

## NEW INSIGHTS ON THE 1600 YEAR-OLD CORROSION RESISTANT DELHI IRON PILLAR

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*(Received 11 May 2000; after revision 24 November 2000)*

The 1600-year old Delhi Iron Pillar has attracted the attention of metallurgists and corrosion scientists for its excellent resistance to corrosion. The present paper summarizes new insights on the Delhi Iron Pillar based on the researches of the author. The paper will first address the identity of Candara and the original location *Viṣṇupadagiri* of the pillar, both of which are mentioned in the oldest Sanskrit inscription on the pillar. Analysis of the archer-type gold coins of the Imperial Guptas provided that Candara should be identified with Candragupta II Vikramāditya. The original location of the pillar has been identified as Udayagiri in Central India based on archaeological evidences. The engineering details of the pillar have been described, including the decorative bell capital of the pillar. The presence of a lead in the pillar has also been analyzed. The manufacturing method of the pillar by side way forge-welding small lumps of iron with the pillar resting in the horizontal position has been described. Finally, the corrosion resistance of the pillar has been addressed. The earlier theories of corrosion resistance have been briefly reviewed along with the microstructure of the DIP iron. The results of a detailed characterization of the DIP's rust have been summarized. Rust characterization clearly established that the major constituents of the scale were crystalline iron hydrogen phosphate hydrate ( $\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ),  $\alpha$ -,  $\gamma$ -,  $\delta$ -FeOOH and magnetite. The iron oxide/oxyhydroxides were present in the amorphous form. The role of slag particles in the matrix of

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the DIP iron in enhancing the passive film formation has been briefly addressed initially. The process of protective rust formation on DIP iron has been outlined based on the rust analysis. Initially, the corrosion rate of iron is high due to the presence of the slag particles. This results in enhancement of surface P content. In the presence of P, the formation of a protective amorphous compact layer of  $\delta\text{-FeOOH}$ , next to the metal surface, is catalyzed 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 iron hydrogen phosphate hydrate, as a thin layer next to the metal-metaloxide 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 Delhi Iron Pillar has been contrasted with rusting of normal and weathering steels.

**Keywords:** Corrosion resistance, Decorative bell capital, Delhi Iron Pillar, Forge welding, Iron hydrogen phosphate, Lead presence, Microstructure, Mixed potential theory, Passive film, Sanskrit inscription,

## INTRODUCTION

The Delhi Iron Pillar (Figure 1) is testimony to the high level of skill achieved by the ancient Indian iron smiths in the extraction and processing of iron. It has attracted the attention of archaeologists and corrosion technologists as it has withstood corrosion for the last 1600 years. It is singularly featured on the emblem of both the National Metallurgical Laboratory and the Indian Institute of Metals, thereby signifying its prime identity as the country's metallurgical pride and heritage. The first systematic scientific study of the Delhi Iron Pillar (DIP) was undertaken by Hadfield.<sup>1</sup> Ever since, there have been a growing number of studies where several aspects of the DIP have been discussed. In the centenary year of the Archaeological Survey of India in 1961, the Delhi Iron Pillar was studied in detail with the co-operation of the National Metallurgical Laboratory (NML).

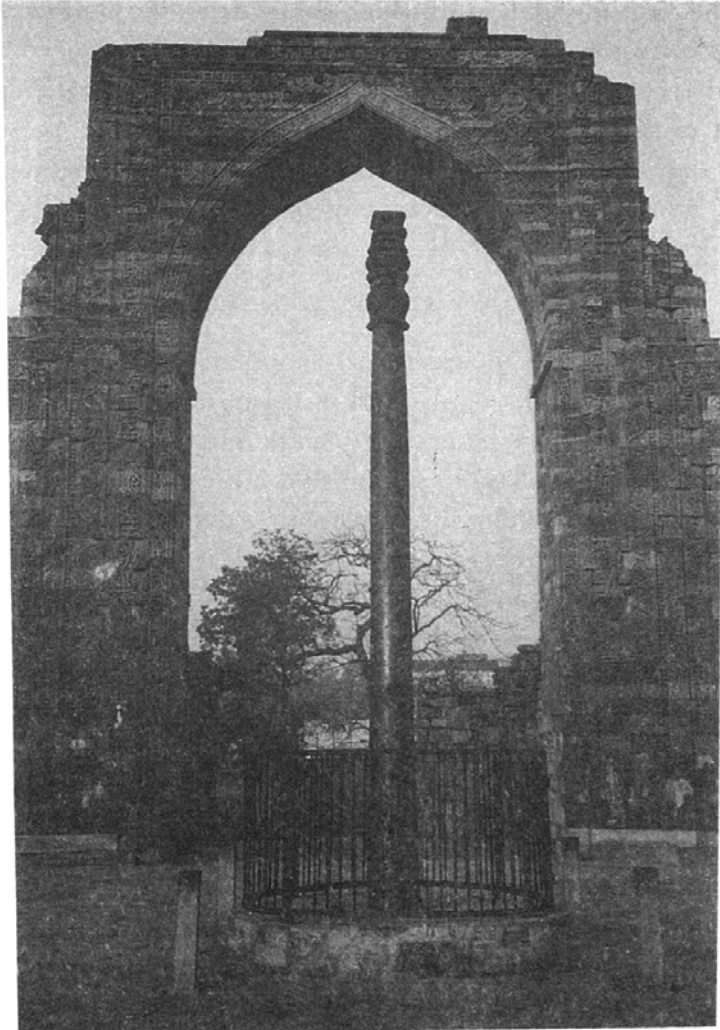


Figure 1: The Delhi Iron Pillar. Notice the iron grill cage around the pillar bottom that has been recently constructed.

The buried underground region of the pillar was examined by archaeological excavation. Moreover, a relatively large iron sample was obtained from the pillar and subjected to several metallurgical analyses at the NML. The results of these scientific studies have been summarized in a special issue of the *NML Technical Journal* (Volume 5, 1963). These studies

provide the firm foundation of which future scientific studies of the DIP were based. A review of the pillar's corrosion resistance later appeared in 1970<sup>2</sup> and recently, the known scientific facts about the DIP have been published in the form of a book by Anantharaman.<sup>3</sup> The present paper will focus on new research insights on the DIP based on research carried out at IIT Kanpur in the last decade of the last millenium.

