On the corrosion resistance of the Delhi iron pillar

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Abstract

The nature of the protective passive layer on the corrosion resistant Delhi iron pillar (DIP) has been addressed based on a detailed characterization of its rust. Rust characterization clearly established that the major constituents of the scale were crystalline iron hydrogen phosphate hydrate (FePO₄·H₃PO₄·4H₂O), α-, γ-, δ-FeOOH and magnetite. The iron oxide/oxyhydroxides were present in the amorphous form. The role of slag particles in the matrix of the DIP iron in enhancing the passive film formation is briefly addressed initially. The process of protective rust formation on DIP iron is outlined based on the rust analysis. Initially, the corrosion rate of iron is high due to the presence of slag particles. This results in enhancement of surface P content. In the presence of P, the formation of a protective amorphous compact layer of δ-FeOOH, next to the metal surface, is catalyzed and this confers the initial corrosion resistance. The critical factor contributing to the superior corrosion resistance of the DIP, however, is the formation of iron hydrogen phosphate hydrate, as a thin layer next to the metal–metal oxide interface. The formation of the crystalline modification of this phosphate from the amorphous form is aided by alternate wetting and drying cycles (i.e. the environmental factor). The rate of corrosion is further lowered due to the low porosity content of the crystalline phosphate phase. The passive film formation on the DIP has been contrasted with the rusting of normal and weathering steels.

Keywords: Delhi iron pillar; Corrosion resistance; Passive film; Mixed potential theory; Iron hydrogen phosphate; Microstructure
1. Introduction

The Delhi iron pillar (DIP) (Fig. 1) is testimony to the high level of skill achieved by the ancient Indian iron smiths in the extraction and processing of iron. The iron pillar at Delhi has attracted the attention of archaeologists and corrosion technologists as it has withstood corrosion for the last 1600 years. The
theories that have been proposed to explain its superior corrosion resistance can be broadly classified into two categories: the environmental [1–3], and material [4–7] theories. These theories have been critically reviewed elsewhere [6,7]. The proponents of the environmental theory state that the mild climate of Delhi is responsible for the corrosion resistance of the DIP as the relative humidity at Delhi does not exceed 70% for significant periods of time in the year (Fig. 2), which therefore results in very mild corrosion of the pillar. It is known from the classic researches of Vernon [8–10] that atmospheric rusting of iron is not significant for humidity levels less than 70%. Interestingly, the data provided on the atmospheric conditions at Delhi by Wranglen [2] were collected over a period of 30 years between 1930 and 1960. It is also important to include the climatic conditions of Delhi over a much longer period, including the recent past, while analyzing the environmental effect on the pillar’s corrosion resistance. Moreover, the climatic conditions of Udayagiri, where the pillar was originally located (it was brought to Delhi in the 11th century [11]), should also be analyzed in detail. On the other hand, several investigators have stressed the importance of the material of construction as the primary reason for its corrosion resistance. The ideas proposed in this regard are the relatively pure composition of the iron used [4], presence of phosphorus and absence of S/Mn in the iron [5], its slag-enveloped metal grain structure [3], passivity enhancement in the presence of slag particles [6,7] and the formation of phosphate film [5–7]. Other theories explaining the corrosion resistance are also to be found in the literature like the mass metal effect [3,12], initial exposure to an alkaline and ammonical environment [2], residual stresses resulting from the surface finishing (hammering) operation [13], freedom from sulfur contamination, both in the metal and in the air [13], presence of layers of cinder in the metal, thereby not allowing corrosion to proceed beyond those layers (cinder theory) [14], and surface coatings provided to the pillar after manufacture (treating the surface with steam [15] and slag coating [16]) and during use (coating with clarified butter) [3]. That the material of construction may be an important factor in determining the corrosion resistance of ancient Indian iron is attested by the presence of ancient massive iron objects located in areas where the relative humidity is high for significant periods in the year (for example, the iron beams in the Surya temple at Konarak in coastal Orissa [17] and the iron pillar at Mookambika temple at Kollur situated in the Kodachadri Hills on the western coast [18]). It is, therefore, obvious that the ancient Indians, especially from the time of the Guptas (AD300–AD500), produced iron that was capable of withstanding corrosion. This is primarily due to the high P content of the iron produced during ancient times, the reasons for which will be explored in detail later. The known facts about the DIP have also been reviewed in a recent book [19].

In order to understand the corrosion resistance of the Delhi pillar, it would have been ideal to study the detailed microstructure and passive film formation characteristics of metallurgical samples from the DIP. However, this is not possible, as specimens from the DIP are not available currently. In view of this, a non-corroding iron clamp, produced during the Gupta period (i.e. the time in
Fig. 2. Atmospheric conditions at Delhi averaged over 30 years (1930–1960) [2]. The well-known effect of atmospheric humidity on the corrosion of iron [8–10] is also shown below.
which the DIP was constructed), was removed from one of the stone blocks in the ruined Gupta temple at Eran, Madhya Pradesh. It exhibited a thin adherent surface layer. Its microstructure [20], aqueous corrosion behaviour [20], and the nature of its protective rust [21] have been studied earlier in detail. The rust from this ancient Indian iron will henceforth be called Eran rust. Rust was also collected from several locations in the DIP just below the decorative bell capital (see Figure 2 of Ref. [22]). This is the location where maximum rusting is observed on the exposed surface of the pillar [23] and, moreover, the rust from this location should be the oldest undisturbed rust as this part of the pillar is inaccessible to the public [24]. The DIP’s rust has been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Mössbauer spectroscopy [22]. The aim of the present paper is to utilize the characterization results to clearly establish the nature of the protective passive layer on the DIP. This layer is clearly responsible for the pillar’s excellent corrosion resistance. It is interesting to note that each of the above characterization techniques provides independent information that individually are incomplete in explaining the passive film nature. However, when the results are viewed in totality, the most probable reason for the excellent corrosion resistance of the DIP can be concluded. The present paper will seek to understand the nature of the protective rust on the DIP.

2. Iron of Delhi pillar

The underlying metal of the Delhi pillar would be briefly discussed here in order to elucidate its characteristic features. Incidentally, these features are also characteristic of ancient Indian iron.

