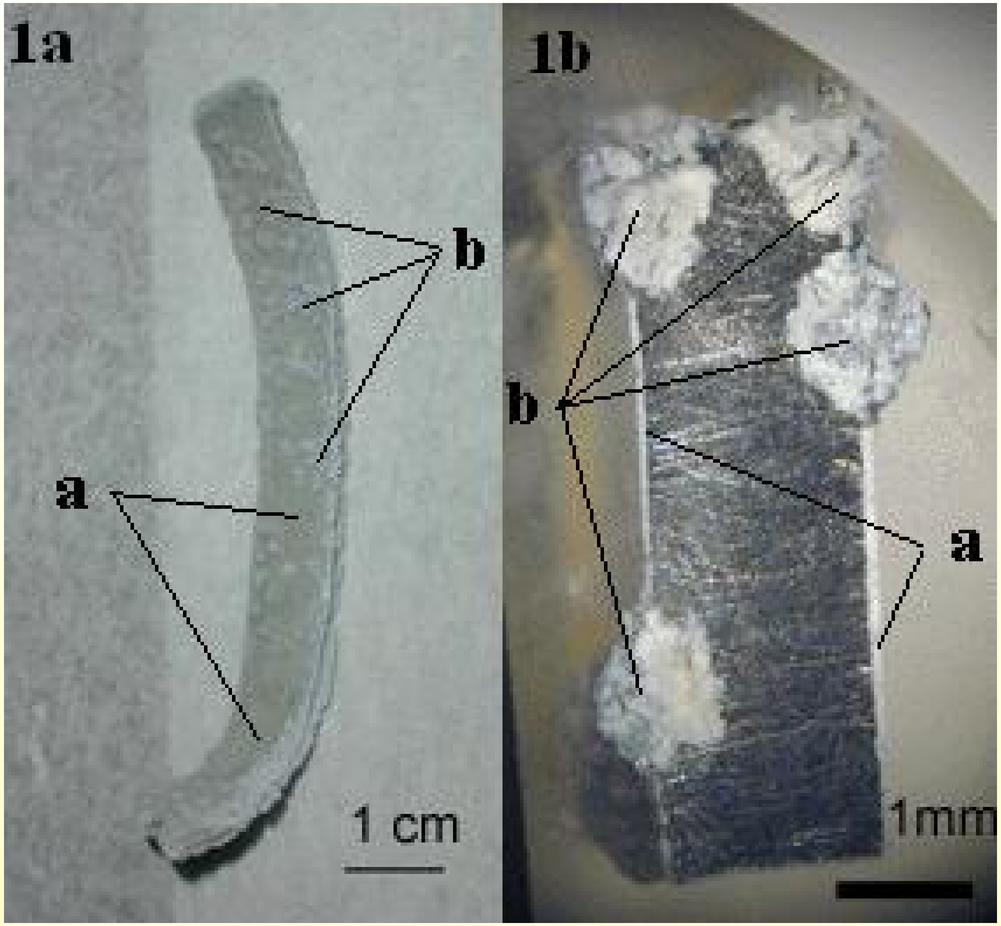
B. Photographical image before and after reduction

