Ancient Rust-Proof Iron Pillar Possibly Protected by Layer of “Misawite” (δ-FeOOH)

A 1600-year-old wrought-iron pillar that stands near New Delhi, India, as a well-known landmark and tourist site has intrigued metallurgists and historians for centuries. Subjected to heat, humidity, and even a direct cannonball hit, the pillar has remained essentially rust-proof. Several theories have been suggested for its virtually rust-free condition. The mystery now appears to have been solved due to the work of metallurgist R. Balasubramaniam from the Indian Institute of Technology, Kanpur.

The Delhi iron pillar was built in the 4th century AD, and stands 23 ft tall with a diameter of 16.5 in. at the bottom and 12.5 in. at the top. It is estimated to weigh ~6.5 tons. It is considered to be the biggest hand-forged block of iron from antiquity. In an article published in the November issue of Current Science, Balasubramaniam demonstrates that the lack of rust is due to the formation of a protective layer of misawite (δ-FeOOH), as well as a layer of crystalline phosphates, catalyzed by the presence of comparatively high levels of phosphorus in the iron.

Rust samples from the pillar have been analyzed using x-ray diffraction, Fourier transform infrared spectroscopy, and Mössbauer spectroscopy. The samples were found to contain amorphous oxyhydroxides, including lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and misawite (δ-FeOOH), magnetite (Fe₃O₄), and crystalline phosphates, mainly iron hydrogen phosphate hydrate (FePO₄•H₂PO₄•H₂O(4H₂O)).

The initial corrosion of the iron, aided by slag inclusions, forms lepidocrocite and goethite, which enhances the concentration of P (<0.1% in the base metal) at the metal-scale interface. This catalyzes the formation of amorphous misawite (δ-FeOOH), which offers significant initial corrosion resistance. In addition, the P reacts with moisture and forms phosphoric acid, which leads to the precipitation of amorphous phosphates at the metal-oxide interface. The phosphates, which form a thin continuous layer next to the metal, minimize corrosion because of their inhibitive nature. Over time, the amorphous phosphates transform to a crystalline phase due to alternate wetting and drying cycles. This further enhances the corrosion resistance due to the low porosity and compactness of the crystalline phase.

Kinetics studies show that an initial fast corrosion rate occurs for about three years until the misawite layer is formed. Subsequently, the corrosion rate is negligible, with corrosion resistance lasting for centuries.

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