2.1. Composition

Several analyses of the DIP iron’s composition are available ever since the first analysis was published by Hadfield in 1912 [25]. The published chemical analyses [5,25–27] of the DIP iron are presented in Table 1 from which the variation in the DIP iron’s composition can be noted. Hadfield stressed that the composition of iron, in his analysis, was determined by actual chemical analysis and not by the difference (i.e. by subtraction of all the other elements compositions from 100%) [25]. A sample of DIP iron was also subjected to microprobe analysis in order to determine the composition of the elements Mn, Cr, Cu and Ni in the near-surface regions and it was found that the composition of Cu (0.05%), Ni (0.05%), Mn (0.07%) and Cr (Nil) was uniform through several millimeters into the sample from the surface [3]. The analysis was made near the area marked A in the microstructure seen in Fig. 3(a). Wranglen utilized the available compositions (excluding that of Lal [26]) and estimated the average composition of the DIP iron as 0.15% C, 0.25% P, 0.005% S, 0.05% Si, 0.02% N, 0.05% Mn, 0.03% Cu, 0.05% Ni and balance Fe [2].
2.2. Microstructure

Some important aspects of the underlying microstructure of the DIP iron would be initially discussed as these have a bearing on its corrosion behavior. The intimate relationship between structure and properties is well established in materials engineering. The DIP possesses a non-uniform grain structure (Fig. 3) [3]. In the unetched condition, the specimens showed slag inclusions irregularly distributed in the microstructure [5,26]. The etched specimens revealed medium to coarse polyhedral grains of ferrite, with slip bands in some grains, near the surface. The surface regions were free from pearlite, which seemed to increase towards the interior. Many slip bands were seen in the surface ferrite grains. Elongated slag particles and oxide particles were also seen in the deformed structure in the near-surface regions. Lahiri et al. [27] also conducted metallographic examination of the DIP iron and the irregular distribution of pearlite was noted. The absence of a uniform distribution of pearlite is indicative of the segregation of P because, in such areas of P segregation, C di/C128uses out and the material becomes poorer in C content [28]. The interior portions were comparatively rich in C [5,27]. Therefore, a wide variation in structure is exhibited by the DIP iron and this is also a characteristic feature of ancient Indian iron. The non-uniform structure could be the reason for the difference in the chemical analyses of the DIP iron’s composition as determined by several investigators (Table 1).

The DIP iron was characterized by a relatively high proportion of slag inclusions and the microstructure near the slags showed wide variations (including normalized and annealed structures) [5]. Moreover, microstructures containing 0.2–0.3% C were present next to the slag particles, in addition to carbon-free grains. As a result of slag particles in the structure, the specific gravity of DIP iron is lower than that of the purest form of Fe (Table 1). It should be noted that

<table>
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<th>Table 1: Published composition analyses of DIP iron</th>
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<tr>
<td>Above</td>
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<td>Others</td>
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<td>Specific gravity</td>
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* 0.100 fixed and 0.180 in solid solution P.
Fig. 3. (a) Entrapped slag inclusions in the iron of the Delhi pillar which appear as large black particles, (b) structure at location A, and (c) at location B marked in (a). The magnification of (b) and (c) are similar [3].
the specific gravity is not uniform, which is also indicative of the non-uniform distribution of the slag particles in the microstructure. The non-uniform distribution of slag particles in the DIP iron can be clearly seen in the microstructures provided by Ghosh [5], and Bardget and Stanners (Fig. 3) [3]. The slag present in the DIP iron is generally microscopic in nature and only a few of them are present in larger sizes (Fig. 3). Slag results in the microstructure due to the processing method employed to obtain iron. Iron was produced in ancient India by solid state reduction of high quality iron ore using charcoal [29,30]. Once the reduction was complete, the iron lumps produced were hammered in order to remove part of the liquid slag formed during the extraction process. Some of the slag invariably remained within the bulk of the material and this is the origin of the entrapped slag inclusions. Moreover, ancient Indian iron also shows the presence of a small amount of unreduced iron oxides. Generally, silica was sprayed on the iron that was extracted and this combined with unreduced iron oxide, resulting in the slag fayelite, Fe$_2$SiO$_4$. Microstructural investigations on iron produced during the Gupta period show that both slag and unreduced iron oxide were present in the main body of Eran iron [20]. These unreduced iron oxides also contained carbon, presumably from the charcoal used for extraction [20]. The presence of carbon in these unreduced oxides would render these oxides cathodic in nature with respect to the surrounding matrix.

It must also be noticed that the slag particles in the DIP iron are in fine microscopic form distributed unevenly in the microstructure. If the slag had enclosed the individual iron lumps that were forge welded (in order to produce the large dimension of the pillar), it would have resulted in poor solid state fusion of the iron lumps. The pillar is a solid body [31] with good mechanical strength (yield strength YS of 23.5 tons/in.$^2$, ultimate tensile strength UTS of 23.9 tons/in.$^2$ and 5% elongation [5]). The relatively high strength, and the similarity of YS and UTS are indicative of the composite structure of the DIP iron. In fact, a cannon ball fired at the DIP in the 18th century (either by Nadir Shah in AD1739 or Ghulam Quadir in AD1787) failed to break the pillar [23], which also suggests that slag does not coat the individual lumps that were forge welded [32].

A very interesting feature concerning the presence of slag particles in ancient Indian iron is that they are generally surrounded by a relatively higher fraction of pearlite compared to regions far removed from the slags. This is observed in the microstructures of DIP iron (see Fig. 3(c)) [3,4] and Eran iron [20,21]. Another typical example is seen in Fig. 4, which shows the microstructure of the Dhar pillar iron. This pillar, which is about 900 years old, is nearly twice the length of the DIP, but lying presently in three broken pieces with a missing fourth piece and a missing decorative capital [33–36]. Note that the pearlite volume fraction is relatively higher near the slag particles. The presence of a large amount of pearlite near the slag inclusions is indicative of P depletion in these regions. Chemical analysis of the P content in DIP iron has revealed that the majority of P content in the DIP is in solid solution while a smaller amount occurs in the slags. In one of the analysis, out of 0.28% P in the material, 0.10% P was in the fixed state (i.e. in slags) with the rest being in solid solution in the metal [5]. The presence of P
was also confirmed, by electron microprobe analysis, in the entrapped slags of the Eran iron and Dhar pillar iron. In the vicinity of slag inclusions, the regions are depleted in P and these are the regions where C will concentrate [28]. This is the reason for the presence of a larger fraction of pearlite near the slag-metal interfaces. The presence of pearlite near the slag inclusions has an important implication as regards understanding potential cathodic sites in ancient Indian iron (i.e. slag regions would act as cathodic reaction sites due to the large volume fraction of cementite present at these locations).