C. Chemical changes induced by reduction process (SR-XRD, XPS)

D. Surface appearance

E. Morphological changes (neutron tomography)

A. Corroded lead objects: coupons from Musée des Arts et Métiers (Paris)



1a Coupon 1b Cross section

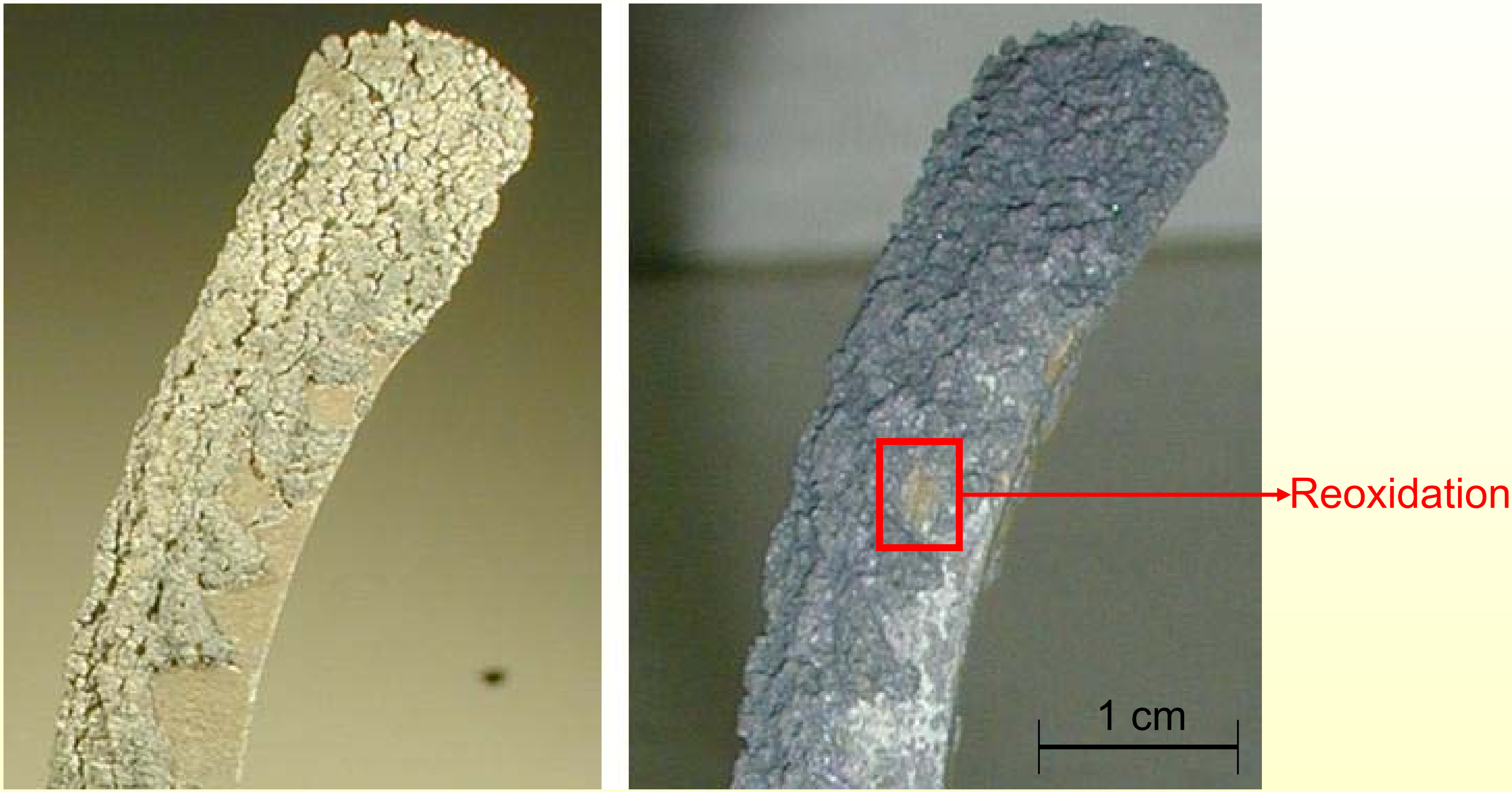
Coupon = corroded lead piece from museum object

Two kinds of corrosion

a. thin corrosion layer which follows the alignment of the bare metal very well (UNIFORM CORROSION)

b. thick porous patches which deform the coupon dramatically (PITTING CORROSION)