### HISTORICAL IDENTITY OF CANDRA

Among the several inscriptions on the pillar, the oldest (and also the largest) is a three-stanza six-line Sanskrit inscription (Figure 2), at a level of about 7' from the stone platform, which states that the pillar was erected as a lofty standard in a Viṣṇu temple on a hill called Viṣṇupadagiri by a king having the name of Candra. The theories that have been proposed to identify Candra have been critically reviewed elsewhere.<sup>4</sup> Based on the nature of the Brāhmī characters, the inscription must be dated to between 400 and 450 AD. Therefore, the Iron Pillar was constructed during the rule of the imperial Guptas in ancient India. The imperial Gupta monarchs were Candragupta I, Śainudragupta, Candragupta II, Kumāragupta I and Skandagupta.

In order to identify Candra, numismatic evidence would be presented. The inscription clearly tells that the king had the name Candra and this is the most important clue to determine his identity. There are several gold coin types in which Candragupta II Vikramāditya's short name of Candra is inscribed. This line of argument has already been stated by many commentators, but this argument alone is not sufficient. The additional crucial argument for the unambiguous identification of Candra from numismatic sources is presented below. The most popular gold coin type which was issued by the Gupta monarchs from the time of Samudragupta was the archer type gold coin. In fact, the archer coin type seems to have been the only issue of some of the later Gupta monarchs. The obverse in these coins depicts the king with a bow and a short name of the issuing king (Figure 3). The Garuḍa emblem is another regular feature of these coins. The most interesting aspect about the archer coin type is that the

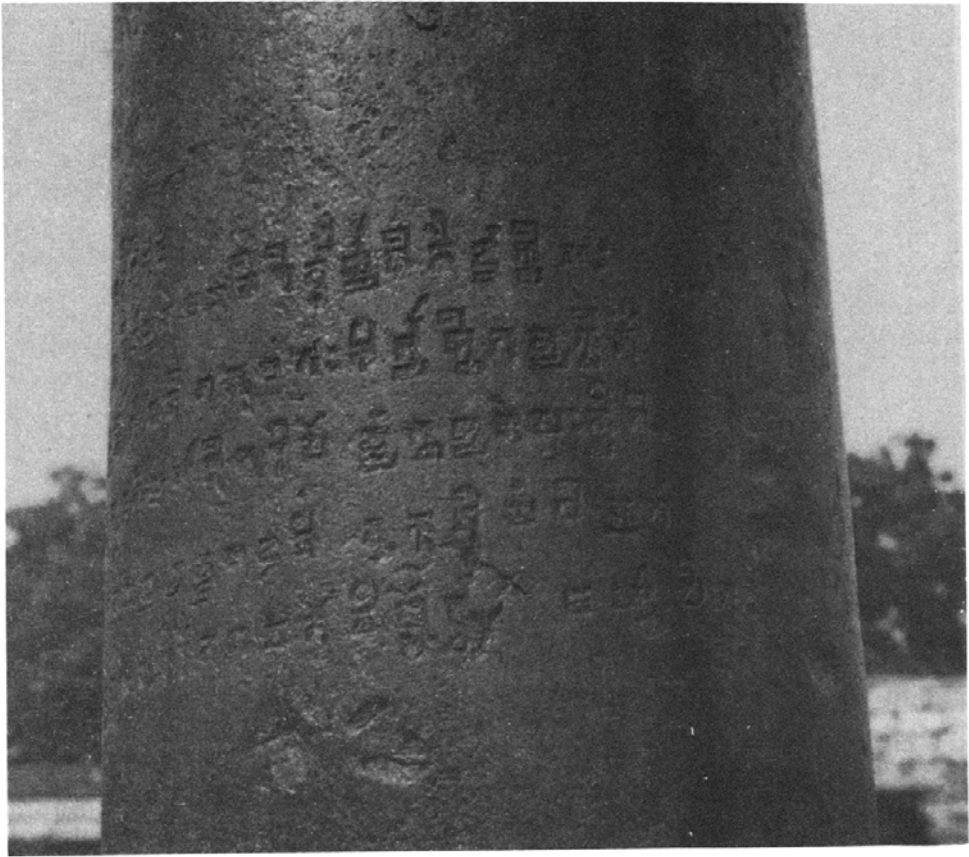


Figure 2: The oldest Sanskrit inscription in the Brāhmī script. Notice that the first line is shorter than the other five lines and that the letters exhibit minimal corrosion damage.

king's short name is inscribed in the obverse field (i.e. region of the figure) with the full name and title of the monarch provided in the circular legend. In the case of Samudragupta's archer coins, *Samudra* is found below his left arm clear of the bow. In *all* the different types of archer gold coins of Candragupta II, the short name of the king is inscribed as *Candra* while the king's complete title and name is provided in the circular legend. Therefore, it is amply clear that Candragupta II Vikramāditya was called in short as *Candra* and this is attested firmly by his most popular coin type. In the archer coins of Kumāragupta I, the king's name provided in the obverse

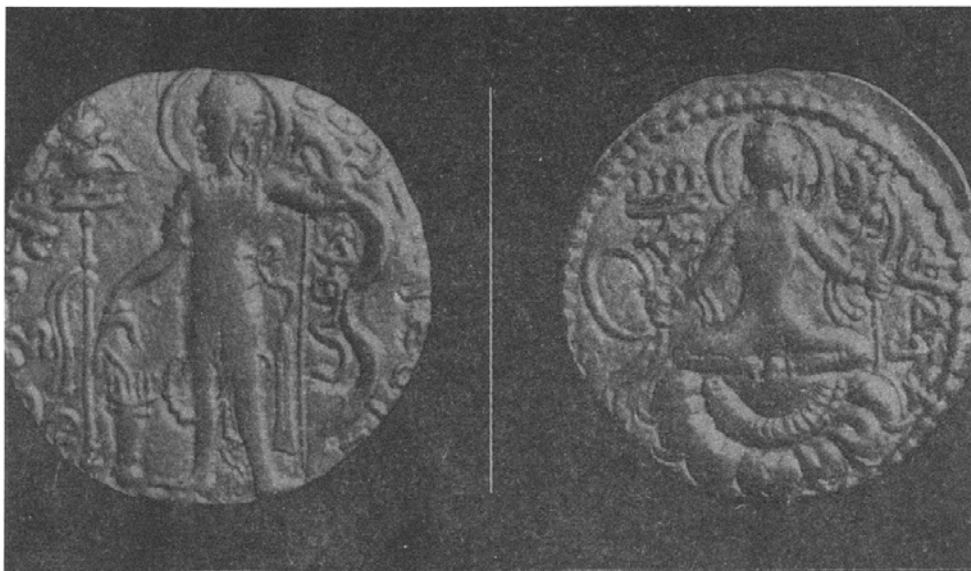


Figure 3: Archer-type gold coin of Candragupta II Vikramāditya. On the obverse, the short name (*Candra*) of the king is provided below his left arm while his full name appears in the circular legend. Photograph courtesy: Ellen M. Raven.