2.3. Origin of P in Metal

It will be shown later that the presence of P is crucial to the corrosion resistance of DIP. As the DIP iron contains a larger amount of P than modern-day iron (produced in blast furnaces), the reason for high P content in the iron is briefly addressed. Interestingly, in nearly all published ancient Indian iron compositions, a relatively larger percentage of P (compared to modern irons) can be noted [5,26]. Modern steels cannot tolerate such high P contents as they would
be susceptible to cracking during the process of hot working due to the formation of liquid phosphides at the grain boundaries (the phenomenon being termed hot shotness). While it was earlier believed that P in ancient steels comes from slag inclusions [37], recent developments in slag chemistry help in understanding the probable reason. The relatively higher P content in ancient iron is related to the kind of slag that was created in the extraction process by solid state reduction. Lime was not added in the ancient Indian furnaces, unlike in modern blast furnaces, and therefore the slag generated in these ancient Indian furnaces were essentially fayelitic slags (consisting of iron orthosilicates Fe$_2$SiO$_4$). This is also corroborated by available compositions of ancient Indian iron-making slags from archaeological excavation sites [26]. The slags do not contain lime [26]. The transfer of P from the metal into the slag is facilitated by the basic components (for example, FeO and CaO) in the slag. The efficiency of removal of P from metal is much higher for CaO compared to FeO in the slag. These facts are well established in slag chemistry [38]. Therefore, the absence of CaO in the slags leads to a lower efficiency for removal of P from the metal, which invariably must have resulted in higher P contents in ancient Indian irons. Thermodynamic analysis of P removal from iron in the absence of CaO in the slag also provides the same answer. As the entrapped slag seen in the ancient Indian iron is generally fayelitic without any CaO, thermodynamics dictates that a higher amount of P should remain in solid solution in iron. This must be one of the reasons for the presence of higher P in ancient Indian iron. It must also be noted that there are indications that P addition was intentional. For example, Buchanan [39], in his detailed description of steel making in Karnataka in the 18th century, describes one primitive furnace operated at Devaraya Durga. In this furnace, conical clay crucibles were filled with a specific amount of wood from the barks of a plant *Cassia auriculata*, and pieces of wrought iron, then sealed and fired. Interestingly, the bark of this plant contains a high content of P, extracted by osmosis from the ground [6,7].

3. Role of slag particles in the passivation process

The method of extraction of iron lumps used in constructing the DIP resulted in the presence of fine slag particles and unreduced ore in the microstructure of the iron. The presence of these second phase particles in the microstructure would result in the creation of mini-galvanic corrosion cells when the iron is exposed to the environment. The metal in the matrix (which is almost pure iron [2,4,5]) would act as the anode and the second phase particles (slag and unreduced iron oxides) as sites for cathodic reactions. This is reasonable as the unreduced iron oxides contain carbon and the slag particles are surrounded by a large volume fraction of cementite (see Fig. 4). Initially, the cathodic reactions that occur on these cathodic reduction sites provide the sink for the electrons liberated by the corrosion of the metal to its ions. The slag particles would therefore accelerate the corrosion of the matrix on exposure to the environment. Relatively high corrosion rates were
observed experimentally in the initial exposure period of Eran iron compared to mild steel of similar C content [20]. Therefore, it is anticipated that the two-phase structure of the DIP iron should corrode at a faster rate compared to iron of similar composition, as the DIP iron is essentially a composite structure. The cathodic nature of the second phase particles in DIP iron should also be relevant in the later stages of corrosion because, in atmospheric corrosion, the cathodic reduction of oxygen must be considered (as ferric oxyhydroxides are also good electronic conductors [40,41]) in addition to the reduction of some of the corrosion products in the rust [42,43].

In order to explain the anomaly of the composite structure of DIP iron exhibiting excellent corrosion resistance, the oxidation and reduction processes occurring on the DIP iron were analyzed using the mixed potential theory [6,7]. The analysis is briefly summarized by considering the Evans diagram presented in Fig. 5. The anodic polarization behavior of iron has been shown to exhibit active–passive behavior, as it is well known that rust layer(s) form on atmospheric corrosion of iron. Moreover, the DIP iron contains a relatively large weight fraction of P (average composition 0.25% [2]) which will aid in inducing passivity in iron [44,45]. The formation of insoluble phosphates is thermodynamically favored [46], even for P contents as low as 0.24% P [47]. Potentiodynamic polarization studies conducted on phosphated steels reveal that the critical current density for the formation of the phosphate layer can be higher by more than three

![Fig. 5. Mixed potential theory analysis for the enhancement in the passivity of the DIP in the presence of slag particles [7].](image)
orders of magnitude compared to that for steel without P [48]. Therefore, it is valid to indicate that the DIP iron will exhibit active–passive behavior on anodic polarization. It is important to stress that the exact nature of the passive film need not be known for this theoretical analysis, and only the formation of a passive film is required while considering the mixed potential analysis.

In case the DIP iron did not contain slag particles, the cathodic activation polarization line would have intersected the anodic polarization curve in the active region. This is reasonable, as relatively large currents are needed to induce passivity in iron containing P because the critical current density for passivation is very high in iron containing P [48]. However, in the presence of slag particles, the exchange current of the cathodic reaction(s) would be higher than in the case when there were no slag particles and the cathodic activation polarization line would shift to the right as shown in Fig. 5. Notice that current is depicted in the X-axis and not current density because this representation is useful in elucidating the effect of second-phase particles in inducing passivity on the DIP iron. A similar representation is also employed in Evans diagrams to understand area effects in galvanic corrosion using the mixed potential analysis [49]. Therefore, in the presence of second phase particles, the higher current demand of the cathodic reaction(s) will demand a higher corrosion current. In this process, the critical current density for formation of the passive film should be attained. Once this is achieved, the passive film covers the surface and the corrosion rate is reduced to minimum. Therefore, the presence of slag particles may be indirectly beneficial in the case of the DIP iron as it helps in the induction of passivity on the surface. The above mixed potential analysis was experimentally validated by potentiodynamic polarization studies using ancient Indian iron of different slag contents [6,7]. The above mixed potential theory analysis establishes that passivity can also be induced on the DIP iron due to the presence of second phase particles in the microstructure. The corrosion resistance of the DIP, therefore, has theoretical support.

