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Electronic properties of iron corrosion product layers at the nanometer scale

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In the double context of the cultural heritage and of the nuclear waste storage, the long-term corrosion of iron has to be studied. For this purpose, the properties (chemical, physical and electrochemical) of the iron corrosion product layers (CPL) must be determined at different scales from global to the nanometer scale in order to have a complete understanding of the corrosion mechanisms and to model the long-term corrosion.

The iron corrosion rate is conditioned by the properties of the corrosion anodic and cathodic reactions. A better understanding of the corrosion mechanisms requires the identification of the limiting steps of these reactions. The major part of publications concerns the description of the anodic reaction. Studies involving the cathodic reaction are less common but its limiting steps are: transport inside the CPL of reducible chemical species in the electrolyte or electrons issued from the iron anodic dissolution.

In our study, to a better understanding of the location of the corrosion cathodic reaction, the electronic properties of the iron CPL are determined at the nanometer scale both on iron archaeological artefacts corroded during some hundreds or thousands of years and on iron coupons corroded in laboratory experiments (some months or years) under controlled conditions.

Conductive Atomic Force Microscopy (C-AFM), unique in its capability to probe electrical characteristics with nanometer-scale resolution, is carried out. In addition, the corrosion product layers are characterized at the micrometer scale by Field Emission Scanning Electron Microscopy (FE-SEM) for the distribution of the different corrosion products and by μ Raman spectroscopy for the determination of their crystalline nature.

Various iron corrosion profiles typical of different environments (deaerated or aerated soils, atmosphere, marine medium) are studied. Particularly the electronic properties of the CPL but also the connectivity of minor corrosion products that can play a role on the electronic properties are researched in order to a better knowledge of the iron corrosion mechanisms.

Concerning the iron corrosion in anoxic soils, the C-AFM study of different corrosion profiles (Fe^{II} carbonates, magnetite entrapped in the carbonate matrix, iron sulfides) have revealed that ferrous carbonate matrix is insulating whereas magnetite and iron sulfides are conductive although not systematically connected to the metal. This suggests that electrons produced by the anodic dissolution of iron metal would be conducted to the

external part of the corrosion product layer through a three-dimensional network of connected magnetite and sulfides strips passing through the insulating ferrous carbonate matrix.

All these data will bring new insights on the iron corrosion mechanisms to model the long-term corrosion.