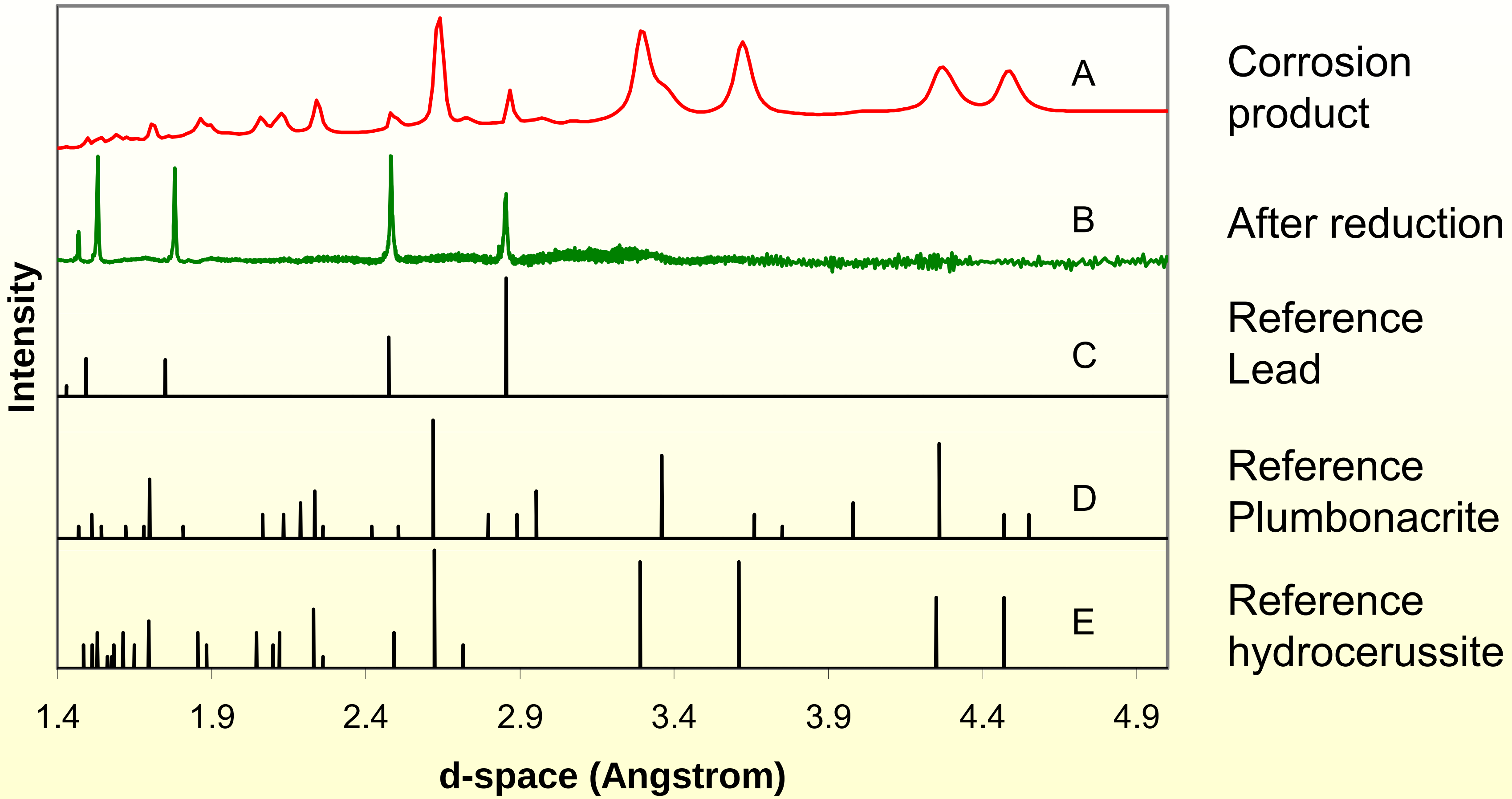
B. Photograpical image before and after reduction treatment



