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A multi-disciplinary materials study as a contribution to evaluate degradation issues of monuments and archaeological sites towards their preservation.

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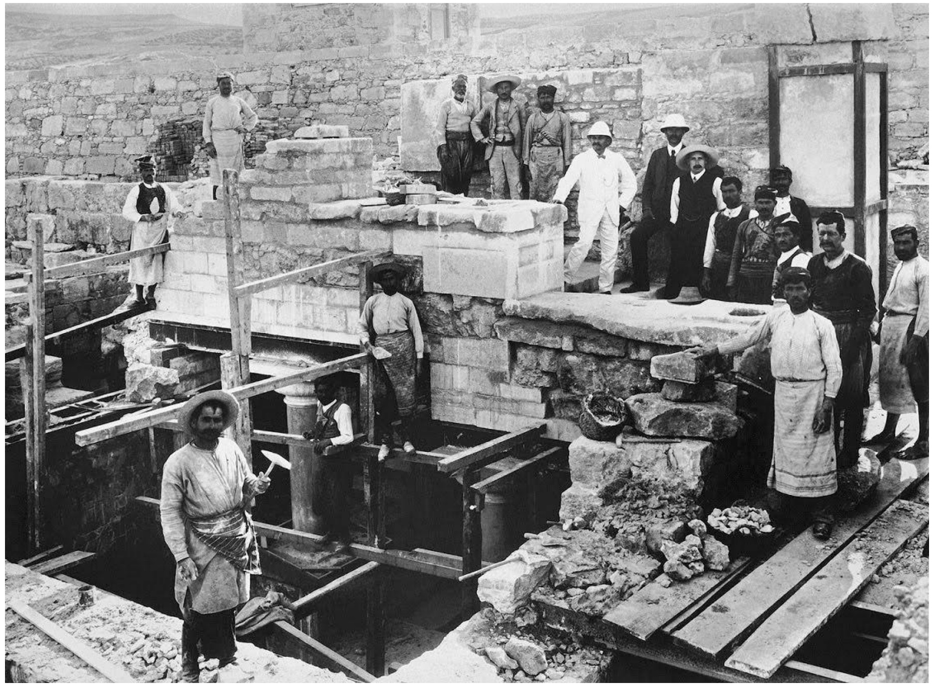

The Palace of Knossos built around 1900 - 1700 BC, can be approximated to a square of about 200m side. Most part of the monument is set up without foundation, on the marly limestone (kouskouras) terrain, or on Neolithic layers.

The Palace was excavated partly by M. Kalokairinos and fully by sir A. Evans between 1900 and 1905. The need for preservation and restoration of the monument was obvious for Sir A. Evans from the first years of the excavation. Since 1905, most of its parts were sheltered, and in some cases restored. With the restoration Sir A. Evans reconstructed entire floors of the monument with **reinforced concrete,** stone masonry and **iron**.

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The detrimental effects of the use of cement and the resulting strategy of the conservation of the restoration (“restauro di restauro”) found a dramatic paradigm in efforts to **conserve Evans’ 1920s restoration of the Knossos Palace in Crete**.

Cement mortars, apart from altering the aesthetic characteristics of the monument, lead to structural and surface failures due to the different chemical and mechanical properties of cement and historical building materials
Deterioration of concrete is particularly visible and widespread at the positions where ancient architectural parts of gypsum are included in the concrete structure.

It is most likely due **to moisture and possibly aggressive agents generally present in the atmosphere** (e.g. carbon dioxide, sulfur dioxide), **as well as to the excessive climate forcing** (strong exposure to rainfalls and solar radiations). In these parts there is **a diffused oxidation of rebars, due to the presence of humidity, efflorescence and local spalling of external layers of material**.

Materials weathering state @ Knossos Palace, in Heraklion

- ✓ **the degradation of selenite (mineral gypsum).**
- ✓ **salt accumulation and efflorescence**
- ✓ **dark encrustations and other external accumulations**
- ✓ **degradation of reinforced concrete** (used by for restoration)

Deterioration of concrete in reinforced concrete elements built during the restoration by Sir Arthur Evans .

