

Effect of material inhomogeneity on protective passive film formation on Delhi iron pillar

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The effect of compositional and microstructural material inhomogeneities on protective passive film formation on the Delhi pillar iron has been analysed. The material inhomogeneities do not affect uniform passive film formation. The important factor deciding the nature of protective passive film is the relatively high P content of the iron. Local variations in P content are not significant in determining the long-term nature of the protective passive film. The protective passive film mechanism for the excellent corrosion resistance of the Delhi iron pillar is valid for the known inhomogeneous Delhi pillar iron.

THE iron pillar (see cover page *Curr. Sci.*, 1997, **73**) located in the courtyard of the Quwwat-ul-Islam mosque, adjacent to the Qutub Minar in New Delhi is famous for its exceptional resistance to atmospheric corrosion. It has, therefore, attracted the attention of metallurgists and corrosion scientists, eager to unravel the mysteries of the pillar^{1,2}. The pillar was built during the reign of Chandragupta II Vikramaditya (375–413 AD) and was originally installed in front of a Vishnu temple in Udayagiri in Central India³. It was moved to its current location in Delhi sometime in the early 13th century AD⁴.

The pillar obtains its excellent corrosion resistance due to the formation of a protective passive film on the surface. The constituents of the protective passive film have been identified by modern characterization methods⁵. The protective passive film consists of crystalline iron hydrogen phosphate hydrate ($\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$), **a**, **g**, **d**FeOOH and magnetite. The iron oxide/oxyhydroxides are present in the amorphous form. The process of protective rust formation on the Delhi pillar iron has been explained based on rust analysis⁶. The Delhi pillar iron contains a relatively high percentage of phosphorus. Initially, the corrosion rate of iron is high due to the presence of entrapped slag inclusions. This results in enhancement of surface P content. The formation of a protective amorphous compact layer of **d**FeOOH is catalysed next to the metal surface in the presence of P, and this confers the initial corrosion resistance. The critical factor aiding the superior corrosion resistance of the Delhi iron pillar, however, is the formation of crystalline iron hydrogen phosphate hydrate, as a thin layer next to the metal–metal oxide interface. The formation and transformation of the amorphous phosphate to the crystalline

state is aided by alternate wetting and drying cycles (i.e. the environmental factor). As the porosity content of the crystalline phosphate phase is low, the rate of corrosion is significantly lowered. Additionally, repeated wetting and drying cycling results in conversion of the iron oxides and oxyhydroxides to nanosized and amorphous structures, which also reduces porosity in the external layer of the atmospheric rust.

The intimate co-relation between processing, structures, properties and performance is well-established in materials engineering. Therefore, the manufacturing methodology has a bearing on the corrosion resistance of the pillar. The Delhi iron pillar was manufactured by the forge-welding technique. The most likely manufacturing methodology, based on critical analyses of various aspects like hammering method, heating method, forging method, use of inserts, use of dies and ease of handling, has been described in detail elsewhere⁷. It is briefly described to provide an overview of the process. The starting material for construction of the pillar were individual iron lumps, extracted by the direct reduction process⁸. As all the lumps were not produced at the same time in the same furnace, it is important to realize that the compositions and microstructures of the individual pieces would not be precisely the same. However, the iron lumps were of fairly consistent quality, as attested by the known compositions of the Delhi pillar iron (Table 1). The heated iron lumps were placed on the heated side surface of the pillar and forge-welded using hand-held hammers. The addition of metal was sideways, with the pillar positioned in the horizontal direction. Visual and scientific proofs for this manufacturing methodology have been provided elsewhere⁷. Moreover, the entrapped slag inclusions in the iron are elongated⁹ along the vertical axis of the pillar, thereby indicating that the dynamic force was applied in a direction perpendicular to the vertical axis in order to forge-weld the lumps onto the pillar body. The vertical and horizontal movements of the pillar were aided by handling clamps provided on the surface of the pillar, the protruding portions of which were chiselled away during the surface-finishing operations. Finally, the surface of the pillar (that was supposed to be exposed and not buried underground) was smoothed by chiselling and burnishing, thereby providing it with a smooth, tapered and cylindrical appearance. Lastly, the Sanskrit inscription was inscribed on the surface of the pillar using cold dies. The decorative bell capital was finally fitted on to the top portion of the Delhi iron pillar, and the pillar erected in the main courtyard of the Vishnu temple.

The detailed description of the manufacturing methodology of the pillar has been provided in order to emphasize that the material of the pillar is not homogeneous. The total weight of the pillar is approximately 6000 kg, while each iron lump weighed between 20 and 40 kg (refs 7, 10). If the microstructures are obtained from sev-

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Table 1. Published composition analyses of Delhi pillar iron

	Hadfield ¹³ (1912)	Ghosh ¹¹			Lal ¹⁴ (1945)
		(1963) Above	(1963) Under	Lahiri <i>et al.</i> ¹⁵ (1963)	
C	0.08	0.23	0.03	0.26	0.90
Si	0.046	0.026	0.004	0.056	0.048
S	0.006	Trace	0.008	0.003	0.007
P	0.114	0.280*	0.436–0.48	0.155	0.174
Mn	Nil	Nil	Nil	Nil	Nil
N	–	0.0065			
Fe	99.720	Diff			99.67
Others	0.246				0.011
Specific gravity	7.81	7.672–7.747		7.5	

*0.100 fixed and 0.180 in solid solution P.