Although the above discussion clearly establishes that the second phase particles in the DIP iron may be beneficial in inducing passivity, it should be borne in mind that alternate wetting and drying conditions are implied while considering atmospheric corrosion. As shall be presented later, this is a very important factor in the formation of the protective film at the metal–metaloxide interface. When iron, possessing similar second-phase particles (slags and oxides), is exposed to a more severe environment (for example, complete immersion in acidic or alkaline solution), rapid localized attack occurs at the second-phase–matrix interfaces, and the material corrodes at a much faster rate than normal mild steel. This has also been experimentally validated for ancient Indian iron by constant immersion corrosion testing and microstructural examination using a scanning electron microscope [20]. In the case of DIP iron, the importance of alternate wetting and drying conditions for its corrosion resistance can be gleaned by analyzing the available corrosion rate data. Wranglen [2] utilized the data of Hudson [1] (who obtained the same for mild steel exposed to Delhi’s environment) to estimate the thickness of the protective film that forms on the surface of the DIP. Assuming
parabolic growth kinetics, he predicted the thickness of the scale to be 200 μm after about 1600 years of growth [2]. The excellent match of the estimated thickness with that experimentally estimated by Bardgett and Stanners [3], using a permanent-magnet type thickness gauge, is proof that the film that forms on the surface is protective in nature as it grows according to parabolic kinetics. It is interesting at this juncture to note that the corrosion rates determined by constant immersion testing of DIP iron samples in 0.001% NaCl and 0.003% SO₂ solutions were 6 mg/sq dm/day (mdd) and 54 mdd, respectively [5]. Utilizing these values, it can be easily seen that had the pillar been completely immersed in an aqueous solution, it would have been corroded much more severely.

The age of the pillar has been stated as 1600 years in the above discussion. The pillar was constructed by Chandragupta II Vikramaditya (AD376–AD414), the Chandra mentioned in the oldest Sanskrit inscription on the DIP and one of the important monarchs of the Gupta Empire. The identity of Chandra has recently been analyzed based on numismatic, archaeological and literary evidence and it has been conclusively proven that the iron pillar should be dated towards the end of Chandragupta II Vikramaditya’s rule [11]. Assuming that the pillar was constructed in the first quarter of the fifth century AD, the pillar is at least 1600 years old.

4. Rust analysis

Rust samples were characterized by XRD [22], FTIR [22], and Mössbauer spectroscopy [22]. The salient results of the characterization studies are summarized. It must be again emphasized that the rust samples were obtained from the region just below the decorative bell capital and therefore, this must be the oldest undisturbed rust on the pillar as the area from where the rust was collected is inaccessible to the public.

The significant result of the XRD analysis of the DIP rust was the identification of iron hydrogen phosphate hydrate in the crystalline form. The FTIR study of the DIP rust clearly established that, in addition to iron hydrogen phosphate hydrate, the scale also consisted of γ-FeOOH (lepidocrocite), α-FeOOH (goethite), δ-FeOOH (misawite), magnetite and phosphates [22]. (The amorphous phase δ-FeOOH is termed misawite in this paper because of the pioneering studies of Misawa and co-workers [44,45] proving its existence and importance in weathering steels). The hydrated nature of these products was also indicated. It was also seen in the XRD pattern that there was a very small amount of iron oxide/oxyhydroxides present in the crystalline form. The identification of the oxide/oxyhydroxides of iron by FTIR clearly established that they are present in the amorphous form. The FTIR study also provided that phosphate ions were present in the rust, confirming the results of XRD. The Mössbauer spectroscopic study of the DIP rust samples proved conclusively that the oxyhydroxides and magnetite were present in the amorphous form and also that iron in the phosphate was in the +3 oxidation state. In summary, while XRD analysis proved the existence of
crystalline iron hydrogen phosphate hydrate, FTIR and Mössbauer spectroscopy proved the presence of magnetite and several oxyhydroxides in the amorphous form.

In order to understand the presence of the identified corrosion products in the DIP rust, the stabilities of these compounds were compared. The free energy of formation of the oxides and oxyhydroxides of iron, iron phosphate and phosphoric acid are provided in Table 2 [46]. Among the compounds listed in the table, the phosphates are very stable based on their relatively large negative values of free energy of formation. This has also been verified by noting that, in the ternary Fe–P–O phase diagram, the formation of phosphate is favorable even when only 0.24% P is present [47].

5. Process of protective rust formation

The process of protective film formation on the exposed surface of the DIP can be outlined based on the detailed characterization of DIP rust. It must be remembered that alternate wetting and drying conditions are implicit in the following discussion on atmospheric corrosion.

Initially, the corrosion of the matrix is relatively fast due to the presence of second phase particles in the microstructure. The usual corrosion products that are observed in the case of mild steels (exposed to atmosphere containing no chloride ions) are generated. It is well known that the corrosion products that form on iron on atmospheric exposure are $\alpha$-FeOOH (goethite), $\gamma$-FeOOH (lepidocrocite), Fe$_3$O$_x$ (magnetite) and X-ray amorphous matter [44,45,50]. In case of exposure to marine environments (i.e. where chloride ions are present), the formation of $\beta$-FeOOH (akaganeite) is favored [51]. In the case of DIP iron, the formation of lepidocrocite and goethite was confirmed by XRD analysis of 1.5-

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<th>Compound formula</th>
<th>Compound name</th>
<th>$\Delta G$ (kJ/mol)</th>
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<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>Hematite</td>
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</tr>
<tr>
<td>Fe$_{0.95}$O</td>
<td>Wüstite</td>
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</tr>
<tr>
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<td>Fe$_3$O$_4$</td>
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<td>−1014.2</td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>Goethite</td>
<td>−490.4</td>
</tr>
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<td>$\gamma$-FeOOH</td>
<td>Lepidocrocite</td>
<td>−471.4</td>
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<tr>
<td>$\delta$-FeOOH</td>
<td>Misawite</td>
<td>−</td>
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</tr>
<tr>
<td>Liquid</td>
<td>−1111.7</td>
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year-old rust from the DIP surface by Lahiri et al. [27]. It is also likely that the sample analyzed by them could have contained amorphous δ-FeOOH (misawite) as the formation of this phase during the initial corrosion of P-containing steel has been conclusively proven by Misawa and co-workers [44,45] utilizing FTIR. This has also been independently confirmed by other workers [52,53].