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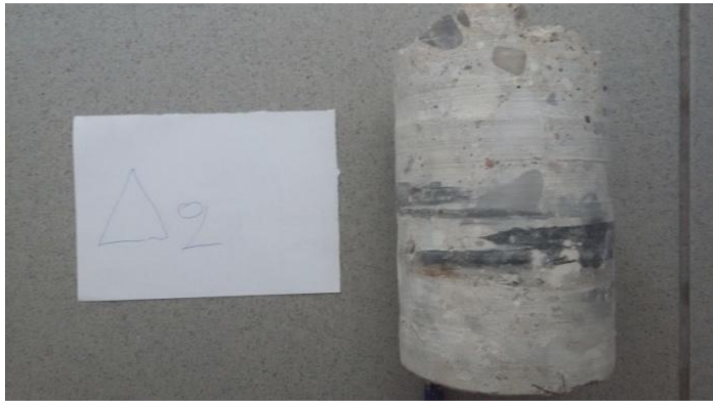
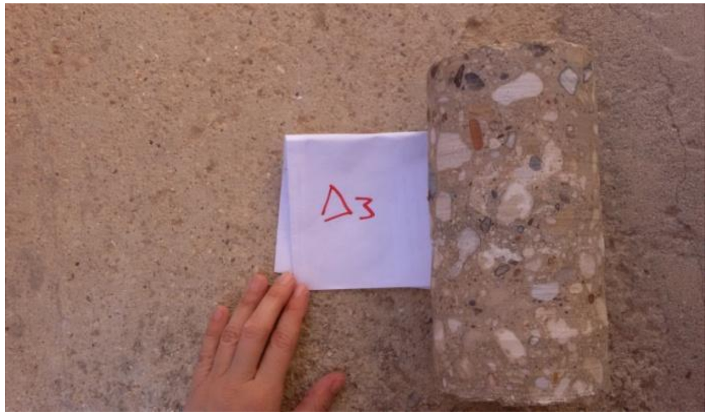
Sample code number D1
Knossos Palace, "Piano Nobile“



Sample code number D2
Knossos Palace, Eastern Wing, "King's Megaron"



Sample code number D 3
Knossos Palace, "East Wing", "Room of the Wooden Posts

Sample code number D 4
Knossos Palace, "Magazine of the Giant Pithoi"

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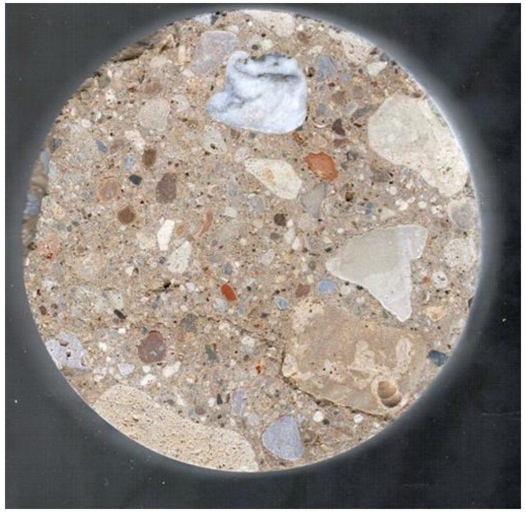
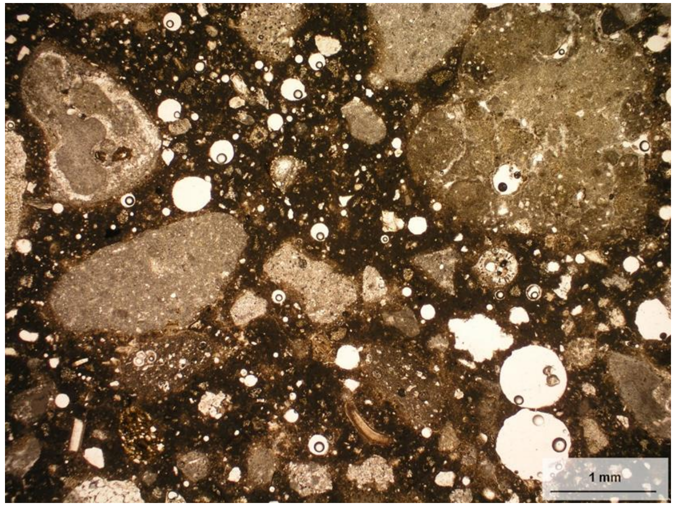
The chemical composition of the concrete core-drillings, called D1, D2, D3 and D4 indicate that the main components are **calcite ($CaCO_3$) and quartz (SiO_2)** and this indication is confirmed by the petrographic analysis**.**



