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The study of anoxic corrosion process of ferrous metals is a matter of concern for industrial sector (pipelines, container for nuclear waste storage….) but also for cultural heritage objects conservation. Indeed, the formation and the presence of sulfide compounds in the corrosion products of buried objects, either in terrestrial or marine environments, can drastically change the corrosion mechanisms and, so, the conservation strategies for these objects. Particularly, in natural environment, the presence of micro-organisms such as Sulfate-Reducing Bacteria (SRB) may influence the corrosion rate of ferrous objects by favoring the precipitation of iron sulfide phases and modifying then the initial corrosion process [1].

The determination of the iron sulfides nature and their distribution in the corrosion product layer is a crucial issue to address in order to anticipate the degradation of ferrous object during extraction, storage or conservation operations. In the present work, archeological ferrous samples, representative of long term corrosion systems, with or without bacteria exposition, have been considered. A multi-technique approach was developed to achieve an overall physico-chemical characterization and to cover the dimensions requirement of the corrosion systems.

First, FE-SEM imaging coupled with EDS and µ-Raman spectroscopy were performed on the archeological ferrous samples enabling the localization and identification of the natural corrosion products. Mix of phases of greigite (Fe_3S_4) and mackinawite (FeS) in a corrosion layer mainly constituted of iron carbonates were observed at a sub-micrometric scale, in consistency with the literature [2], showing the precipitation of greigite, mackinawite and/or pyrite (FeS_2) in the presence of bacteria or in sulfur environment. Then, Nano-Auger spectroscopy, owing to its local chemical characterization capability, was investigated to obtain a chemical diagnostic at a nanometric scale. Scanning Auger Microscopy (SAM) was performed to evaluate the ability of this technique to spatially discriminate different phases (iron sulfides, oxides and carbonates) at a local scale and extreme surface sensitivity (5nm escape depth). Then, thanks to µ-Raman mappings, specific areas presenting only one component were selected and identified for the acquisition of reference Auger spectra, and especially high energy resolution spectra of Fe-MVV and S-LVV regions. Finally, the spatial distribution of the different phases obtained with SAM could be compared with nano-SIMS experiments informing about the sulfur isotopic composition variations and the bio-origin of the sulfur phases.

[1]   H.A. Videla et al., Int. Biodeterior. Biodegrad. 63 (2009) 896–900.
[2]   S. Grousset et al., Corrosion Science 112 (2016) 264–275.