field is *Kumāra* or *Ku* or absent in some, but appearing as *Kumāragupta* in the circular legend. Kumāragupta's successor was Skandagupta, who also issued the archer coin type in which his name appears in the field as *Skanda* and his full name is provided in the legend in the obverse. The dates of the Gupta monarchs after Skandagupta and their line of succession are not known with certainty and therefore we shall not provide the dates. However, the existence of the later Gupta monarchs and rivals is provided from the archer coin types of the later Guptas.<sup>4</sup> One of the known rivals of Skandagupta by the name of Purugupta issued archer type coin with his name in the obverse field mentioned as *Puru* and the biruda *Śrīvikramaḥ* ("the valorous one") on the reverse. The rebellious son of Kumāragupta I, Ghaṭotkacagupta issued an archer type coin with his name *Ghaṭo* on the obverse field. Skandagupta was succeeded by Narasiṃhagupta I Bālāditya with his short name provided as *Nara*, and then he was followed by Kumāragupta II Kramāditya (with the short name *Ku* and the legend *Kramāditya* ("progress-sun") in the reverse. He was succeeded by Budhagupta

Vikramāditya whose archer coin type spells his name as *Budha* and the legend *Śrīvikramaḥ* on the reverse. Vainyagupta Dvādaśāditya succeeded Budhagupta and his archer coins have his name *Va(in)ya* with the reverse legend *Dvādaśāditya*. The last known imperial Gupta ruler was Viṣṇugupta Chandrāditya whose archer type gold coins provides his name as *Viṣṇu* in the obverse field and the legend *Śrīcandrāditya* in the reverse. Therefore, analysis of the archer coin type of the imperial Guptas provides conclusive evidence that Candra was the short name for Candragupta II Vikramāditya.<sup>1</sup>

### LOCATION OF VIṢṆUPADAGIRI

Opinions vary on the identity of the Viṣṇupada hill and all of them have been summarized elsewhere.<sup>4,5,6</sup> We need to seek Viṣṇupadagiri in the region which was well within the territory of Candragupta II and which was also renowned for Vaishnavite worship from times even before the Gupta period. The centre that satisfies this important criterion is the region comprising present Udayagiri-Besnagar-Vidisha-Sanchi. The importance of this region for Vaishnavism and for the religious activities of the Guptas is attested by the fact that the Guptas created their first rock-cut temples in this region, i.e. at Udayagiri. The Udayagiri cave temples also possess the unique distinction of being the only works which can be personally associated with one Gupta monarch, Candragupta II Vikramāditya. Harle<sup>7</sup> notes that “the nearest that we can actually come to visualizing an Imperial Gupta monarch is here, among the low hills and the wide plains of Central India. Candragupta II must have almost certainly have walked, surrounded by his retinue, along the narrow roads that run past the caves and made his devotions here.”

The most well-known and imposing of the Udayagiri sculptures is the great panel of the Varāha (Boar) incarnation of Viṣṇu designated as Cave 5 (Figure 4). It is actually a bas-relief and the second largest one in India measuring nearly 7m by 4m. Harle rightly points out that the larger kneeling human figure in front of Varāha must be Candragupta II Vikramāditya. The appearance of the object on which Varāha sets his foot is more like a mountain, the living image of Viṣṇupadagiri. It must also be noticed that

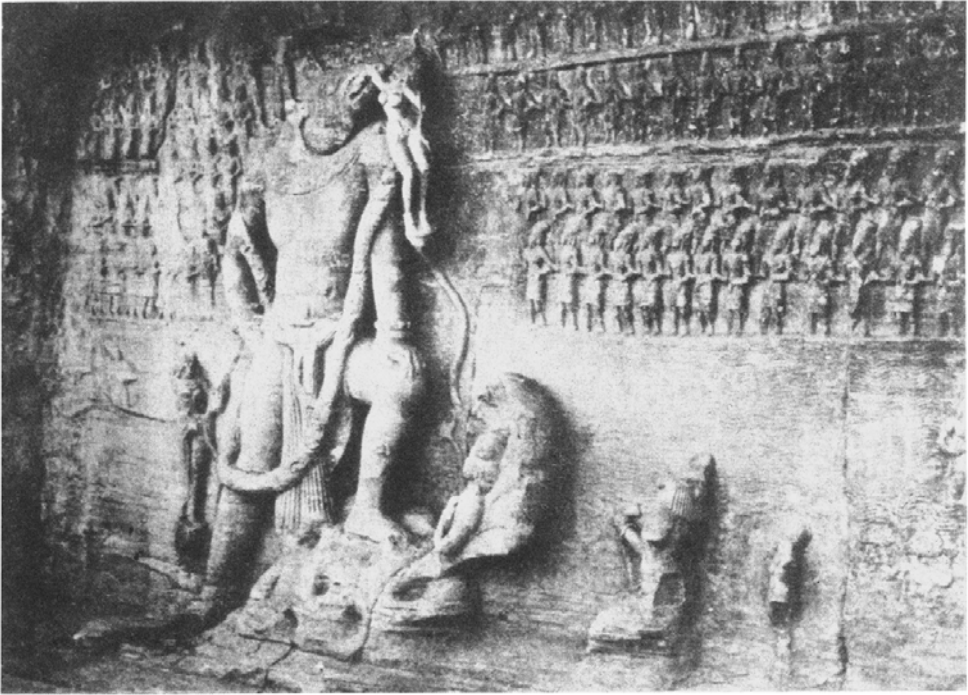


Figure 4: Bas-relief in Udayagiri in front of which the Iron Pillar was originally located as Garuḍastambha.

the rock, on which Varāha sets his foot, contains cave-like cavities carved out of the rock and this is similar in appearance to the Udayagiri itself with its cave temples. This evidence very strongly suggests that the Udayagiri mountain must possibly be the Viṣṇupadagiri mentioned in the Delhi Iron Pillar inscription. The imagery supplied by the panel in Cave 5 further strengthens this argument. It is noted that Garuḍa, the *vāhana* of Viṣṇu, is missing in the Varāha panel. There is no Garuḍa-stambha presently seen in front of the bas-relief. The Iron Pillar could have formed the Garuḍa-stambha of this temple. The language of the inscription of the Delhi Iron Pillar also indicates that this pillar could have been possibly located in front of the Varāha panel in which Candragupta II is depicted looking up to Varāha. The scene depicted in the Iron Pillar inscription, i.e. “having in



faith fixed his mind upon (the god) Viṣṇu”, is literally presented in the Varāha panel.