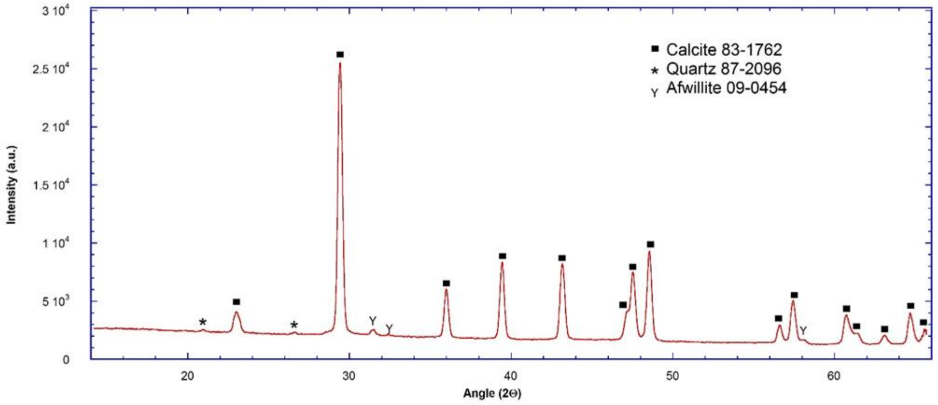
Sample D3



Sample D3 in plane-polarized light.

The aggregate is composed of lithic fragments, monocrystalline grains and diffuse calcium carbonate remains.

XRD of sample D3



XRD revealed, in addition to the presence of calcite and quartz, **the diffraction pattern of afwillite ($Ca_3Si_2O_4(OH)_6$) a calcium silicate hydrate characteristics of Portland cement**

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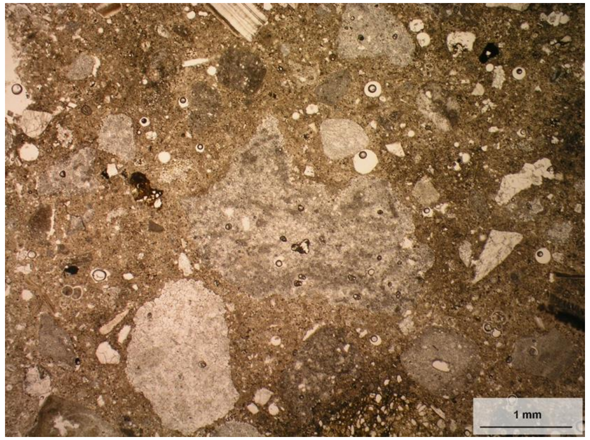
Sample D4

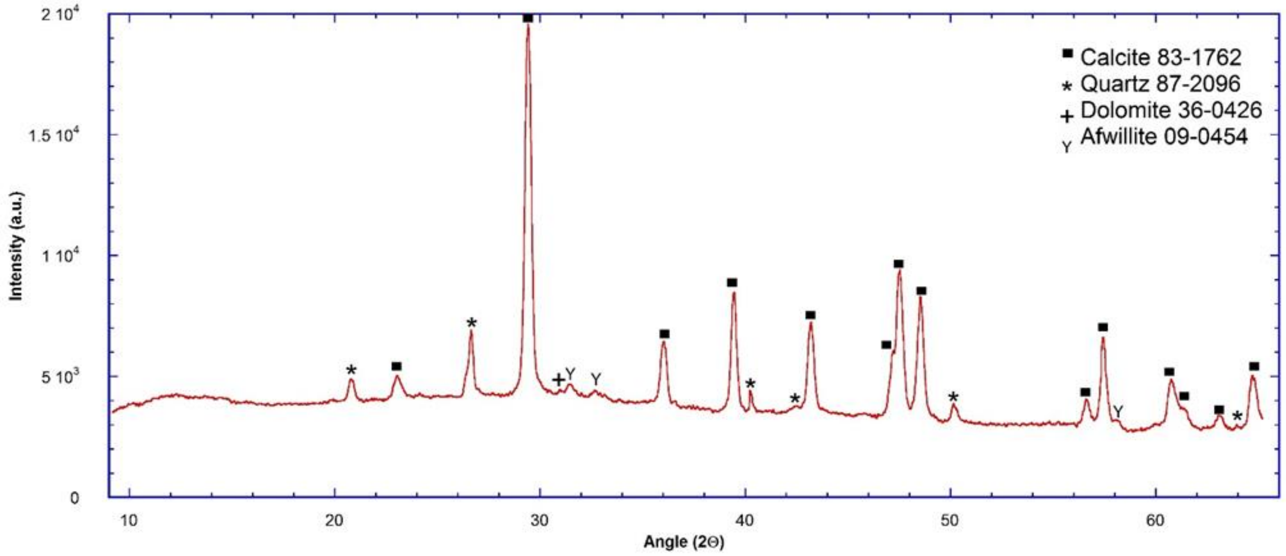


Sample D4 in plane-polarized light.