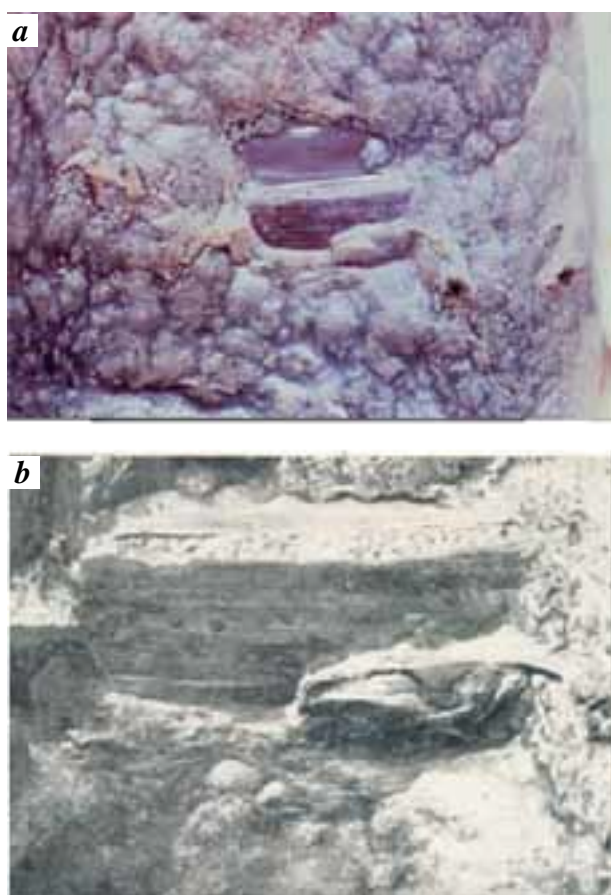


Figure 1. *a*, Location above the ground from where samples were obtained in December 1959. The same location, when examined in 1993, revealed that a uniform thin protective passive film has completely covered the previously-cut surface; *b*, Cut surface of the pillar photographed after removal of the sample in 1959 (ref. 11).

eral locations on the iron pillar (for example, by *in situ* metallography), they will exhibit wide variations. This inherent inhomogeneity in the material is not unique to the Delhi pillar iron, but, in fact, a common feature of ancient Indian irons¹¹. As the iron pillar obtains its excellent corrosion resistance due to the formation of a pro-

TECTIVE passive film, the effect of material heterogeneity (both compositional and microstructural) on the protective passive film nature must be understood. This is addressed in the present communication.

The earliest chemical analyses of the iron pillar material were performed by Murray Thompson from Roorkee Engineering College and Percy from the School of Mines, based on two samples sent by Cunningham¹². Both established that it was wrought iron of specific gravity 7.66. Hadfield¹³ published the first chemical analysis of the iron in 1912 and determined the specific gravity as 7.81, quite close to that of pure iron (7.84). Lal¹⁴, from the Archaeological Survey of India (ASI) published, in 1996, a report of a chemical analysis of the pillar iron which was originally conducted in September 1945 at the Laboratories of the Chief Metallurgical Inspector, Jamshedpur.

A detailed study of the Delhi pillar iron was undertaken by the National Metallurgical Laboratory (NML), Jamshedpur in the late 1950s. The buried underground regions of the pillar were excavated in 1961, on the eve of the centenary celebrations of the ASI, for observing the state of iron and related conservation activities. A sample from the buried underground region was obtained during excavations in 1961, and its chemical composition also analysed (Table 1). On 16 December 1959, two relatively large iron samples were removed from the pillar surface above the ground. The samples were taken from the Delhi pillar from a hump on the rough upper portion of the pillar (see Figure 1*a*). One small piece was obtained by a vertical cut along the surface and another piece was obtained by a partial horizontal cut with a hacksaw. The horizontally-cut piece was hammered-off from the surface by thrusting a chisel into the groove and in the process, grains of fracture were left on the surface of the pillar (Figure 1*b*). The outer surface possessed hammer marks and was dark brown in colour (Figure 2*a*). In one of the fractured corners (due to process of hammering to remove the sample), traces of rust were observed in an original cavity in the sample (Figure 2*b*).

The samples that were obtained from the rough region above the ground level are important because they were exposed to the atmosphere. Moreover, the surface, from where the specimens were removed, has been, ever since, exposed to the environment (Figure 1a). These iron samples were extensively characterized for their microstructure, composition, surface composition of minor elements and for the distribution of phosphorus and sulphur. Studies were conducted at the Tata Iron and Steel Company (by Ghosh and Visvanathan) and at NML (by Lahiri, Banerjee and Nijhawan). Moreover, a small sample (measuring approximately $1.1\text{ cm} \times 0.6\text{ cm} \times 0.4\text{ cm}$ and weighing 2.05 g) was taken from a larger sample (4.47 g) that was undergoing atmospheric tests at NML and provided to Bardgett of the United Steel Companies, UK and Stanners of the British Iron and Steel Research Association, UK for analysis of surface elemental compositions using a electron probe microanalyser. The results of these studies were published in a special volume of the *National Metallurgical Laboratory Technical Journal* (1963, V), appropriately called the 'Delhi Iron Pillar Number'. These studies are significant because they provide deep insights on the effect of material heterogeneity on protective passive film formation.