Before reduction

After reduction

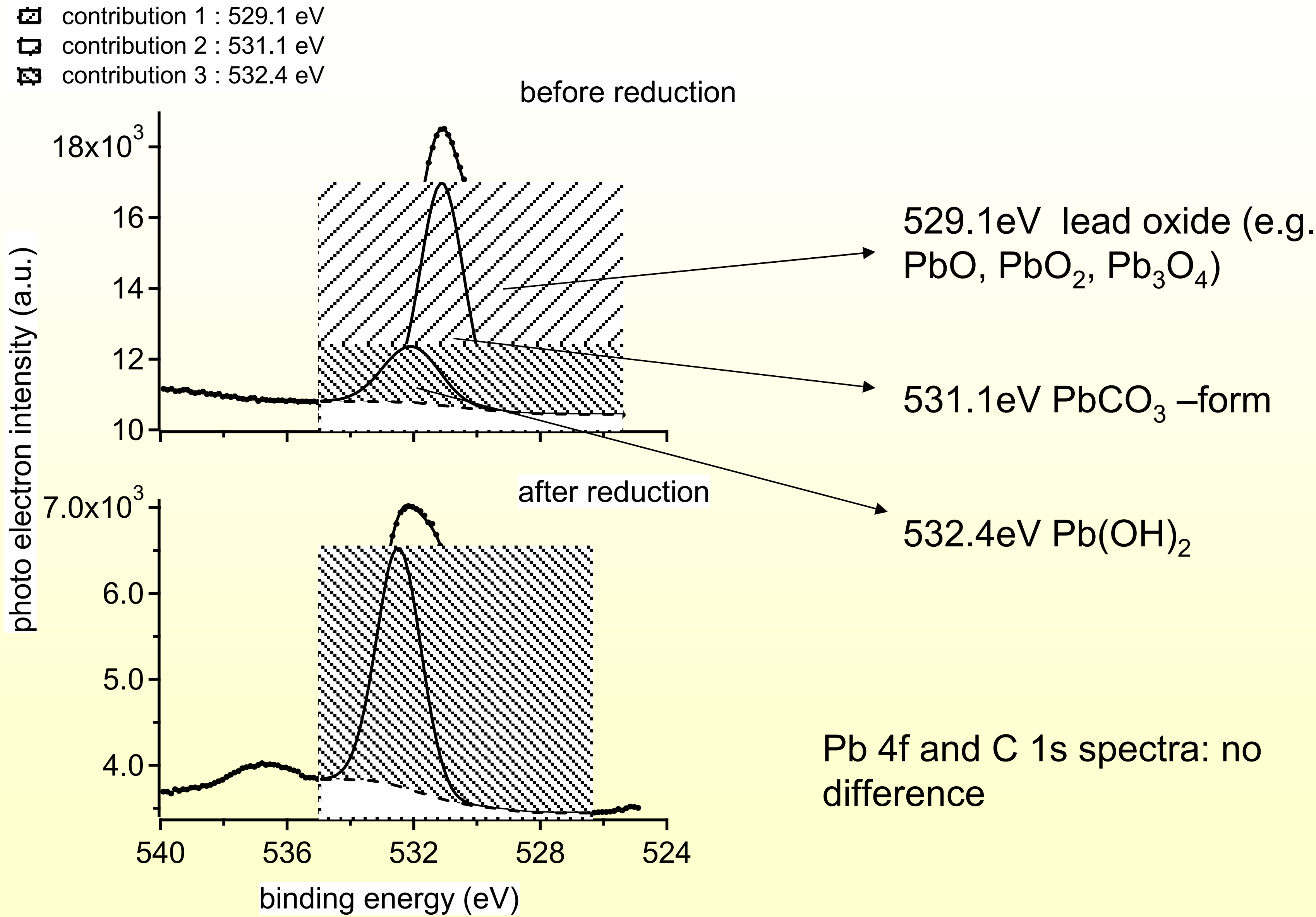
C. Chemical changes corrosion layer (SR-XRD)