Concrete composed of a poorly sorted aggregate and it is is composed of lithic fragments, monocrystalline grains and diffuse calcium carbonate remains. The lithologies are predominantly carbonatic sedimentary rocks

XRD analysis revealed, in addition to the presence of calcite and quartz, the diffraction pattern of **afwillite ($Ca_3Si_2O_4(OH)_6$)** and **dolomite**.

XRD of sample D4



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The **mechanical properties of the concrete samples** have been generally estimated in terms of **compressive strength, tensile strength and elastic modulus**.

The results highlight that the concrete constituting the structural interventions made by Evans at the beginning of the 20th Century is characterized by a low mechanical strength, both in tension and compression. In particular, it should be noted that **D1** has been taken form a recent concrete slab (dating back to about 1950), **D2** and **D3** from an Evans concrete slabs directly exposed to the environmental actions (sun radiation, rainfall and more), and **D4** from an Evans concrete slab recently coated with inclined concrete for managing the rainwater.

Test layout used in the uniaxial compression test of the concrete core-drillings.

Image of the D3 sample at failure in compression

Test layout used for the estimation of the elastic modulus of concrete core-drillings through the application of strain gauges

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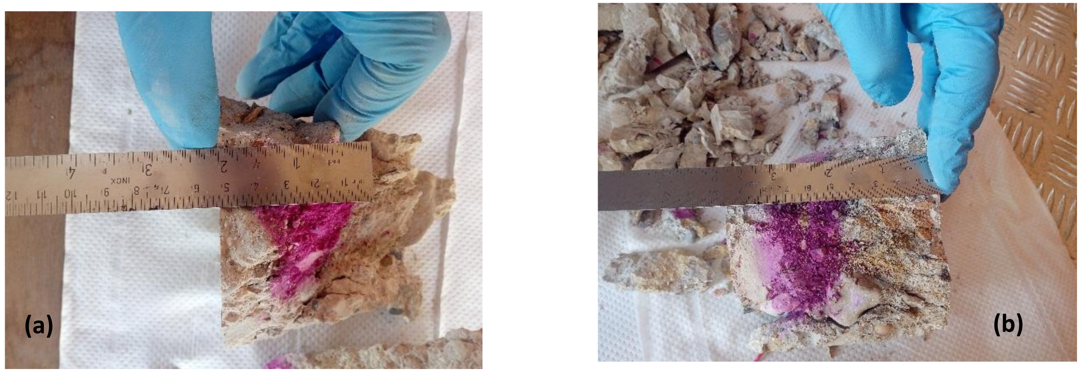
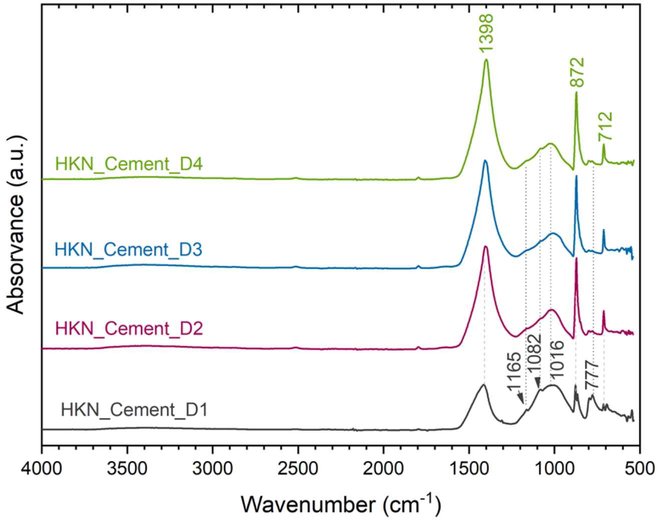
The samples **D3** and **D4** have been also analyzed to evaluate the depth of the **carbonation layers** of the material through the **phenolphthalein indicator test**. The core layer of the slabs with non-carbonated material has a depth of about **4-5 cm** for the sample **D3** and **2-3 cm** for the sample **D4**. For both the cases the carbonated layer is about 5-6 cm thick, highlighting a high level of carbonation, exposing the internal rebars to corrosion.