These are the available data sources, in which all information about the Delhi pillar iron is contained.

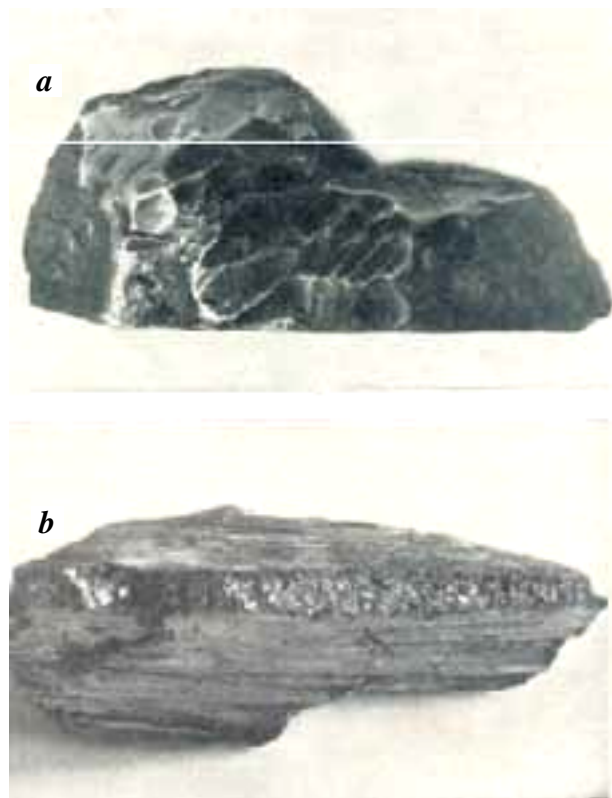


Figure 2. *a*, Surface appearance of the sample from the Delhi pillar showing hammer marks; *b*, Cut section of the sample (ref. 11).

The original saw-cut section of the sample removed in 1959 was first studied for sulphur segregation by the sulphur-printing method. It did not reveal any segregation of sulphur¹¹. When the same section was polished and etched with hydrochloric acid, the etching was heterogeneous (Figure 3a). This indicates non-uniform distribution of the entrapped slag inclusions. In order to reveal the distribution of phosphorus, the section was again polished and etched with Stead's reagent. After treating with this reagent, regions poor in P are revealed by the deposition of copper, while regions rich in P do not exhibit Cu-deposition. In the case of the Delhi pillar sample, copper deposits were observed only at cavities and spongy areas¹¹ (Figure 3b), thereby indicating that a relatively high amount of P was present on the surface, although there existed point-to-point variations in the same.

The available compositions of the pillar iron are provided in Table 1. Hadfield published the first chemical analysis in 1912 (ref. 13). Lal's analysis was performed in 1945, but published only in 1996 (ref. 14). The pieces that were cut out from the Delhi iron pillar were also chemically analysed by Ghosh¹¹ and Lahiri *et al.*¹⁵. They both reported high P content in the Delhi pillar iron. The results of Ghosh (for the sample obtained from above the ground level) are particularly important because they were obtained from specimen shavings that were machined along the cut surface (Figure 2b). Therefore, his analysis provides the macroscopic composition of the cut surface.

The actual analysis of the Delhi pillar iron varies with the source of the iron, as can be noticed in Table 1. Although the carbon and phosphorus contents vary depending on location, it is established from the known

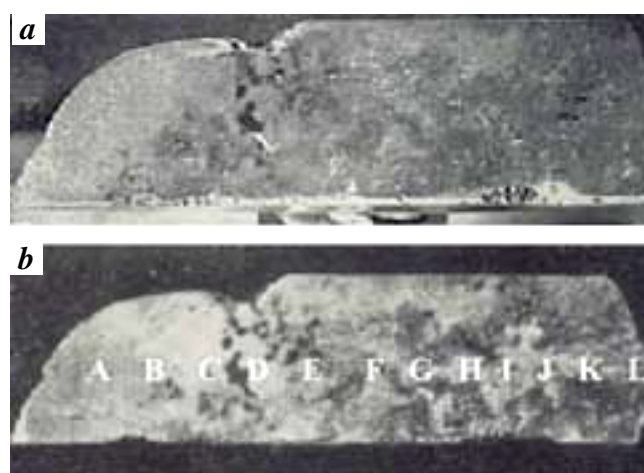


Figure 3. *a*, Heterogeneous etching of the Delhi pillar sample section using HCl as etchant, indicating non-uniform distribution of entrapped slag inclusions¹¹. *b*, Polished section after etching in Stead's reagent¹¹. Bright regions are those where P content is higher. Variation in P content and the relatively high percentage of P in the surface must be noted. Microstructures marked at the letter locations are provided in Figure 6.