The initial enhanced corrosion of the matrix leads to the enrichment of P concentration at the metal–scale interface. In the presence of P at the interface between the metal and rust, the formation of a compact layer of amorphous δ-FeOOH layer next to the metal–metaloxide interface should be favored like that observed in the case of P-containing weathering steels [44,45]. Moreover, experiments have shown that H$_2$PO$_4$ ions prevent crystal growth of the corrosion products [44,45]. The formation of amorphous δ-FeOOH confers the initial corrosion resistance to the DIP iron. The δ-FeOOH phase forms in a discontinuous manner in normal mild steels whereas it forms a compact layer next to the metal–metaloxide interface in the case of P- or Cu-containing weathering steels due to catalytic action [44,45]. The superior corrosion resistance of P- and Cu-containing weathering steels has been attributed to this compact δ-FeOOH layer next to the metal surface, which is also enriched with the element(s) added to provide weathering resistance (i.e. Cu and P). This mechanism may not apply to Cr-containing weathering steels [54]. While the α-FeOOH and γ-FeOOH can be identified by X-ray diffraction, it is generally not possible to identify the δ-FeOOH phase by this characterization technique [44,45].

It is important to note that the oxyhydroxides and magnetite present in the old DIP rust are amorphous in nature and not crystalline. As it is known that the initial oxide and oxyhydroxides that form on the DIP iron are crystalline in nature [27], the long-term conversion of the crystalline forms of these oxyhydroxides to the amorphous form is indicated. The crystalline oxide/oxyhydroxides of iron are converted to the amorphous state by the process of alternate wetting and drying, as has been shown in P-containing weathering steel [44].

The enrichment of P in the δ-FeOOH layer continues with prolonged exposure and this has been observed in P-containing weathering steels [44,45]. This enrichment should be responsible for the precipitation of the insoluble phosphate identified by XRD. The process of formation of crystalline iron hydrogen phosphate hydrate would be understood based on the literature available on phosphating of steels [55,56]. This exercise would also be useful in further understanding the reason for the DIP’s excellent corrosion resistance.

Phosphating of iron is a commercially important coating method that involves the formation of relatively insoluble, electrically non-conducting thin films of metal phosphates on the surface. It is known that the formation of a protective phosphate layer on Fe surface involves the following four steps [55]. In the first step, electrochemical attack of iron by orthophosphoric acid occurs over a wide range of concentration and temperature. In the case of DIP iron, the formation of orthophosphoric acid next to the metal surface has to be first understood. The enrichment of P at this location was earlier established due to the initial corrosion
of matrix. Moreover, it is also important to note that the concentration of P is relatively higher near the surface regions of the DIP iron than within the bulk [32]. It was earlier noted that the surface regions of DIP contain a high amount of ferrite (depleted of carbon) which is due to the final surface finishing operation provided to the pillar during its manufacture [32]. It is known that P diffuses and concentrates in regions where C is depleted [28] and therefore, concentration of P is relatively higher near the surface regions of the pillar. Therefore, enrichment of P in the \( \delta \)-FeOOH layer is expected.

This P enrichment has been experimentally determined by Ghosh [5] who mentioned that the P content in the DIP rust was 0.35% whereas the P content in the DIP iron was 0.18%. The enrichment of P in the rust would initially result in the formation of phosphoric acid at the metal–metaloxide interface due to the presence of P at this location and also as free energy considerations favor its formation. The moisture for phosphoric acid formation is obtained in the alternate wetting and drying cycles. In contact with phosphoric acid, the dissolution potential of iron becomes less noble and it causes the dissolution of Fe to sparingly soluble dihydrogen phosphate according to

\[
2\text{H}_3\text{PO}_4 + \text{Fe} \rightarrow \text{Fe(H}_2\text{PO}_4)_2 + \text{H}_2
\]

The transient oxides of iron (in which Fe is in the +2 oxidation state) will also be corroded by phosphoric acid to provide \( \text{Fe(H}_2\text{PO}_4)_2 \) according to

\[
2\text{H}_3\text{PO}_4 + \text{FeO} \rightarrow \text{Fe(H}_2\text{PO}_4)_2 + \text{H}_2\text{O}
\]

Among the above two reactions, mainly the first one occurs [55].

In the second stage, the contact of the metal shifts the equilibrium in such a way that massive precipitation of monohydrogen phosphate \( \text{FeHPO}_4 \) and tribasic iron phosphate \( \text{Fe}_3(\text{PO}_4)_2 \) occurs. The precipitation reactions are

\[
3\text{Fe(H}_2\text{PO}_4)_2 \rightarrow \text{Fe}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4
\]

\[
\text{Fe(H}_2\text{PO}_4)_2 \rightarrow \text{FeHPO}_4 + \text{H}_3\text{PO}_4
\]

It is interesting to notice that iron is in the +2 oxidation state in these phosphates. Both these phosphates are insoluble in nature. Moreover, these phosphates are also amorphous in nature and this is well corroborated by experimental evidence [55].