Two kinds of corrosion consist both of

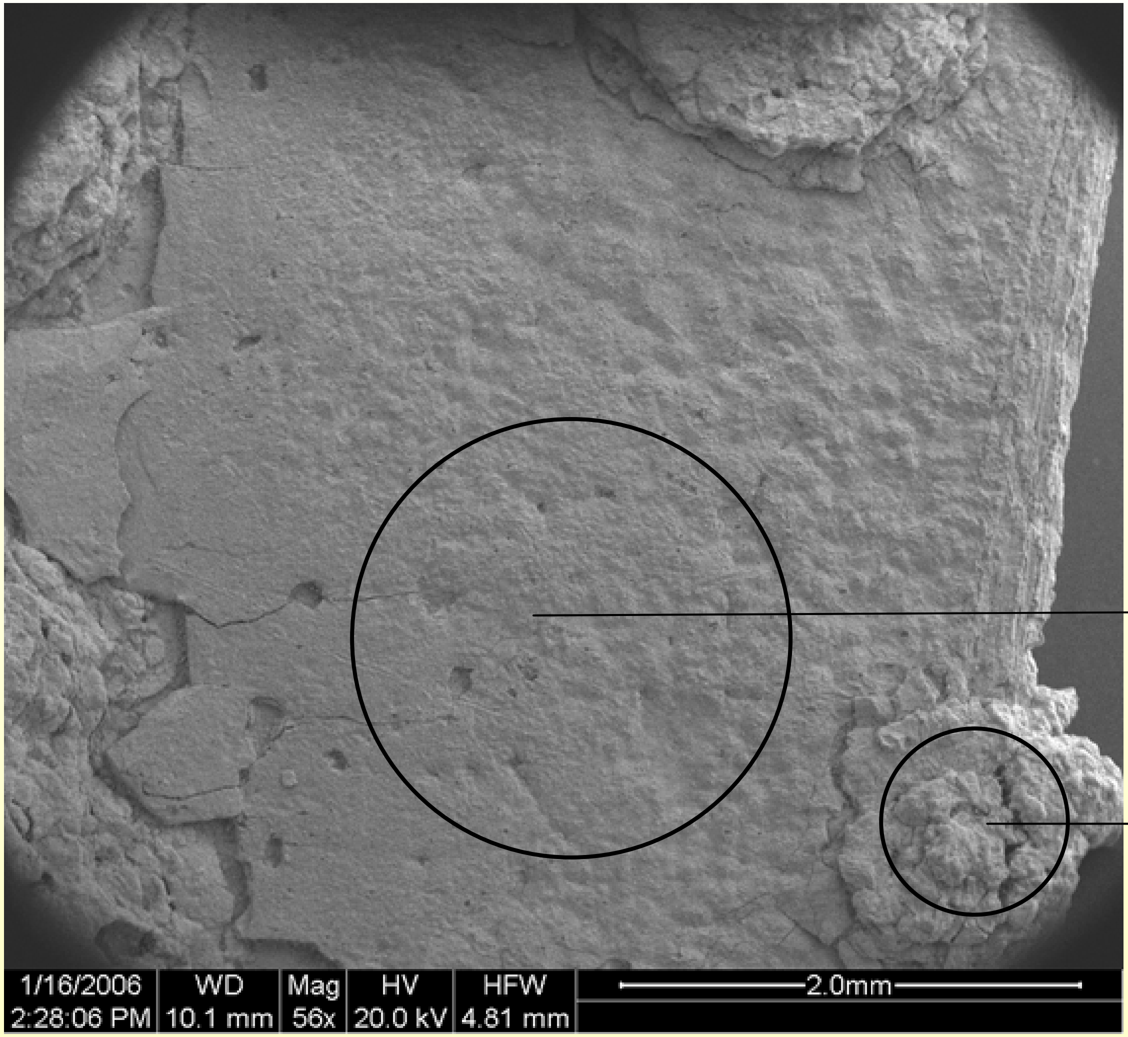
- Hydrocerussite $2\ PbCO_3.Pb(OH)_2$
- Plumbonacrite $6\ PbCO_3.3PbO.Pb(OH)_2$

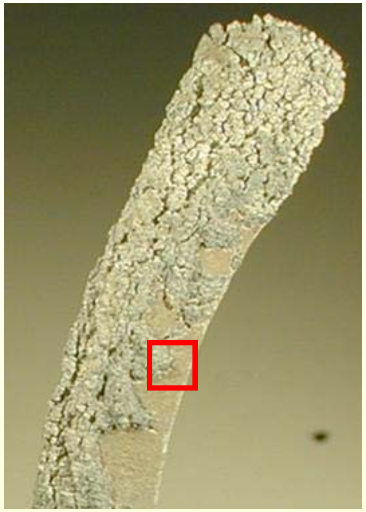
C. XPS measurements (O 1s spectra)



