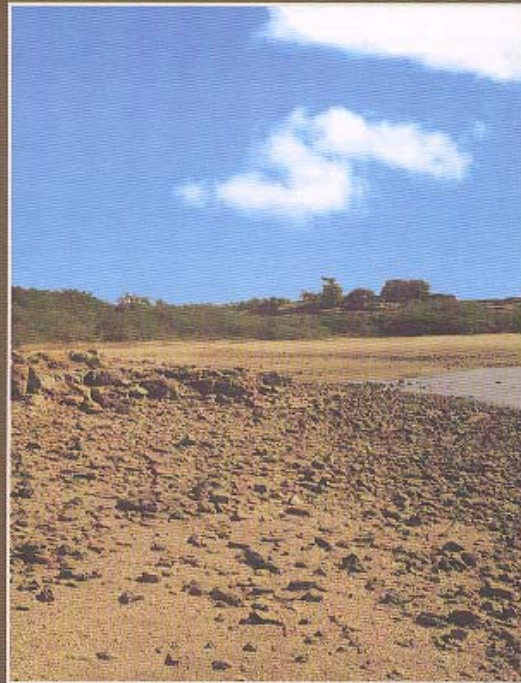


Volume 82 Number 11

10 June 2002

# CURRENT SCIENCE



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Current Science Association ■ Indian Academy of Sciences

## On the growth kinetics of the protective passive film of the Delhi iron pillar

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**A kinetic model for the evolution of atmospheric rust on the Delhi iron pillar (DIP) has been presented. The model is based on the known nature and structure of rusts on DIP and other corrosion-resistant ancient Indian irons. The initial fast rate of corrosion is aided by the entrapped slag inclusions and this results in enrichment of P at the metal-scale interface. The presence of P at the metal-scale interface promotes protective film formation processes (catalytic formation of  $\delta$ -FeOOH and phosphates), thereby reducing the corrosion rate. Growth rates have been roughly estimated for these two regions based on available DIP rust thickness measurements.**

The corrosion resistance of the 1600-year-old Delhi iron pillar (DIP; Figure 1) is due to the formation of a protective passive film on the surface, which is capable of withstanding atmospheric corrosion<sup>1</sup>. Characterization of the oldest rust on the pillar revealed that it contained amorphous iron oxyhydroxides and magnetite, and crystalline phosphates. The amorphous oxyhydroxides identified were lepidocrocite ( $\gamma$ -FeOOH), goethite ( $\alpha$ -FeOOH), misawite ( $\delta$ -FeOOH) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The phosphate identified was iron hydrogen phosphate hydrate ( $\text{FePO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ) (ref. 2). In addition to the nature and constituents of the long-term atmospheric rust, the structural features of DIP rust have also been analysed<sup>1</sup>. The process of protective rust formation can be summarized as follows. In the initial stages, the rust comprises of lepidocrocite and goethite. These forms of rust do not offer excellent protection and therefore the rate of corrosion is still maintained on the higher side. Conversion of part of this rust to magnetite does result in lower corrosion rates. However, the cracks and pores in the rust allow for diffusion of oxygen and complementary corrosion reactions. Moreover, reduction of lepidocrocite also contributes to the corrosion mechanism in atmospheric rusting<sup>3,4</sup>. The first step in enhanced corrosion resistance of the DIP results from the catalytic formation of  $\delta$ -FeOOH (ref. 1). This phase is amorphous in nature and forms as an adherent compact layer next to the metal-scale interface. Its formation is catalysed by the presence of phosphorus in the DIP. Upon its formation, the corrosion resistance enhances significantly because  $\delta$ -FeOOH forms a barrier between the rust and the metal.

Such a mechanism is operative in the corrosion resistance of Cu- and P-containing weathering steels<sup>5,6</sup>. A modified scheme has also been proposed for these steels based on long-term observations<sup>7</sup>. In the special case of DIP and in the general case of ancient Indian irons, the presence of significant amounts of P in the metal (> 0.1%) leads to further effects, which have a direct bearing on their corrosion resistance. Due to the initial corrosion of metal, there is enhancement of P at the metal-scale interface. This P reacts with moisture and conditions are created in the rust that are ideal for formation of phosphoric acid, which eventually leads to the precipitation of phosphates in the long term. There are several phosphate-formation reactions<sup>8</sup>. The nature and type of phosphate will depend upon exposure conditions<sup>9</sup>. The nature of phosphate can provide ideas, in a qualitative manner, about the time period of the rust. For example, the phosphate identified in the DIP rust was crystalline in nature<sup>2</sup> and therefore, this indicated the relatively old age of the rust, because the phosphates that precipitate initially are amorphous in nature<sup>8</sup>. The formation of phosphates is beneficial to the corrosion resistance, because of their inhibitive nature. Added benefits accrue when the phosphate forms as a continuous layer next to the metal. In case of alternate wetting and drying cycles, like those obtained in atmospheric corrosion, the amorphous phosphates can transform to crystalline modifications and in this process there is a large reduction in porosity in the phosphate<sup>8</sup>. This transformation results in excellent corrosion resistance

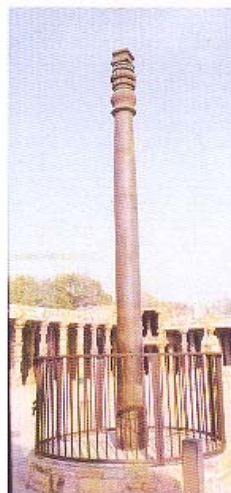


Figure 1. Corrosion-resistant Delhi iron pillar.

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