In normal phosphating processes, the phosphating reactions generally discussed are up to the sequence of events provided above. In normal practice, other cations such as Zn or Mn are also added to phosphoric acid. In some cases, oxidizing agents are added so that iron may appear in the coating as ferric phosphate [56]. This is beneficial to corrosion resistance because the crystal reorganization of amorphous phosphates to ferric phosphates results in a large reduction in the porosity of the phosphate and subsequently, much improved protective properties [55].
The oxidation of iron to ferric phosphate can also be achieved by alternate wetting and drying cycles [55]. The $\text{H}_2\text{PO}_4^-$ ions accelerate the air oxidation of Fe$^{2+}$ to Fe$^{3+}$ under alternate wetting and drying cycles and prevents the crystal growth of the corrosion products [44,45,57–59]. Over time, Fe$_3$(PO$_4$)$_2$ is oxidized by atmospheric oxygen and H$_3$PO$_4$ to iron hydrogen phosphate hydrate according to

$$2\text{Fe}_3(\text{PO}_4)_2 + 8\text{H}_3\text{PO}_4 + (3/2)\text{O}_2 + 21\text{H}_2\text{O} \rightarrow 6(\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O})$$

In this compound, iron is in the +3 state and this can be understood if one considers the above reaction in parts as follows:

$$2\text{Fe}_3(\text{PO}_4)_2 + 2\text{H}_3\text{PO}_4 + (3/2)\text{O}_2 + 9\text{H}_2\text{O} \rightarrow 6(\text{FePO}_4 \cdot 2\text{H}_2\text{O})$$

$$\text{FePO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_3\text{PO}_4 + 2\text{H}_2\text{O} \rightarrow \text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$$

The dissolution and reprecipitation reaction also leads to a change in the pH of the metal–solution interface, which leads to a crystalline reorganization and followed, most importantly, by a large decrease in porosity. The crystalline reorganization is a very deep-seated reaction (at the metal–phosphate interface) because it modifies the porosity of the passive layer and decreases markedly the exposed metallic surface [55]. Therefore, the formation of the crystalline modification of iron hydrogen phosphate hydrate from the amorphous phosphate is critical in providing excellent protection against further ingress of moisture and oxygen to the metal surface.

The continuous layer of crystalline iron hydrogen phosphate hydrate (formed at the metal–metal oxide interface) is, therefore, responsible for the superior corrosion resistance of the DIP. Ghosh anticipated this mechanism in his excellent study of the DIP iron [5]. He stated that ‘P accumulates in a new phase at the base of the main oxide layer in the oxide form in combination with iron’ and ‘so long as the new phase at the base of the main oxide film was not formed, the metal behaviour was similar to that of the exposure surface of ordinary irons’ [5]. Ghosh performed some simple experiments with the DIP iron piece to assess the influence of P on rusting. The sample was polished and allowed to rust. When a thin and unequally distributed film of rust was formed, it was photographed and then slightly polished to remove the rust from the surface. This surface was treated with Stead’s solution to observe the distribution of P on the surface. It was found that P was generally low in the areas where rust appeared more intensely.

It is important to also note that the crystalline modification of iron hydrogen phosphate hydrate was obtained in the XRD analysis [22], thus indicating that the phosphate in the rust is relatively old. This validates the statement that the analyzed DIP rust must be the oldest rust on the pillar as it was obtained from a region inaccessible to the public (i.e. the region just below the decorative bell capital).

Alternate wetting and drying conditions play an important role in the case of atmospheric corrosion of the DIP because they accelerate the precipitation of
protective crystalline phosphate and the amorphization of the DIP rust. The amorphization of rust is also aided by the presence of $\text{H}_2\text{PO}_4^-$ ions [44,45]. The iron pillar’s weight is estimated to be approximately 6 tons and therefore, the large mass of the metal plays a contributory role in aiding the alternate wetting and drying processes. Sanyal and Preston [12] and, later, Bardgett and Stanners [3] proposed that the large mass of the pillar implies a large heat capacity and therefore, the pillar will heat up or cool down faster than the surroundings. This provides the right conditions of alternate wetting and drying of the iron pillar surface. The intensity (i.e. rate) of wetting and subsequent drying would be much more in the case of DIP iron because of the large mass of the pillar.

In summary, the phosphate film theory, originally presented by Ghosh [5] and elaborated in detail later [6,7], is valid. It is the crystalline iron hydrogen phosphate hydrate layer (and not amorphous as originally proposed [6,7]) at the metal–scale interface that is responsible for the excellent corrosion resistance of the DIP. The conclusion drawn is unambiguous as it has strong experimental support from DIP rust characterization.

6. Rust cross section

The process of protective film formation outlined above can also be understood by analyzing the only published cross section microstructure of the DIP rust [5]. The rust was obtained from the buried underground region when the pillar was excavated in 1961. The stone platform currently seen around the base of the pillar was not present until the middle of the nineteenth century [60]. It was erected by Beglar [61] after he explored the underground regions of the courtyard area where the iron pillar is located. When the pillar was re-erected by Beglar, the stone platform was constructed and a coating of lead was provided on the buried underground surface of the pillar. This uneven coating of lead (of about 3 mm in thickness) was found to be in an excellent state of preservation when the buried region of the pillar was again excavated in 1961 on the eve of the centenary of the Archaeological Survey of India [26]. However, the buried portion was found covered with rust layers ranging from a few mm to 15 mm [5,26]. Interestingly, there were numerous cavities and corrosion pits were also observed on the surface. The composition of the rust in the buried underground was chemically analyzed and they were found similar to the rusts obtained above the ground [5]. The soil samples in the nearby vicinity was found loaded with soluble sulfates and chlorides [26]. The iron in the buried regions is corroded more than the exposed surface due to the galvanic action with the lead layer, as lead is cathodic with respect to iron [23]. Simulation experiments conducted with lead-coated mild steel in soil environments [62] has clearly established the deleterious nature of the lead coating as the corrosion is intense in areas where coating defects exist. Under such circumstances, it is anticipated that cross sectional analysis of the rust layer in the buried underground would provide a picture of the rust nature, but on an amplified scale. (A new lead coating was provided on the pillar in the buried
underground region when it was relaid in a new foundation in the 1960s, much against the wishes of the Chief Chemist of the Archaeological Survey of India [26]. Therefore, the iron in the buried underground region is currently subjected to intense galvanic corrosion. It is important to replace this lead coating with another suitable coating for proper preservation of this important cultural and scientific object.