analyses that the carbon content is relatively low and the phosphorus content is relatively high in the Delhi pillar iron. Variation in carbon content is due to the variation in different heats as well as spot-to-spot variation in the same heat¹¹. The non-uniformity is due to the solid-state direct reduction method of producing iron in ancient India⁸. Interestingly, Hadfield¹³ published detailed analyses of several iron specimens from Sri Lanka dated to the fifth century AD. For example, an iron nail (specific gravity 7.69) contained traces of carbon, 0.11% Si and 0.32% P; an iron chisel (specific gravity 7.69) contained traces of carbon, 0.12% Si and 0.28% P; and an iron bill hook (specific gravity 7.50) contained traces of carbon, 0.26% Si and 0.34% P. The higher phosphorus and lower carbon content in these iron samples must be noted. The origin of high phosphorus content in ancient Indian irons has been analysed elsewhere⁸. The high P content results because of the absence of CaO in ancient iron-making slags, thereby lowering their efficiency of dephosphorization. Limestone was not charged in ancient furnaces unlike modern blast furnaces and, therefore, a higher P content resulted in ancient irons. In modern technology, high P content cannot be tolerated because it leads to embrittlement of the material during cold working operations, the phenomenon being termed as 'cold shortness'^{16,17}. This problem must have been overcome in ancient forge-welding operations by hot-working the iron lumps. Therefore, the higher P content of the Delhi pillar iron also provides important clues to its method of manufacture, i.e. by hot-working. In the operation of heating the lumps and subsequent hot-working, there was loss of carbon from the surface regions (as revealed by the predominantly ferritic microstructure in the near-surface regions). Moreover, phosphorus will segregate to regions that are poor in carbon¹⁸, and therefore enrichment of P in the surface regions is an added consequence of the hot-working process.

The major portion of P in the Delhi pillar iron is in solid solution. Chemical analysis showed that out of the total 0.28% P, only 0.10% was in the fixed form (i.e. in the entrapped slags as phosphates), with the rest (0.18%) in solid solution¹¹. Experiments conducted by Ghosh to assess the influence of P on the rusting process are revealing. It is important to note that these experiments were conducted on the surface of the sample that was cut from the pillar and therefore, the analysis also applies to the surface of the pillar from where the piece was taken, as this is a mirror image of the cut sample surface. The piece of iron pillar was polished and allowed to rust. A thin and unequally distributed layer of rust formed on the surface initially (Figure 4a). The same piece was slightly polished to allow for removal of the rust only, and the surface was etched with Stead's agent to observe the distribution of P on the surface. It was found that generally copper deposited on spots where the rust appeared more intensely (Figure 4b). Therefore, Ghosh rightly con-

cluded that as long as the new phase did not appear at the base of the oxide film, corrosion behaviour of the Delhi iron was similar to that of normal irons. This experiment also demonstrated that short-term tests (like *in situ* aqueous electrochemical tests) will not be useful in concluding information about the long-term atmospheric corrosion of Delhi pillar iron.

The published microstructures of the Delhi iron pillar exhibit a wide variety of structures; these will be discussed now.

The first published structure of the pillar iron by Hadfield¹³ in 1912 (Figure 5) revealed that the material was almost pure iron. The grain size ranged between 47 and 380 μm . Entrapped slag inclusions were not identified in his published micrograph. Based on the microstructural and composition analyses of the pillar iron, Hadfield stated that the iron was designed to be corrosion-resistant and suggested that 1600 years ago, metallurgical knowledge existed for manufacturing corrosion-resistant steels¹³. He also opined that the Delhi pillar iron was one of the purest samples of steel that he had studied. Hadfield measured the density of the iron sample that was taken from the pillar as 7.81, thereby indicating that the particular sample obtained by him was relatively free of slag inclusions. The presence of entrapped slag inclusions reduces the density of ancient iron.

Nearly half a century elapsed after Hadfield's study before other microstructures of the Delhi pillar iron were published in 1963, utilizing the cut samples obtained in 1959. One of the saw-cut sections was prepared and examined under a microscope¹¹ (Figure 3b). In the unetched condition, slag particles were distributed rather hetero-

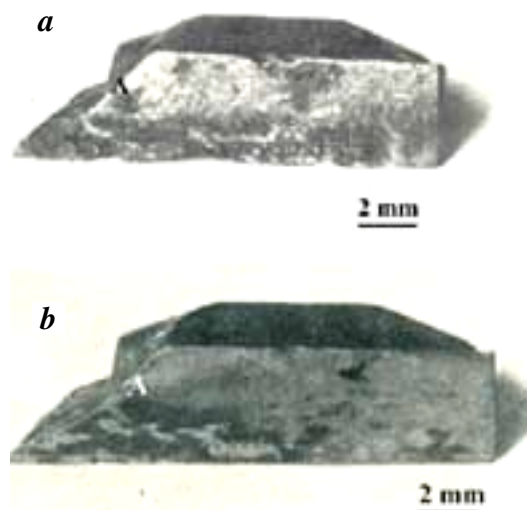


Figure 4. *a*, Non-uniform development of rust on polished surface of Delhi pillar iron sample¹¹; *b*, Distribution of P on the surface of the Delhi pillar sample after removing the rust seen in (*a*) and etching with Stead's reagent¹¹. P content is higher in locations where the rust layer did not appear prominently.