Results of the phenolphthalein indicator test for D3 (a) and D4 (b) concrete samples.



For the mortars formulated with only the **Portland cement**, $Ca(OH)_2$ produced $CaCO_3$, and this compound during time can be progressively washed away by the action of **acid rains**, transforming calcium carbonate in soluble calcium bicarbonate (**carbonation phenomena**) or in soluble calcium sulphate (**sulphation**).

Carbonation phenomena plays an important role in the weathering of the material. It is a chemical reaction where firstly carbon dioxide present in the air, dissolves in rain water forming carbonic acid, which in turn combined with calcium carbonate forms calcium bicarbonate, highly soluble in water.

In addition, the **phenomena of sulphation** has to be considered, where sulfuric acid, deriving from the reaction between SO_2 and rain water reacts with calcium carbonate, and generates the decomposition of $CaCO_3$, and the formation of calcium sulphate $CaSO_4$.

These phenomena lead to an increase of the porosity, thus inducing a rapid decline of the mechanical resistance, compromising the material durability and functionality.

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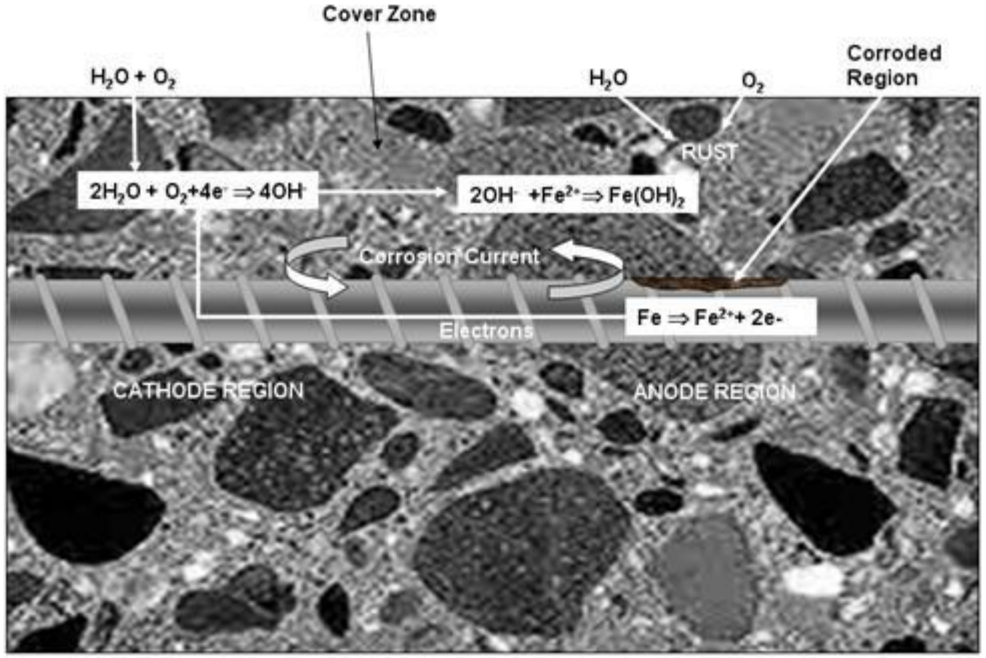
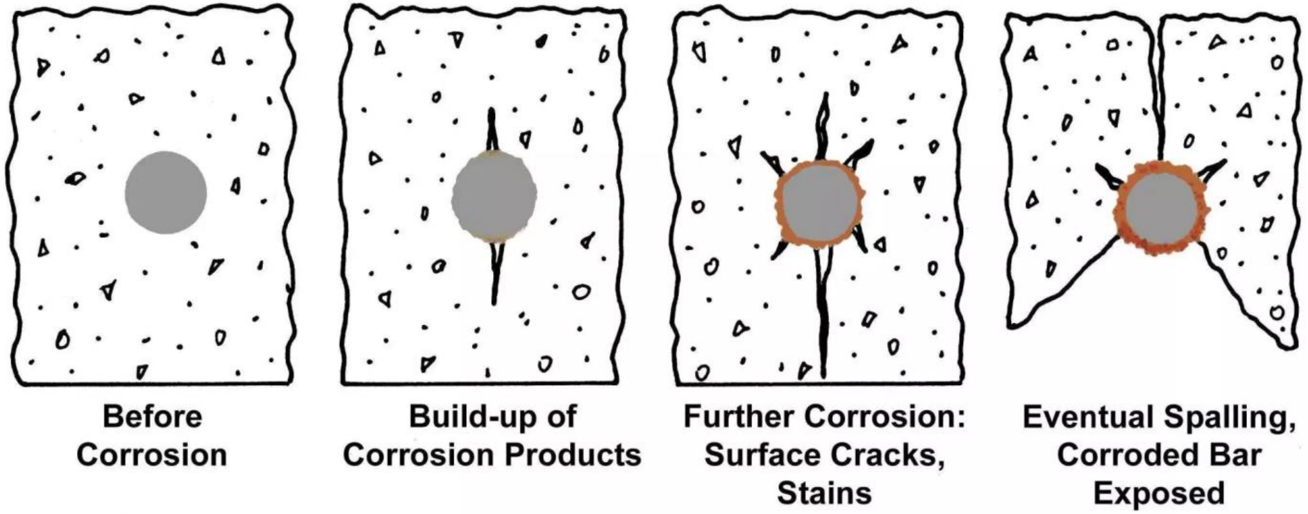
Iron bars Corrosion