It is also to be noted that the surface film that forms on the iron pillar in the buried underground region would be slightly different from that which forms on the exposed surface. This is due to the restricted nature of the buried soil environment. Under conditions of restricted oxygen supply, it is well established that the major corrosion product on iron is magnetite [44]. Such a situation should be obtained in the case of the DIP rust in the buried underground regions. Ghosh analyzed a sample of rust from the buried underground region and it was seen that it was essentially magnetic in nature, based on the attraction of the rust to a magnet [5]. It is not possible to conclusively prove that the magnetic portion is entirely composed of magnetite as the other oxyhydroxides of iron are also paramagnetic [63] and therefore will also be attracted to a magnet. The magnetic portion of the rust was analyzed by XRD and it was shown to consist of magnetite in addition to lepidocrocite and goethite [5]. Ghosh did not mention the relative amounts of these phases based on the XRD study as he was quoting the results of the XRD work done at Bern. However, it can be reasonably predicted that a higher amount of magnetite must have been present in the rust obtained from the buried underground when compared to that obtained in the exposed regions. Apart from this the nature of the phosphate layer should be different on the exposed and buried surfaces of the DIP.

The rust from another ancient Indian iron clamp taken from the buried conditions in a stone block were earlier analyzed and the results of its rust characterization provide valuable insights into the possible nature of the rust in the buried underground regions of the DIP. This is important as both of these irons were in a restricted environment. The Eran rust did not exhibit any characteristic diffraction lines as they were diffused in nature, which indicated that the corrosion products in the rust were in a fine state of aggregation. However, FTIR spectroscopy revealed the presence of \( \alpha \)-FeOOH, \( \gamma \)-FeOOH, \( \delta \)-FeOOH, magnetite and phosphates [21]. Mössbauer spectroscopy of the rust confirmed the amorphous nature of the oxyhydroxides and indicated that magnetite was doped with some ions [21]. Scanning electron microscopy of the cross section of the rust indicated that it composed of a loose outer layer and an adherent inner layer [21]. Compositional analysis using an electron probe microanalyzer indicated that the inner rust layer was enriched in P and the concentration of P was maximum at the metal–metaloxide interface [21]. It was concluded, based on the rust analysis, that the inner layer providing the protection was \( \delta \)-FeOOH in the amorphous form and this was enriched in P at the metal–metaloxide interface. Although the presence of phosphates was indicated in the FTIR spectrum, they could not be identified by XRD and therefore, it is clear that the phosphate layer that was present must also have been amorphous in nature. Moreover, they must be
present at the metal–metal-oxide interface based on the compositional analysis of the rust. It was earlier seen that the phosphates that form on the surface of steel are generally amorphous in nature and the formation of crystalline phosphate (which incidentally is the most protective due to its low porosity content) takes place either in the presence of oxidizers or due to a large number of wetting-and-drying cycles (i.e. by the process of dissolution and re-precipitation) [55].

Therefore, in addition to the phases identified by Ghosh in the rust layers in the buried underground portion of DIP, the presence of amorphous phases like $\delta$-FeOOH and amorphous phosphates is likely. XRD analysis would not have revealed these phases. Having established the general similarities in the rust that forms above and below the ground on the DIP, it is illuminating to view the published microstructure of the rust formed in the underground buried regions of the DIP [5]. It is reproduced in Fig. 6. It is clearly noticed that the rust is composed of three distinct layers, with the outer layer (marked A) being optically active while the inner two layers (marked B and C) being optically dull. The inner most layer (marked C) is present as a thin layer next to the metal–metaloxide interface. The layered structure of the protective rust in weathering steel is well established [44,45,54]. Regarding the optical nature of the layers on weathering

Fig. 6. Cross section of DIP rust in the buried underground [5]. Note the presence of three distinct layers in the rust with the inner two layers being optically dull indicating their amorphous nature.
steels, Okada et al. [64,65] pointed out that the inner optically isotropic layer of the surface rust is composed of X-ray amorphous spinel type iron oxide which can protect the steel matrix. Yamashita et al. [54] also observed, by microscopic observation using reflected polarized light and crossed nicols, that the rust layer present on a weathering steel exposed for 26 years could be divided into two parts: an outer layer which was optically active (i.e. illuminated) and an inner layer which was optically isotropic (darkened). On the other hand, the surface rust formed on mild steels was of the mottled structure consisting of the optically active and isotropic corrosion products [54]. It is also established that weathering steels obtain their protection due to the presence of the amorphous (dark) inner layer [54]. Therefore, based on the above studies, it is reasonable to state that the inner two layers seen in the underground DIP rust microstructure of Fig. 6 are amorphous in nature while the outer layer is crystalline in nature. The innermost thin layer seen next to the metal surface must be due to the precipitation of phosphates (most likely in the amorphous form as the rust did not undergo drastic alternate wetting and drying) because of the enrichment of P at this location. The optically dull layer appearing next (B) should correspond to δ-FeOOH. Of course, the major difference between the rust seen in the buried underground and above-the-ground portions is that there should be a lower amount of crystalline oxide/oxyhydroxides in above-ground rust due to alternate wetting and drying cycles. Moreover, the phosphate layer would be in the crystalline form in the above-the-ground dust on prolonged wetting-and-drying cycling. This is also corroborated by the characterization of DIP rust [22]. Therefore, Fig. 6 literally provides the visual picture for the nature of protective passive film that forms on the DIP. In the rust exposed to the atmosphere, the outermost two layers (A and B) would be optically dull, while the two innermost layers (C) would be optically bright.

7. Color of rust

The color of rust on a freshly cut surface of the pillar exposed to the environment was studied by Ghosh [5]. He stated that in one year’s time, after the surface was freshly cut, some brown oxide could be removed by rubbing but an adherent thin layer of rust was formed, though very thin and unequally distributed. The oxyhydroxides of iron are brownish in color while magnetite is black in color [54]. After 14 months, a thin film was formed but again it was not uniformly distributed. After another 6 months (i.e. for a total of 20 months), the color of the film was almost the color of the main surface and the film was still thin and non-uniformly distributed. The rust was still bright at some places and rusting pits were also found, some of which could be removed by rubbing. At this point, the surface was rubbed with emery paper to remove the rust and this came off under slight rubbing though the pits remained. After another 15 months of this rubbing exercise, the surface was observed. The pits had smoothed out excepting one or two but the location was still bright and had not taken the color of the
surface nearby. The above studies clearly indicate that the formation of the protective film on the freshly cut surface takes time.