Pb 4f and C 1s spectra: no difference

D. Surface appearance

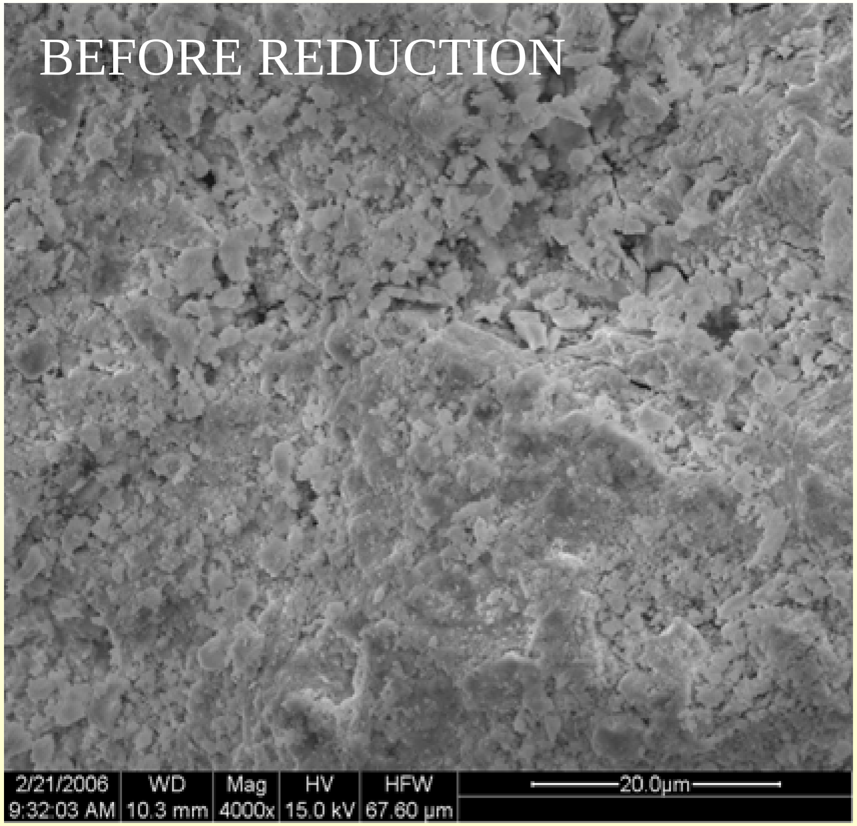


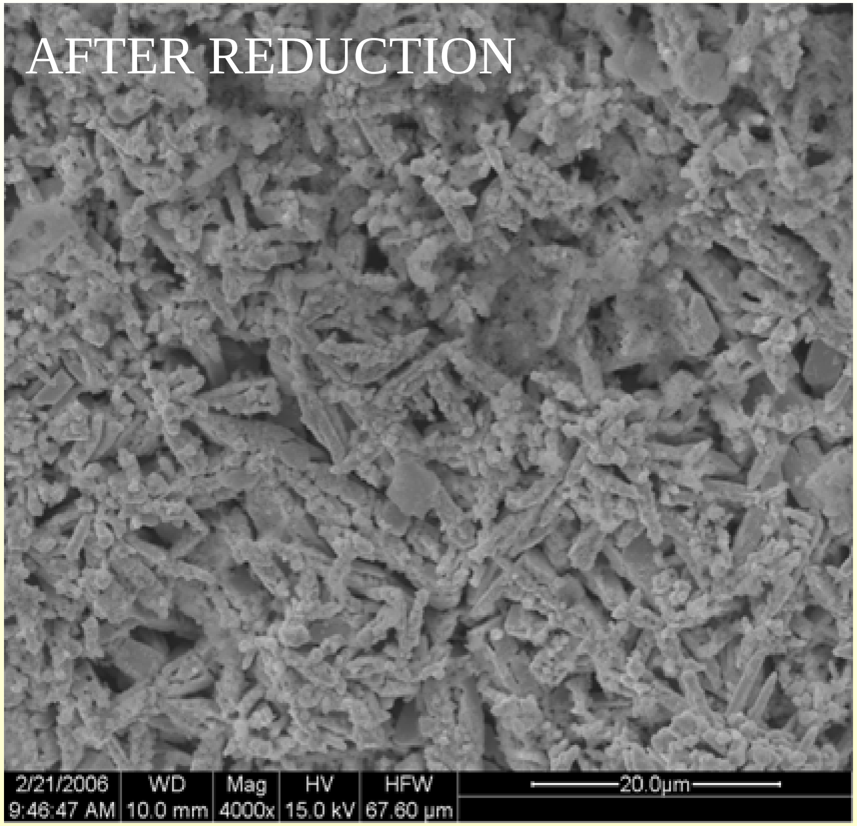