### LATER HISTORY

The pillar was later moved from this location. Although it is not known if the pillar was taken to another location, it is known that it was erected in the main temple at *Dillī* (Delhi) when it was developed around 1050 AD by the Tomar king Anangapāla.<sup>5</sup> The fortress city of *Lāl Kot* changed hands after the defeat of Prithvīrāj Chauhān by Qutb-ud-din Aibak, the slave army commander of Muhammad Ghori in 1191 AD. Aibak erected a mosque, between 1192 and 1199 AD, called the *Quwwat-ul-Islam* (Might of Islam) to commemorate his victory. The pillar currently stands in the open courtyard of this mosque, the first to be built in India. Archaeological evidence<sup>6</sup> and facts based on temple architecture indicate that the pillar must have been located in the original temple complex in Delhi, but at a different location from the current one. The pillar has, ever since, been lying in this location.

### ENGINEERING DESIGN OF PILLAR

The current burial level of the pillar was not the original burial level of the pillar when it formed a part of the temple. Hammer-marked cavities are still visible on the surface of the pillar in the rough region just below the smooth surface-finish region (Figure 5). The rough portion of the pillar was originally buried in the courtyard of the temple and later left exposed outside when the iron pillar was displaced from its original position. The stone platform around the base of the Iron Pillar was constructed in the last century by Beglar.<sup>8</sup> Sketches<sup>9</sup> and earlier published photographs of the pillar taken before<sup>10,11</sup> (for example, Figure 6)<sup>10</sup> attest to this.

A critical analysis of the dimensions of the main body of the pillar provides conclusive evidence for the original burial level of the pillar and also an appreciation of the pillar’s symmetrical design.<sup>5</sup> If the start of the smooth surface section is taken as the original burial level, the relative dimensions of the pillar are as provided in Figure 7. The rough surface

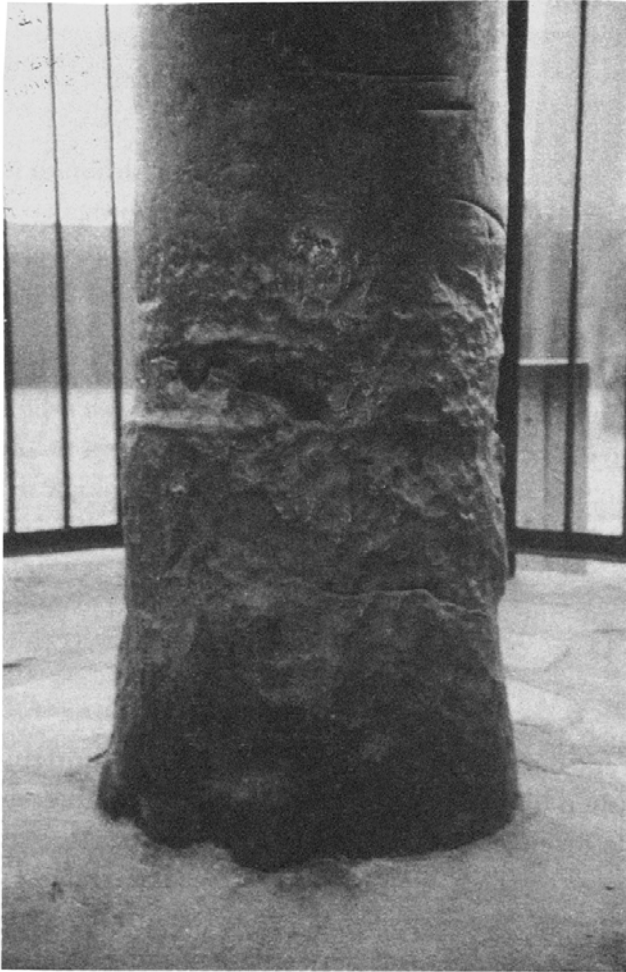


Figure 5: Bottom region of the Iron Pillar. The rough portion was originally buried in the ground.

occupies one-fourth (60U) and the smooth surface three-fourths (180U) of the pillar main body length, excluding the decorative top. The burial of the pillar body to one-fourth of its height would have provided the necessary stability to the structure. The decorative bell capital<sup>12</sup> is again a symmetrical object and its relative dimensions are provided in Figure 8. The Garuḍa

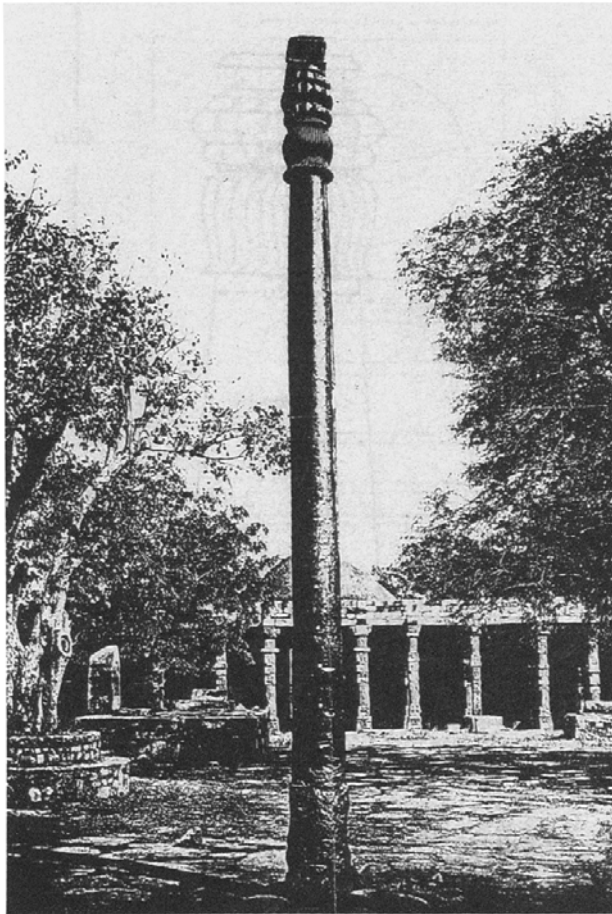


Figure 6: One of the oldest published photographs of the Delhi Iron Pillar.<sup>10</sup> Notice the absence of the stone platform around the base of the pillar.

idol would have been approximately 20U in length thereby providing the total length of the decorative top as 60U. The length of the decorative capital (60U) would now be exactly one-fourth of the total pillar height exposed above the ground level (240U). Therefore, it is reasonable to state that the depth of burial below ground level was equal to the height of the decorative capital, indicative of the engineering design of the pillar. The unit U is equal to 1 inch (1 *angula*).