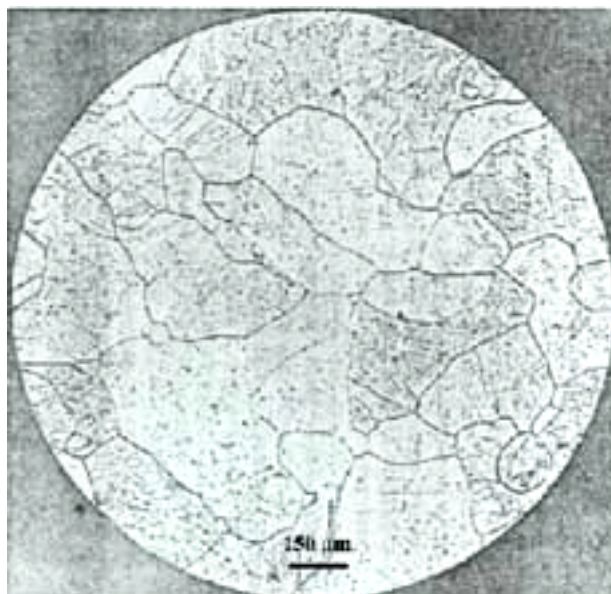


Figure 5. Microstructure of Delhi pillar iron (Published by Hadfield¹³).

generously all over the surface. The presence of entrapped slag inclusions was also indirectly indicated by the lower specific gravity (7.672 to 7.747) measured by Ghosh¹¹. The highly heterogeneous nature of the material was revealed by etching and studying the structure in an optical metallograph. The microstructures obtained at the locations marked in Figure 3*b* are provided individually in Figure 6. Entrapped slag inclusions are clearly visible in Figure 6*b*, *f* and *g*. Coarse grains of ferrite were observed near the surface (Figure 6*c–e*), and they generally possessed slip bands (Figure 6*d*). The surface was free from pearlite (Figure 6*a* and *b*). Small-to-medium grains of ferrite were seen in the next area along with a small amount of pearlite at the grain boundaries (Figure 6*f–h*). The amount of pearlite increased on progressing towards the interior (Figure 6*h* through *l*). In some locations, nitride needles were also observed at the grain boundaries between coarse pearlite (Figure 6*c* and *e*). The hardness obtained from various locations on the microstructure¹¹ further confirmed that the material microstructure was highly heterogeneous. It is important to emphasize that these locations within a relatively small sample exhibited such wide variations. Therefore, it is anticipated that microstructures obtained from several different locations on the Delhi iron pillar will also reveal a wide variation. This is one of the basic features of ancient Indian irons¹¹ and the Delhi pillar is an excellent example of the same.

The heterogeneous nature of the Delhi pillar iron was also confirmed by Bardgett and Stanners⁹ by metallography. The general structure of the sample is shown in Figure 7*a*. As stated earlier, this sample was obtained by sectioning from a larger piece. The mating surface of this section is seen in Figure 4*a* and *b*. Location A, indicated in Figure 7*a*, has been marked in the mating surface

(Figure 4*a* and *b*). Bardgett and Stanners also noted the relatively large amount of entrapped slags in their microstructure. The slag inclusions were generally elongated in a direction parallel to the surface, i.e. along the vertical axis of the pillar. Based on the macrostructure, they commented that their sample did not exhibit such wide variations as exhibited in the sample (Figure 3*b*) analysed by Ghosh¹¹. However, they confirmed that the microstructures near the surface locations were almost pure ferrite with some slag (Figure 7*b*). The microstructures near large slag particles in the interior of the sample, exhibited microstructures typical of 0.1–0.2% carbon steel (Figure 7*c*). The microstructure in Figure 7*c* was analysed by image analysis for determining the percentage of pearlite and based on this, the carbon content was estimated as 0.17%. Bardgett and Stanners also observed peculiar ‘coring’-type of etching (‘ghost’ structures) in some grains. These are locations of high P content. The ‘ghosting’ effect following nital etching is typical of iron containing phosphorus¹⁶. The ‘ghosting’ phase is a differential etching effect resulting from local phosphorus enrichment, and this phase is commonly observed in phosphorus-rich ancient Indian irons¹⁹.

One of the samples that was cut from the Delhi iron pillar in 1959 was also analysed by Lahiri *et al.*¹⁵. The specific gravity of the sample was 7.5. The metallographic analysis of a small piece taken from the sample also revealed the heterogeneous nature of the iron. The presence of large slag particles was noted (Figure 8*a*) and Lahiri and coworkers stated that the sample showed extraordinarily high content of slag¹⁵. The distribution of pearlite was not uniform (Figure 8*b*). The microstructure in Figure 8*b* yielded a carbon content of 0.30% by image analysis. Lahiri *et al.*¹⁵ stated that microstructures exhibited carbon content from as high as 0.3% to completely carbon-free structures. Several regions were identified to be very rich in carbon (Figure 8*c*). The very high local carbon content in a few locations could have resulted in the structure observed in the middle of Figure 8*c*. Lahiri *et al.*¹⁵ attributed the non-uniform pearlite distribution to non-homogeneity in carbon and phosphorus contents. It is well-known that carbon diffuses out of regions rich in P¹⁸. Although they did not publish any micrograph of the structures next to slag inclusions, Lahiri *et al.* stated that the structure of the metal in the region adjoining the slag particles exhibited wide variations (Widmanstätten, normalized and annealed structures). The origin of the Widmanstätten structure was speculated to be due to prolonged holding of the spongy iron lumps at temperatures above the upper critical temperature range in order to forge-weld them¹⁵. They also confirmed the heavily deformed condition of the material by noting the presence of a large number of slip bands in the ferritic grains. The regions adjoining the surface, particularly, exhibited signs of heavy deformation. Sharp needles within the ferrite grains were speculated by Lahiri *et al.*¹⁵ to be