Uniform
corrosion structures

Volumineous
Corrosion structures

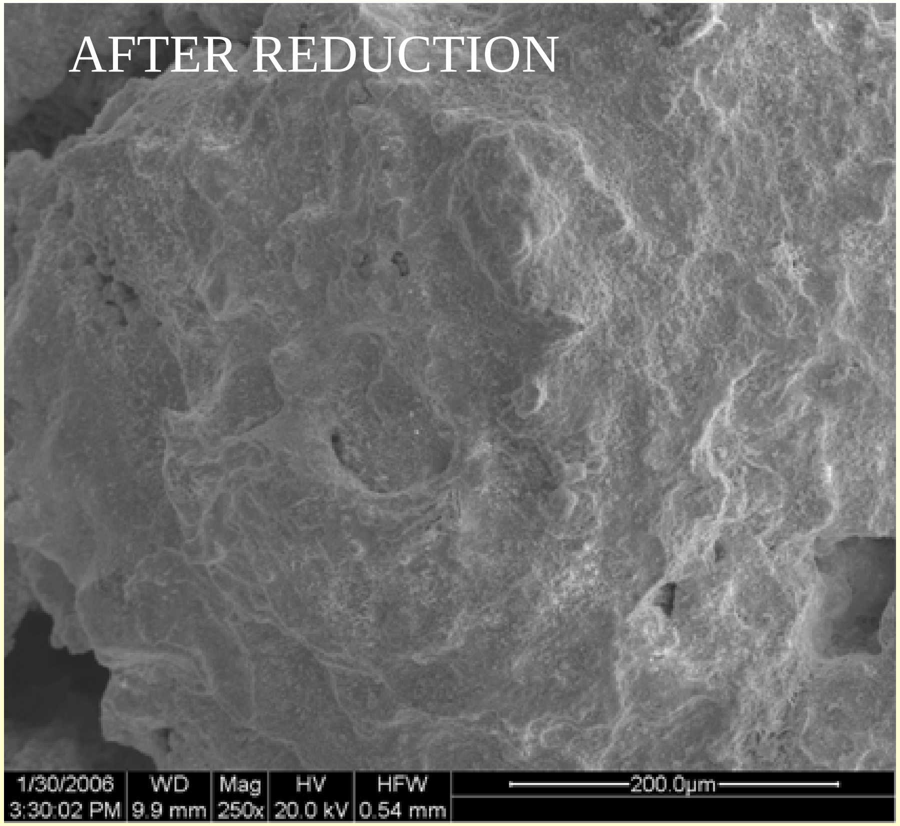
D: Characterization of uniform corrosion





