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Electronic properties at the nanometer scale of iron anoxic corrosion product layers

Florence MERCIER-BION⁽¹⁾, Jiaying LI⁽¹⁾, Ludovic TORTECH⁽²⁾, Delphine NEFF⁽¹⁾

Philippe DILLMANN⁽¹⁾

(1) LAPA-IRAMAT-NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

(2) DRF/IRAMIS/NIMBE/LICSEN, CEA Saclay, 91191 Gif-sur-Yvette, France

In the double context of the *in situ* preservation of archaeological objects and nuclear waste disposal in deep geological media, the corrosion of iron metal buried in anoxic carbonated soils has to be studied.

The iron corrosion rate is conditioned by the characteristics of the corrosion anodic and cathodic reactions. Therefore, for a better understanding of the corrosion mechanisms, the limiting steps both for the anodic and for the cathodic reactions need to be identified. As far as the corrosion mechanisms of iron are considered, the major part of publications concerns the anodic reaction study and there is a serious lack of data linked to the corrosion cathodic reaction. The limiting steps of this latter can be: transport inside the corrosion product layer (CPL) of the electrolyte, of the chemical species (such as H₂) or electrons issued from the iron anodic dissolution.

Therefore we investigated the corrosion cathodic reaction for iron corroded in anoxic medium by studying iron nails corroded from the 16th century in anoxic carbonated soils (archaeological site of Glinet Seine-Maritime, France). We intend to identify the limiting step and the location of the corrosion cathodic reaction by measuring local conductivity of the CPL. The description of the crystalline nature of the iron CPL, distribution, electronic

properties and porosity at the different scales from global to the nanometer scale are important to have a complete knowledge of the corrosion mechanisms.

Indeed the electrical properties of the CPL were probed by Conductive Atomic Force Microscopy (C-AFM) which provides measurements within the range of nanometers. In addition the corrosion product layers was characterized by μ Raman spectroscopy for the determination of the crystalline nature of the corrosion products and by Field Emission Scanning Electron Microscopy (FESEM) for the distribution phases from metal to the metal/soil interface. Different patterns representative of the anoxic CPL of the 400 years old iron archaeological nails were identified: CPL constituted of only ferrous carbonates such as siderite FeCO_3 and chukanovite $\text{Fe}_2(\text{OH})_2\text{CO}_3$, CPL composed of mainly ferrous carbonates but with the minor presence of magnetite Fe_3O_4 under strips or under nodules inside the ferrous carbonates matrix, or showing locally iron sulfides borders.