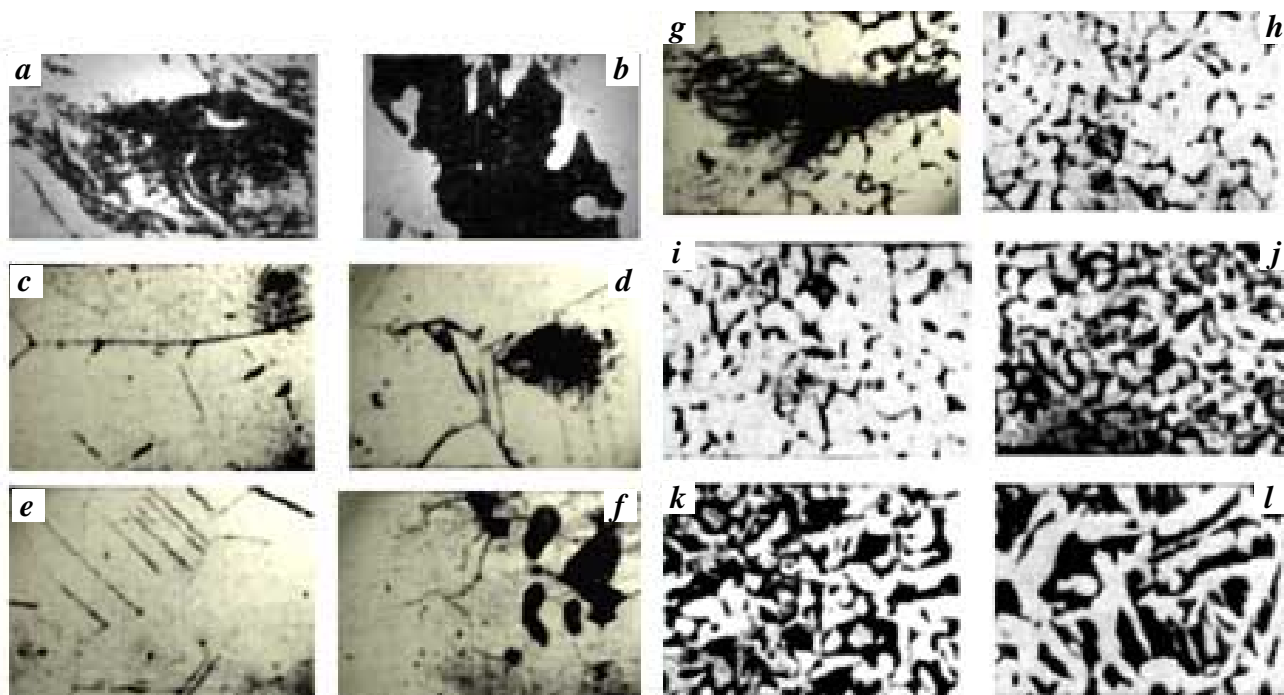


Figure 6. Individual microstructures¹¹ at locations marked in Figure 3 *b*: *a*, A; *b*, B; *c*, C; *d*, D; *e*, E; *f*, F; *g*, G; *h*, H; *i*, I; *j*, J; *k*, K and *l*, L.

either nitride or carbide. In the regions near the forge-welded joints, the slag inclusions were elongated and the structures resembled those of carbon-free wrought iron or mild steel. The forge-welded joints were also heavily deformed. Lahiri *et al.*¹⁵ concluded that the small piece of Delhi pillar iron exhibited wide variations in microstructures.

It is important at this juncture to note that the ancient Indian blacksmiths, particularly during the Gupta period, did not master the art of melting and casting iron, because the ancient iron-making furnaces could not attain temperatures required for melting iron and steel. Iron was produced by the direct reduction method, wherein the iron ore was reduced in the solid state by utilizing charcoal in bloomery furnaces⁸. Therefore, solidification structures will not be generally noticed in Delhi pillar iron. However, there is one location where solidification microstructures can be obtained and this is the region near the topmost surface of the pillar. The top surface of the pillar (see figure 14 in ref. 20) indicates evidences for metal flow. The local melting and solidification of the metal at this location may have presumably resulted due to lightning strikes on the top surface of the pillar during its lifetime. A similar feature was also observed by Anantharaman²¹ on the top portion of the iron pillar at Kodachadri hill.

It has been seen that the most important aspect of the Delhi pillar iron material is its inherent compositional and microstructural inhomogeneity. The non-uniform distribution of slag particles and phases in the structure is

a consequence of the direct-reduction iron-extraction method. Variations in local C and P contents manifest as variations in pearlite fractions in the microstructure.