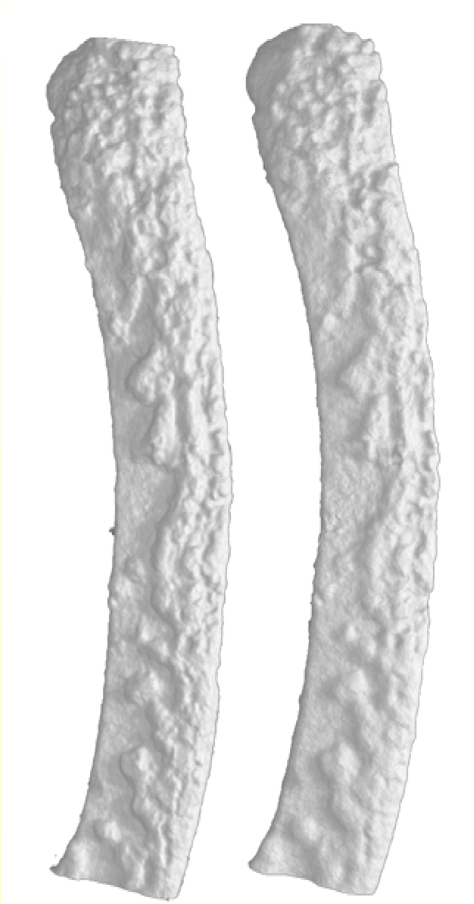
Large specific surface finish → Reoxidation

D: Characterization of pitting corrosion

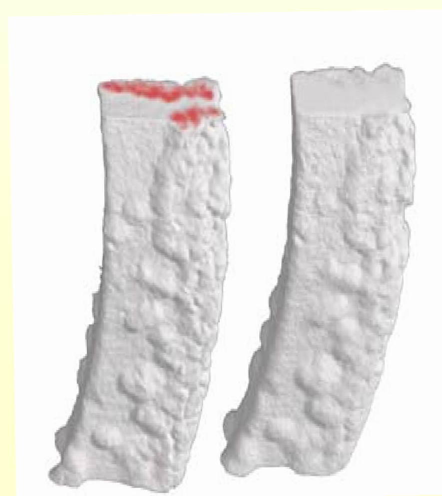


Volume reduction
Profile still present

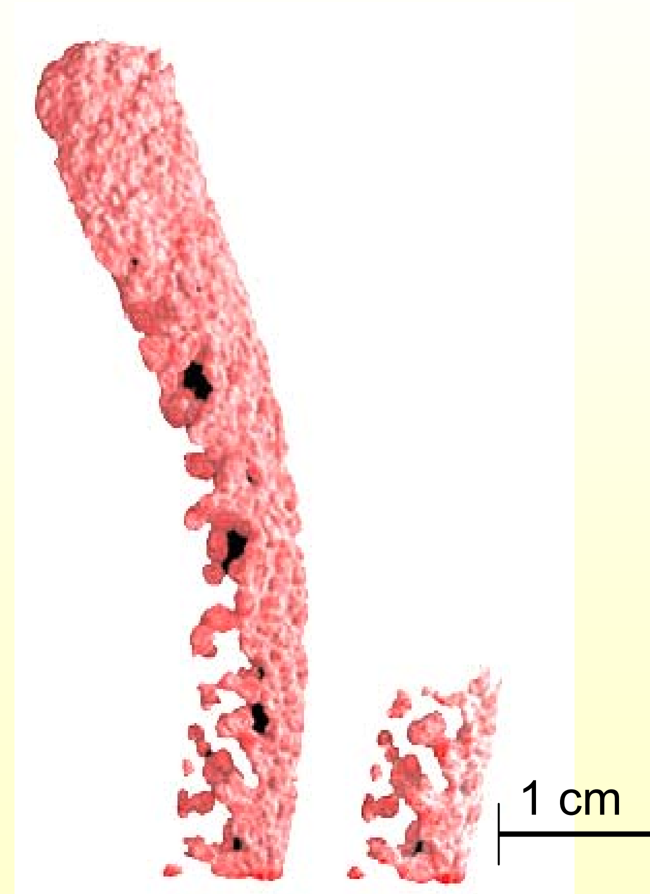
E. Morphological changes (NT)



Surface appearance



Cross section



Corrosion products

6. Conclusions

- Electrolytic reduction
  - Reduction of the corrosion structures to metallic lead
  - Surface contains still some oxides and hydroxides, probably due to reoxidation during drying
  - Surface appearance before and after reduction is different depending corrosion structure
    - Uniform: increase in specific area
    - Pitting: volume reduction
- Better to prevent than to stabilize!

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