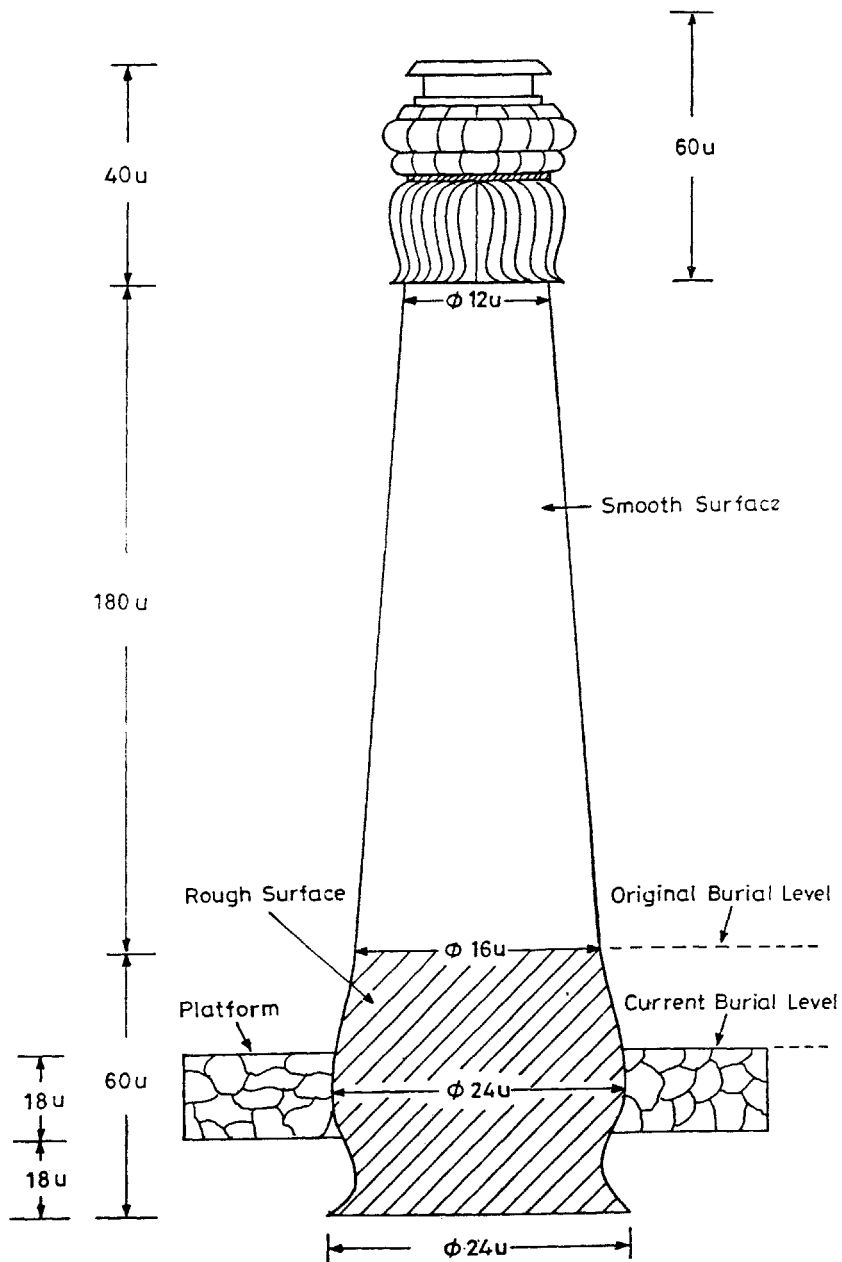


Figure 7: Relative dimensions of the Delhi Iron Pillar. The unit U measures 1" and is equal to 1 *angula*.

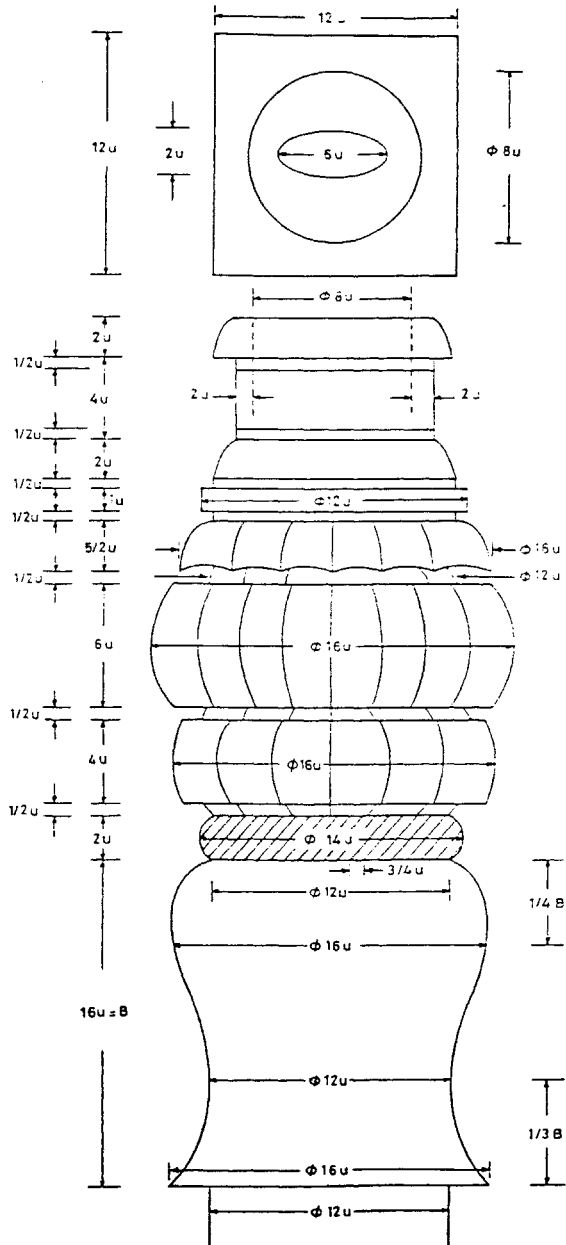


Figure 8: Relative dimensions of the decorative bell capital of the Delhi Iron Pillar.