The surface of the sample that was cut-out in 1959 is a mirror image of the surface on the pillar from where the sample was removed. Therefore, it is proved that the inhomogeneity observed in the structure of the cut samples (Figure 6) would also be present on the surface of the pillar from where the pieces were taken (Figure 1*b*). Variations in local C and P contents on the surface of the pillar must be similar to those of the cut section. In spite of these local variations in microstructure and composition, an important observation is that the surface is now uniformly covered with a protective passive film (Figure 1*a*). The uniform coverage of the protective passive film is confirmed by the uniform optical appearance of the surface. Therefore, variations in microstructures are not reflected in the nature of the protective passive film. This implies that even if the underlying structure of the iron pillar is heterogeneous, the protective passive film will cover the surface uniformly. Interestingly, Ghosh mentioned that an earlier cut made on the pillar in 1956 by NML was not visible when observed in 1959, because it had acquired the uniform colour of the entire pillar. A direct proof for the lack of effect of material inhomogeneity on protective passive film nature was provided earlier⁵. Old rust samples obtained from two different locations just below the decorative bell capital of the Delhi pillar were analysed by modern characterization methods and the rusts from these different locations were

similar in nature⁵. This conclusively proves that the nature of the protective passive film is relatively uniform, irrespective of the underlying material structure.

The heterogeneous microstructure plays a role in the initial stages of atmospheric corrosion. The rate of corrosion is relatively high in the initial stages due to the presence of the entrapped slag inclusions. Enrichment of P at the metal–metal oxide interface is aided by the initial high rate of corrosion of iron⁶. The role of entrapped slag inclusions in aiding passive film formation by modifying the complementary cathodic reactions has been analysed earlier by the mixed potential theory²². The important factor that determines passive film formation is the relatively high P content of Delhi pillar iron. Although there

are variations in the local P content, the overall P content of the Delhi iron pillar material is quite high (Table 1). The non-uniformity of P content evens out over longer periods of atmospheric corrosion due to the enrichment of P that occurs at the metal–metal oxide interface, which results in protective passive film formation⁶. The mechanism by which the accumulated P, at the metal–metal oxide interface, results in protective film formation has been described in detail elsewhere⁶. The enrichment of P is further carried over to the rust, as the analysis of Ghosh¹¹ has revealed that the rust of the Delhi pillar contains a higher amount of P than the metal. In the case of ordinary mild steel, he determined that %P in the metal was 0.028, while that in the rust 0.072%. Utilizing

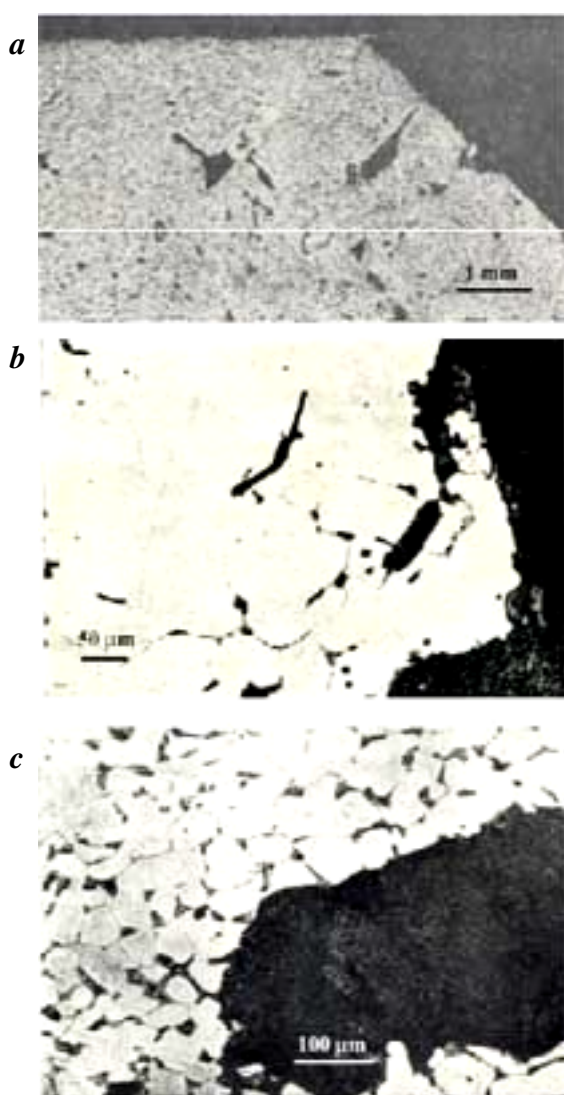


Figure 7. Heterogeneous nature of the Delhi pillar iron confirmed by Bardgett and Stanners⁹. *a*, General structure of the sample; *b*, Microstructure at location A near the surface showing almost pure ferrite with some slag, and *c*, Microstructure at position B near the large slag particle showing microstructures typical of 0.1–0.2% carbon steel. ‘Ghost’ structures observed in some grains indicate locations with high P content.

