Role of green rusts in corrosion and biocorrosion of carbon steel in marine environment

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The corrosion products of steel in seawater are associated with micro-organisms, extracellular polymeric substances and other species of organic origin. When steel is immersed in seawater, the sulfated green rust GR(SO_4^{2-}) with composition $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 8H_2O$, is the first corrosion product that forms. During the initial aerated period of the corrosion process, GR(SO_4^{2-}) is oxidized by dissolved O_2 into lepidocrocite γ-FeOOH (mainly), goethite and magnetite. The corrosion product layers are thus made of two strata, an inner one mainly composed of GR(SO_4^{2-}), growing on the metal surface, and an outer one, mainly composed of lepidocrocite, resulting of the oxidation of the GR. Microbiological analysis of this layer shows that numerous bacterial species are associated with the corrosion products. Sulfate reducing bacteria (SRB) were identified on coupons left only one month in seawater. In agreement, FeS could be detected locally on the same coupons. This shows that at that time, SRB have already begun to grow in the most deaerated zones.

After some time (>6 months), FeS is a major corrosion product, associated with GR(SO_4^{2-}) and SRB in the inner part of the rust layer [1]. This shows that in most cases the corrosion process remains rather uniform because the whole steel surface, placed in anoxic conditions, can finally be colonized by SRB. The behavior of steel in anoxic conditions was then studied in the laboratory using seawater-like electrolytes [2]. Carbon steel electrodes were polarized anodically at a potential ~100 mV higher than the open circuit potential, in an electrolyte continuously de-aerated by an argon flow. X-ray diffraction and µ-Raman analysis performed after 23 h of polarization demonstrated that a layer mainly composed of GR(SO_4^{2-}) had grown on the steel surface. In parallel, carbon steel coupons immersed for 11 years in the harbor of La Rochelle (Atlantic coast) were removed from seawater for analysis. The inner part of the rust layer (7-8 mm thick) proved to be mainly composed of magnetite, GR(SO_4^{2-}) and iron sulfide FeS [2]. This definitively confirms that GR(SO_4^{2-}), as Fe_3O_4 and FeS, can also form from steel during the anaerobic period of the corrosion process.

Laboratory studies finally demonstrated that SRB could grow using the sulfate species coming from GR(SO_4^{2-}), thus using the GR as a source of sulfates. The consumption of sulfate induces the transformation of the GR and the formation of mackinawite FeS [3]. This suggests that the ratio FeS/GR(SO_4^{2-}) can measure the importance of the influence of SRB on the corrosion process.

References:

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