Ideas about the film formation can be obtained from the color of the growing rust on the DIP. The ASI has constructed an iron grill cage surrounding the DIP in 1997 to prevent visitors from damaging the pillar. The surface of the ‘metallurgically’ polished bright surface, occurring at a height of about 5 feet from the ground, (when the pillar was in intimate human contact) was photographed at periodic intervals to obtain insights on the rust formation. The presence of a rectangular metal insert at this location provided the reference frame. After about a year of the cage construction, the previously bright area was covered with a thin dark-brown layer which was adherent on the surface. In the location of the forge welded joints, the rust was black in color indicative of magnetite formation in these areas of enhanced corrosion caused by the presence of the interface. Interestingly, there were some regions above the polished region which were bright yellow in color. These observations are in conformity with that of Ghosh on the initial rust formation on the DIP. The results of Lahiri et al. further indicate that the rust must be composed of \( \gamma \)-FeOOH, \( \alpha \)-FeOOH and magnetite in addition to X-ray amorphous matter, as discussed earlier. Observations in early 2000 indicated that the rust layer was black in color. In some regions of the previously-bright surface, the color approached that of the undisturbed.

It is also interesting to note the color of the stable protective film that forms on the pillar after a long exposure to the environment. Some early observers of the pillar have stated that the pillar possessed a golden hue. When the DIP is viewed normally, it appears black in color with good reflectivity, indicating that the passive layer is relatively thin. However, when the DIP surface (especially the region inaccessible to the public, i.e., above the oldest Sanskrit inscriptions) is viewed at an acute angle in bright sunlight, the color of rust is yellowish-red in nature and it provides the visual effect of a golden hue. Interestingly, yellow specks can be seen distributed all over the rust layer and this is the crystalline phosphate. Therefore, the golden hue of the pillar is related to the nature of the protective passive film that forms on its surface.

### 8. Comparison of corrosion of DIP iron with weathering steels

The protective passive film that form on the DIP would be contrasted with the films forming on mild and weathering steels on atmospheric exposure. Structure-related issues of the rusts are discussed as the compositional factors have already been outlined earlier.

The rusting of normal mild steel and weathering steel is first addressed. When iron is exposed to the environment, the first oxides that form are the oxyhydroxides of Fe which are oxidized from Fe(II) complexes. Although several different allotropic modifications of the oxyhydroxides have been proposed to form on the surface of iron on initial exposure to the environment, there are firm evidences in the literature to suggest and prove that the first oxyhydroxide to
form is γ-FeOOH [44]. After this forms, a part of it begins to transform to another allotropic modification (α-FeOOH) and the rust at later times is composed of both these oxyhydroxides. Both these oxyhydroxides are not protective against corrosion and they readily crack allowing for ingress of oxygen and moisture to reach the metal surface and cause further corrosion. However, with time, a part of the FeOOH formed transforms to magnetic oxides of iron, which are much more protective than these oxyhydroxides [44]. There is also debate on the exact nature of the magnetic oxide that form on exposure of the iron to the environment. This is because the diffraction peaks of Fe3O4 and γ-Fe2O3 occur at the same location. However, Mössbauer studies of rust formed on steel exposed to the environment does indicate that Fe3O4 (more precisely called Fe1.5O4) forms first and this is later converted to γ-Fe2O3 [21]. The formation of this magnetic oxide results in protection and the oxidation (corrosion) rates decrease once these oxides form on the surface from the oxyhydroxides. In addition to α- and γ-FeOOH, there can be another oxyhydroxide of nature δ-FeOOH which can form on atmospheric exposure of iron. It is interesting to note that δ-FeOOH is generally amorphous in nature and therefore no diffraction peaks would be observed from this phase [44]. In ordinary mild steels, this phase does not develop as a continuous layer but rather in a discontinuous manner (Fig. 7) as it results from the dehydration–oxidation of the Fe(II) complexes [44]. Therefore, the δ-FeOOH that forms on ordinary mild steels is not protective in nature. However, it is possible for this δ-FeOOH to form, next to the metal surface, a continuous layer such that the steel obtains corrosion resistance (Fig. 7), as the oxyhydroxide is also amorphous in nature. The formation of δ-FeOOH as a continuous layer next to the metal surface is catalyzed by the presence of P and Cu in the material [44]. Moreover, the δ-FeOOH is enriched with P and Cu, elements that are added for improving atmospheric corrosion [44]. The presence of this amorphous layer is the reason for the excellent corrosion resistance of the weathering steels [44,45] although the time required for forming the protective layer is determined by the exposure conditions. Several schemes for the formation of rust on steels as a function of pH and environmental factors are available [44].

In the case of DIP, the process of protective rust formation has been outlined in detail earlier. The structure of the passive film on the DIP is also provided, schematically, in Fig. 7 for comparison with the films that form on mild and weathering steels. Cross sectional microstructural analysis of DIP rust (see Fig. 6) confirms the structure of DIP rust presented.

9. Conclusions

The nature of the protective passive layer on the corrosion resistant DIP has been addressed based on a detailed characterization of its rust. The rust is composed of iron hydrogen phosphate hydrate (FePO4·H3PO4·4H2O) in the crystalline form in addition to α-, γ-, δ-FeOOH and magnetite, all in amorphous form. The process of protective rust formation on DIP iron is outlined based on
the rust analysis. The passive film formation on the DIP has been contrasted with rusting of normal and weathering steels. The critical factor aiding the superior corrosion resistance of the DIP is the formation of crystalline iron hydrogen phosphate hydrate, as a thin layer next to the metal–metaloxide interface, which drastically lowers the rate of corrosion due to its low porosity content. The process of protective crystalline phosphate formation is aided by alternate wetting and drying cycles, which is an important contribution of the atmosphere to the DIP’s corrosion resistance. Therefore, the corrosion resistance of the Delhi Iron Pillar is due to both Delhi (the environment providing alternate wetting and drying conditions) and iron (with its high P content conferring protection by the formation of the crystalline iron hydrogen phosphate).

Fig. 7. Schematic comparing the rust structure formed on mild steel, weathering steel and Delhi iron pillar.
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References