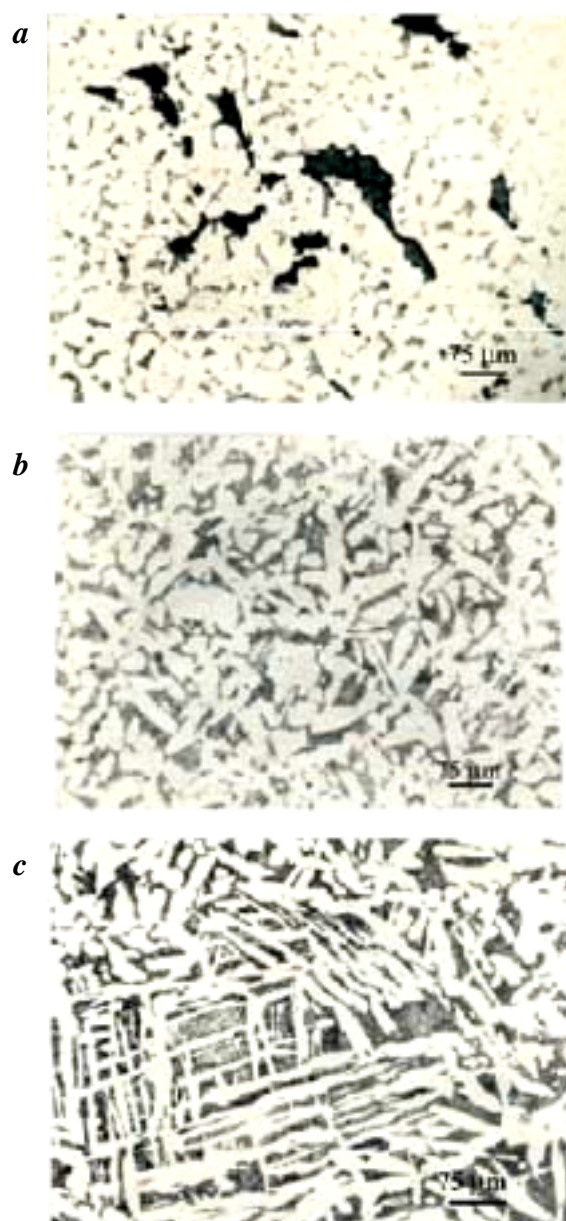


Figure 8. *a–c*, Microstructures of the Delhi pillar iron (Published by Lahiri *et al.*¹⁵).

the same method of analysis, he determined that while the %P in the metal of Delhi pillar was 0.18 (in solid solution), the same in the rust of the Delhi pillar was 0.35%. Therefore, although there was P enrichment in both the rusts, higher amount of P in the Delhi pillar iron resulted in a higher P content in the rust of the pillar.

It is important to note that sufficient atmospheric exposure is required before a uniform protective passive film is formed. Short-term immersion testing and polarization studies will not reveal the characteristics of passive film formation on the surface due to atmospheric exposure¹¹. The kinetics of the protective passive film formation on the Delhi pillar has been analysed recently, by considering the known thickness of the protective passive film on the surface and visual observation of protective passive film growth on the surface²³. It has been concluded that approximately three years will be required for the initial formation of the protective film. Once the protective passive film forms, it grows and covers the surface, and the underlying microstructural variations may be of no consequence. This conclusion is also in agreement with well-established science that surface-sensitive properties like general corrosion and passive film formation in ambient temperature aqueous corrosion or protective oxide formation in high-temperature oxidizing conditions are significantly dependent on the composition of the underlying material, with the material microstructures generally playing only a minor role^{24,25}.

In summary, the microstructural and compositional inhomogeneities of the Delhi pillar iron do not have any influence on the protective passive film that forms on the surface. The deciding factor that is important in imparting the excellent corrosion resistance is the high P content of the Delhi pillar iron.

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ACKNOWLEDGEMENTS. I thank the Archaeological Survey of India for co-operation during my studies on the Delhi iron pillar and Mr S. Sankaran from my department for efficient technical assistance with image analysis.

Received 23 August 2002; revised accepted 7 November 2002

Photocatalytic oxidation of As(III) to As(V) in aqueous solutions: A low cost pre-oxidative treatment for total removal of arsenic from water

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Nonionic nature of As(III) in aqueous solutions, pH less than nine makes it a difficult form of arsenic which cannot be efficiently removed from drinking water by conventional ion exchange and adsorption chromatographic techniques. In the presence of TiO₂ photocatalyst and UV radiation, nonionic H₃AsO₃ can be readily oxidized to the anionic form of As(V) with no formation of metallic arsenic. The rate of oxidation is found to be less pH dependent. The suggested mechanism for the holes and electrons consuming steps are: $\text{H}_3\text{AsO}_3 + 2\text{h}^+ + 4\text{OH}^- \rightarrow \text{HAsO}_4^{2-} + 3\text{H}_2\text{O}$ and $2\text{H}^+ + 2\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O} + 3/2\text{O}_2$ respectively.

HETEROGENEOUS photocatalytic mineralization has been studied extensively by many research workers as a non-toxic purification technique for water contaminated with heavy metals and organic pollutants^{1–3}. Removal of heavy metal pollutants such as mercury⁴ is based on photocatalytic reduction with the deposition of metallic

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