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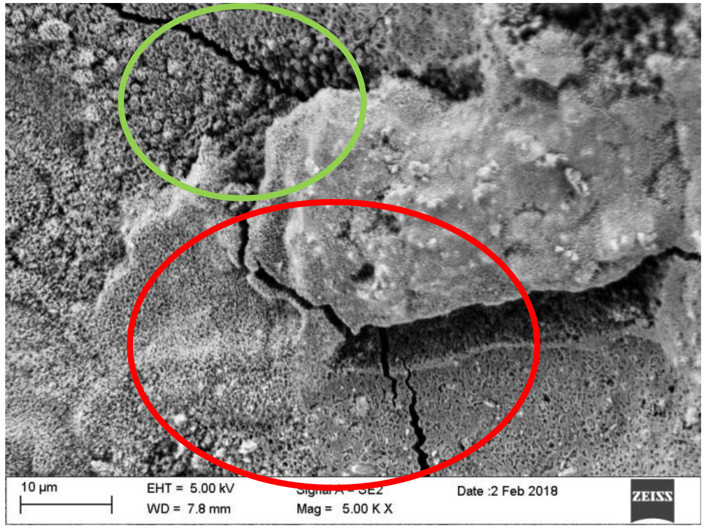
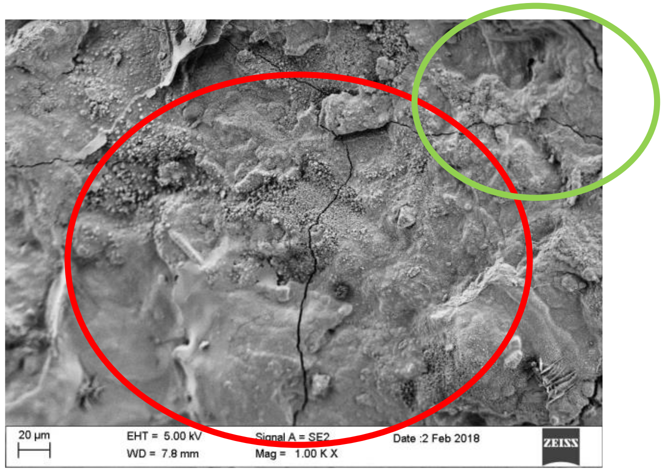
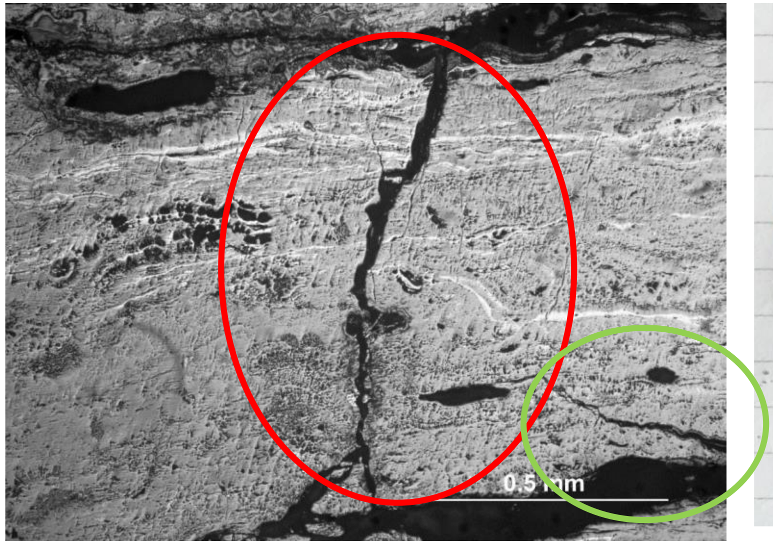
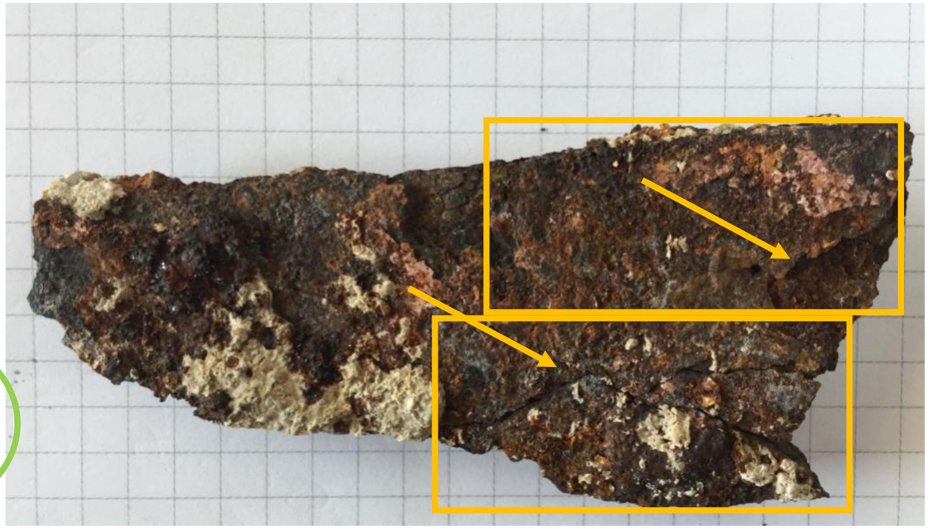
The **observation at metallurgical microscope reported revealed cracks that propagated in two different directions: along the rolling axis and in a direction perpendicular to it.** The corrosion propagated on layers parallel to the surface as **in exfoliation corrosion**. The corrosion product that formed had a greater volume than the volume of the parent metal. The increased volume forced the layers apart, and caused the metal to exfoliate. **The presence of a strong exfoliation combined with the load, generated a stress corrosion attack** (i.e. the result of the combined and synergistic interaction of mechanical stress and corrosion reactions) . **The stress corrosion produced vertical cracks**.



