

Mineralogy of ferrous corrosion products formed in natural seawater

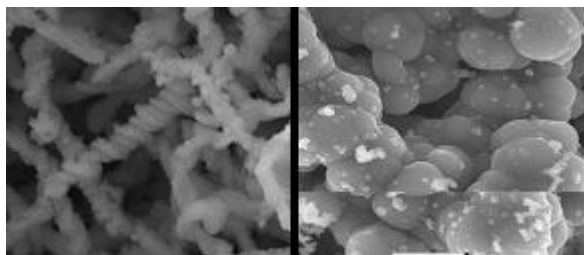
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Carbon steel 1020 coupons were exposed to natural Key West, FL seawater over a one-year period in both stagnant and alternate immersion conditions with varying concentrations of dissolved oxygen (DO) in both the seawater and the atmosphere. A two-tiered oxide layer of lepidocrocite/goethite formed during exposure to stagnant oxygenated seawater (~7 ppm DO). The inner layer was extremely tenacious and resistant to acid cleaning. Under hypoxic conditions (~0.2 ppm DO), dissolved oxygen was completely consumed in the first week by bacterial respiration and corrosion reactions. Numbers of sulfate-reducing bacteria increased and dissolved sulfide could be measured in the bulk seawater. The corrosion product was initially a non-tenacious sulfur-rich corrosion product, mackinawite, with enmeshed bacteria. As more sulfide was produced the mackinawite was transformed to pyrrhotite. Energy dispersive spectroscopy confirmed an increase in sulfide concentration within the corrosion products. Encrusted bacteria were observed using an environmental scanning electron microscope (ESEM) in all cases and corrosion morphology varied with sample orientation and DO concentration.

In alternate immersion, all exposure conditions produced a two-tiered corrosion layer. The outer extremely fragile layer was reddish orange and x-ray diffraction (XRD) indicated halite, lepidocrocite and goethite. The inner layer was black, tenacious and XRD indicated maghemite. Bacteria were associated with all corrosion products.



Chemistry of metallic iron nanoparticles

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Our work with metallic iron nanoparticles has focused on a search for evidence of nanometer-scale size effects on the rate at which they react and on their fundamental chemistry. Iron nanoparticles, synthesized by borohydride reduction (Fe^{BH}) or by thermal reduction of oxide particles under a hydrogen atmosphere (Fe^{H_2}), and micron-sized iron particles, synthesized electrolytically (Fe^{EL}), were characterized by a variety of spectroscopic, microscopic, and electrochemical techniques, and then reacted with either benzoquinone (BQ) or carbon tetrachloride (CT). Surface-area normalized reaction rates showed little difference among the three types of Fe, although Fe^{H_2} had a slightly slower rate than the other two forms in reactions with BQ.

To assess the fundamental chemistry of the three forms of Fe, we measured the branching ratio for the reductive dechlorination of CT. This reaction branches between a pathway that yields chloroform (CF) as its primary product and one or more pathways that yield other, as yet unidentified, products. The results depended in part on initial CT concentration. At low initial CT concentration (4 μM), the yield of CF (Y_{CF}) was typically < 0.4 for the Fe^{H_2} form and > 0.4 for Fe^{BH} and Fe^{EL} forms suggesting that the non-CF pathway was favored when the Fe^{H_2} form was used. At higher CT concentrations (0.9-2.4 mM), however, differences among the forms of Fe were smaller with Y_{CF} values of about 0.46 observed for the Fe^{H_2} form and 0.50 for the Fe^{BH} form.

To help identify the factors that control the branching ratio, we have initiated a series of experiments using electron paramagnetic resonance (EPR) spectroscopy to nondestructively probe the reactivity of Fe^{H_2} and Fe^{BH} particles over time. Aging of the particles (i.e., oxidation by H_2O), and the possible role of nonpolar solvents such as CT in this process, are the primary foci of these experiments.