### IRON OF DELHI PILLAR

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

#### COMPOSITION

Several analyses of the DIP iron's composition are available ever since the first analysis was published by Hadfield<sup>1</sup> in 1912. The published chemical analyses<sup>1,13,14,15</sup> 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 analysis and not by the difference. 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 millimetres into the sample from the surface.<sup>16</sup> Wranglen<sup>2</sup> utilised the available compositions (excluding that of Lal<sup>15</sup>) 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.

#### MICROSTRUCTURE

Some important aspects of the underlying microstructure of the DIP iron would be initially discussed as these have a bearing on its corrosion behaviour. The intimate relationship between structure and properties is well established in materials engineering. The Delhi Pillar iron possesses a non-uniform grain structure<sup>13,16</sup> (Figure 9). In the un-etched condition, the specimens showed slag inclusions irregularly distributed in the microstructure. 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.

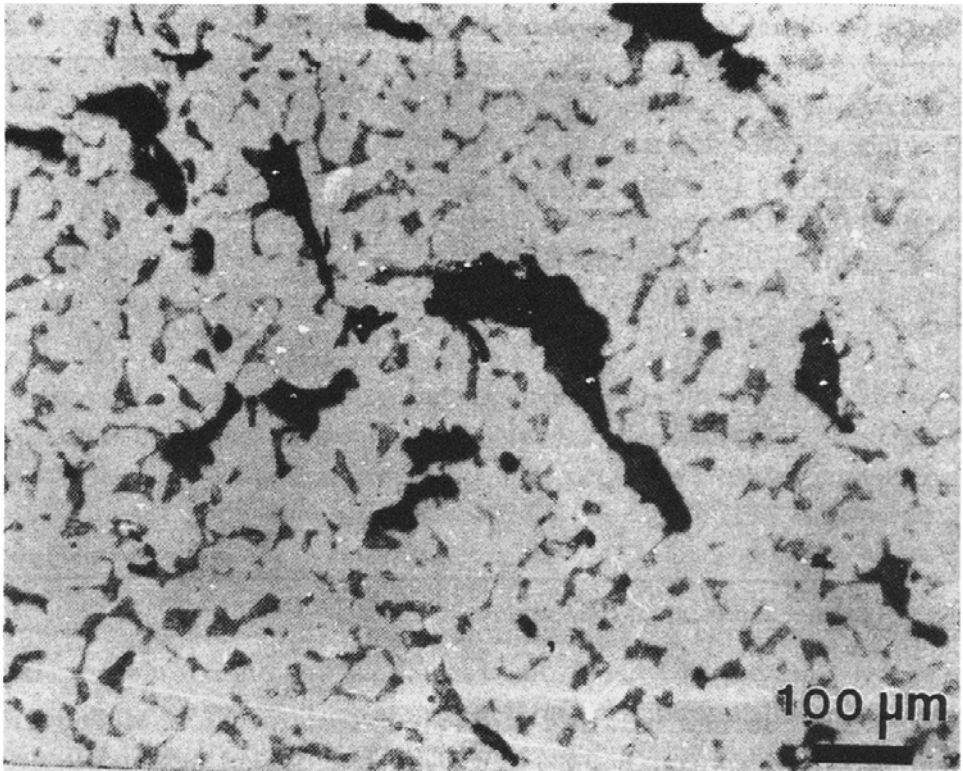


Figure 9: Microstructure of the Delhi Pillar iron.

Elongated slag particles and oxide particles were also seen in the deformed structure in the near surface regions. Lahiri et al<sup>11</sup> also conducted metallographic examination of the DIP iron and the irregular distribution of pearlite was also noted. The absence of a uniform distribution of pearlite is indicative of segregation of P because, in such areas of P segregation, C diffuses out and the material becomes poorer in C content. The interior portions were comparatively rich in C.<sup>13,16</sup> Therefore, a wide variation in structure is exhibited by the DIP iron and this is 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

Table 1 : Published Composition Analyses of DIP Iron

	Hadfield <sup>1</sup> (1912)	Ghosh <sup>13</sup> (1963) Above	Lahiri <i>et al</i> <sup>11</sup> (1963) Under	(1963)	Lal <sup>15</sup> (1945)
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

(including normalised and annealed structures).<sup>13</sup> Moreover, microstructures containing 0.2% to 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 for the purest form of Fe (Table 1). Note also that the specific gravity is not uniform indicative of the non-uniform distribution of the slag particles in the microstructure. The non-uniform nature of the slag particles in the DIP iron can be clearly seen in the microstructures provided by Ghosh,<sup>13</sup> and Bardget and Stanners.<sup>16</sup> The slag present in the Delhi Iron Pillar iron is generally microscopic in nature with a few of them in larger sizes. 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.<sup>17</sup> 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 in 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 to the iron that was extracted and this combined with unreduced iron oxide, resulting in the slag fayalite  $\text{Fe}_2\text{SiO}_4$ . 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.<sup>18,19</sup> These unreduced iron oxides also contained carbon, presumably due the charcoal used for the extraction.<sup>18</sup> The presence of carbon in these unreduced oxides would render these oxides cathodic in nature with respect to the surrounding matrix.

It must be also noticed that the slag particles in the DIP iron are in fine microscopic form distributed unevenly in the microstructure. Had the slag 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<sup>20</sup> with good mechanical strength (yield strength YS of 23.5 tons per sq. in., ultimate tensile strength UTS of 23.9 tons per sq. in. and 5% elongation<sup>13</sup>). 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 Delhi Iron Pillar in the 18th century (either by Nadir Shah in 1739 AD or Ghulam Quadir in 1787) failed to break the pillar also suggesting that slag does not coat the individual lumps that were forge welded.