The SEM observation of the fracture surface **showed a crack propagation both transgranular and intergranular,** confirming the occurrence of a double mechanism exfoliation and stress corrosion.







Delamination of iron bars

The restoration/reconstruction made by Evans, using concrete, **is nowadays considered an integral part of the monument and its history, to be protected. This is the reason why we studied and developed cementitious mortars, generally not applicable in the CH field**.

In this framework, the HERACLES project approach involves the design and synthesis of a cement mortar to face and to stop both the degradation of the reinforced concrete and the loss/deterioration of the original materials.

Taking into account the diffused degradation of building, the restoration/maintenance action has to **include the removal of carbonated concrete in each portion, presenting cracking phenomena, swellings or delamination.**

There is also the progressive oxidation of visible metal reinforcements that in some cases led to the bar section reduction. Integration of metal reinforcements should be provided to counterbalance the original damaged ones.

The common structural and non-structural repair actions for reinforced concrete involve:

1. **The complete degraded concrete portions removal, which are therefore carbonated, detached or delaminated**

2. The surface metal reinforcement cleaning to remove dust, iron oxide and debris

3. Treatment of the metal reinforcements using a protective corrosion inhibitor

4. Missing portions reconstruction in order to restore the original profile through cement mortar. In order to guarantee the perfect cohesion between concrete and mortar.

This requirement is fundamental to guarantee the monolithic restoration.

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