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<sup>13</sup> and Eran iron.<sup>18</sup> An example of the same is provided in Figure 10. The pearlite volume fraction is relatively greater near the slag particles. The presence of a larger 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 major portion of P content in the DIP is in solid solution while a smaller amount occurs in the slags. 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.<sup>13</sup> The presence of P was also confirmed, by electron microprobe

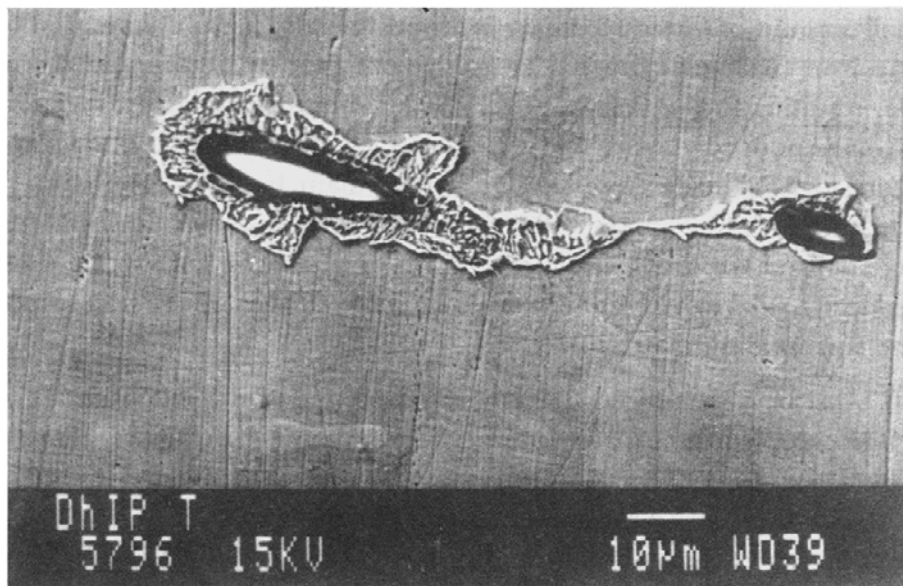


Figure 10: Microstructure of the Dhar Pillar iron. Notice the significant pearlite volume fraction near the entrapped slag particle.

analysis, in the entrapped slags of the Eran iron.<sup>19</sup> In the near vicinity of slag inclusions, the regions are depleted in P and these are the regions where C will concentrate. Therefore, this is the reason for the presence of a larger fraction of pearlite near the slag-metal interfaces. The presence of more 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).

#### ORIGIN FOR 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 the blast furnaces), the reason for the high P contents 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 (Table 1). Modern steels cannot tolerate such high P content as they would be susceptible to cracking

during the process of hot working due to the formation of liquid phosphates at the grain boundaries (the phenomenon being termed hot shortness). While it was earlier believed that P in ancient steels comes from slag inclusions,<sup>21</sup> 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 today's blast furnaces, and therefore the slag that formed in these ancient Indian furnaces were essentially fayelitic slags (i.e. consisting of iron orthosilicates  $\text{Fe}_2\text{SiO}_4$ ). This is also corroborated by available compositions of ancient iron-making slags from archaeological excavation sites.<sup>15</sup> The slags do not contain lime.<sup>15</sup> The removal 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.<sup>22</sup> 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.<sup>23</sup> As the entrapped slag seen in ancient Indian iron is generally fayelitic without any CaO, thermodynamics dictates that a higher amount of P should remain in solid solution in Fe. 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 also intentional. For example, Buchanan,<sup>21</sup> in his detailed description of steel making in Karnataka in the 18th century, describes that in one primitive furnace operated at Devaraya Durga, conical clay crucibles were filled with a specific amount of wood, from the barks of a plant *Cassia auriculata*, pieces of wrought iron, then sealed and fired. The bark of this plant contains a high content of P, extracted by osmosis from the ground.

#### MANUFACTURING METHODOLOGY

The manufacturing methodology of the main body of the pillar will be addressed initially<sup>20</sup> and later the decorative bell capital's design<sup>12</sup> would be explained. The section finally deals with the connection of the decorative

bell capital to the main body. It should be noted that the starting material is, of course, iron lump and the method used to fuse the lumps together was forge welding. The individual iron lumps obtained from the metal extraction process had to be joined in order to produce large objects. This was accomplished by forge welding. Forge welding is an operation in which iron lumps are joined together by forging them in the hot state such that fusion is obtained between them. This process initially involves heating of the lumps to a relatively high temperature in a bed of charcoal in order to make them soft and amenable for deformation. One lump is then placed on top of another and force is applied in order to weld them in the solid state. As the force is dynamic in nature, it is called forge welding.

### MAIN BODY

The likely method by which the Delhi Iron Pillar could have been manufactured is briefly described to provide an overview of the process. This is based on the critical analysis of the various aspects concerning the manufacturing methodology like hammering method, heating method, forging method, use of inserts, use of dies and ease of handling.<sup>20</sup> The heated iron lumps were placed on the side surface of the pillar and hammered on to the same by the use of hand-held hammers (Figure 11). The addition of metal would have been sideways with the pillar in the horizontal direction. The pillar's vertical and horizontal movements would have been aided by handling clamps provided on the surface of the pillar, the protruding portion of which must have been chiseled away during the surface finishing operations. Visual proof for the presence of these clamps is available at two locations on the pillar. The first location is the previously-polished surface where the presence of a rectangular insert is seen (Figure 12). The region where the insert is located was previously brightly polished due to visitors clasping their hands around the pillar, before the construction of the iron cage around the pillar recently. A close-up view of the same, when the region appeared brightly polished, is provided in Figure 8 in Balasubramaniam.<sup>20</sup> This insert (originally containing the holding clamp) appears to have been inserted on to the surface of the pillar and this is

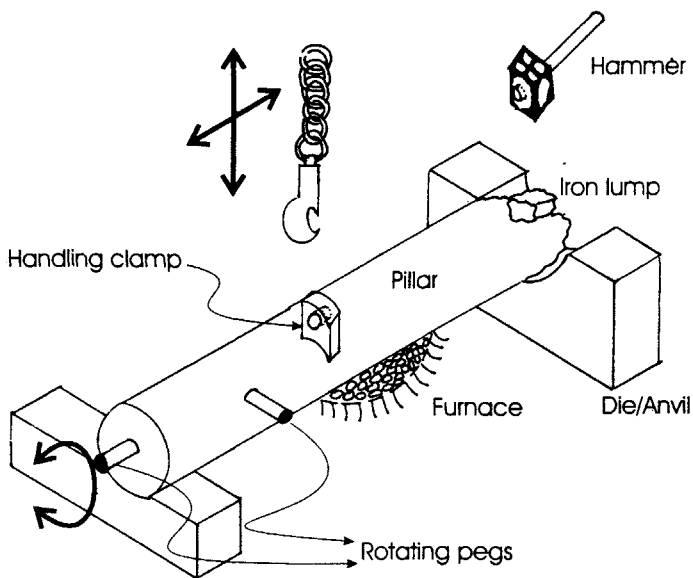


Figure 11: Horizontal forge welding technique for manufacturing the pillar's main body.

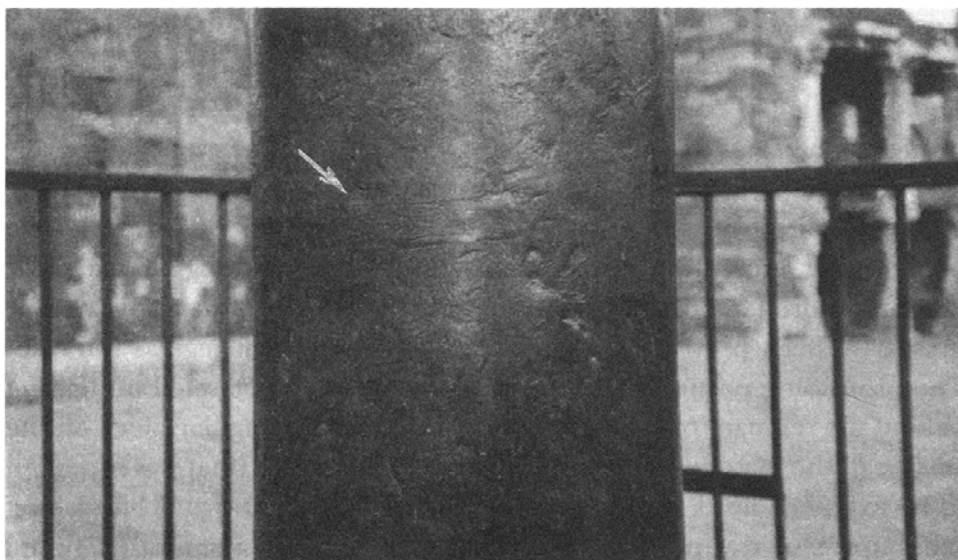


Figure 12: Evidence for a rectangular insert (arrowed) in the previously brightly polished region of the pillar. A close-up view of the same, when the region appeared brightly polished, has been provided in Figure 8 in Balasubramaniam.<sup>20</sup>

indicated by the presence of cracks emanating from the insert periphery on to the surrounding lumps of iron. The second location where a handling clamp could have been present is situated approximately about one fourth of the height from the top of the main body of the pillar. There is a horizontal rectangular object currently missing from the surface at this location (Figure 13). Close observation of this region reveals that this rectangular slot is exactly of the same dimensions as that of the rectangular insert (i.e. the remnant of the handling clamp) seen in the bright polished region. Moreover, it occurs exactly in line with the bottom insert (i.e. it is aligned with respect to the bottom rectangular insert). The location of these inserts with respect to the pillar body dimensions should also be appreciated. The location of the top missing insert appears at a distance of approximately 60" from the top of the pillar main body (i.e. excluding the decorative capital). The rectangular insert seen in the bright polished region appears at a distance of 150" from the top of the pillar main body and, therefore, 90" from the bottom of the pillar. The distance between these two inserts is 90". These dimensions should be compared to the overall dimensions of the pillar which has been analyzed in detail earlier. The body would have been rotated with the aid of rotating pegs inserted in the holes provided on the surface for this purpose. These holding supports would have aided heating the surface to be forged and then bringing this heated surface on top of an anvil. The anvil would have served additionally as a die. The hot lump to be forged is placed on top of this side section and then forged with the aid of hand-held hammers. Once a certain length of the pillar must have been manufactured, the handling of the pillar becomes more tedious and therefore to aid this process, handling clamps must have been provided on the surface of the pillar at regular intervals. The protruding portion of the insert must have been chiseled off leaving behind the remnant of the insert in the form of a rectangular block on the surface of the material. Finally, the surface of the pillar (that was supposed to be exposed) must have been smoothed by chiseling and burnishing the surface of the pillar and, thereby, providing it a smooth tapered cylindrical appearance. Lastly, the Sanskrit inscriptions are inscribed on to the surface of the pillar. Cold dies must have been used for inscribing the



Figure 13: Missing clamp located at a vertical distance of about 6 feet above the insert seen in Figure 12.

inscriptions with the metal surface being inscribed possibly being locally heated before inscribing. The decorative bell capital must have been finally fit on to the top portion of the Delhi Iron Pillar and then the whole pillar erected in the main courtyard of the Viṣṇu temple.

### DECORATIVE BELL CAPITAL

The decorative bell capital of the DIP has been described in great detail in Balasubramaniam.<sup>12</sup> The main features of the capital will be summarized. The decorative bell capital consists of seven distinct parts (Figure 14). The bottom-most part is the reeded bell structure which has been manufactured by utilizing iron rods of uniform diameter (Figure 15). Atop this comes the slanted rod structure (Figure 16). Notice the presence of a black filling in between the joints. There are several evidences at the joints between these two members to indicate that lead solders were utilized for joining the pieces together.<sup>25,26</sup> The next three members are rounded structures, with the top one being only half rounded (Figure 17) because when the pillar is viewed from the bottom, in perspective this part would appear curved. A round disc comes above this and finally the box pedestal is placed on the top of the capital. The box capital contains holes that are empty at the four corners<sup>12</sup> and these must have been originally utilized for holding figures of lions, based on the architecture of Gupta Garuḍa capitals.<sup>12</sup> The top of the pillar presently contains a hollow slot<sup>12</sup> in which an idol of Garuḍa must have been originally present (Figure 18). The fitting methodology of the various components is illustrated in Figure 19, where the individual components are shown shrunk fit around a hollow cylinder. Evidence for this kind of fitting method has been presented earlier.<sup>12</sup> The cylinder would also have helped handling of the pillar and also for joining the capital with the main body by the aid of inserts. It is interesting to note the cross markings in Figures 15 and 17, which are being reported here for the first time. These markings could be related to the alignment of the individual components, although they are not strictly aligned with each other in the overall context of the decorative bell capital.



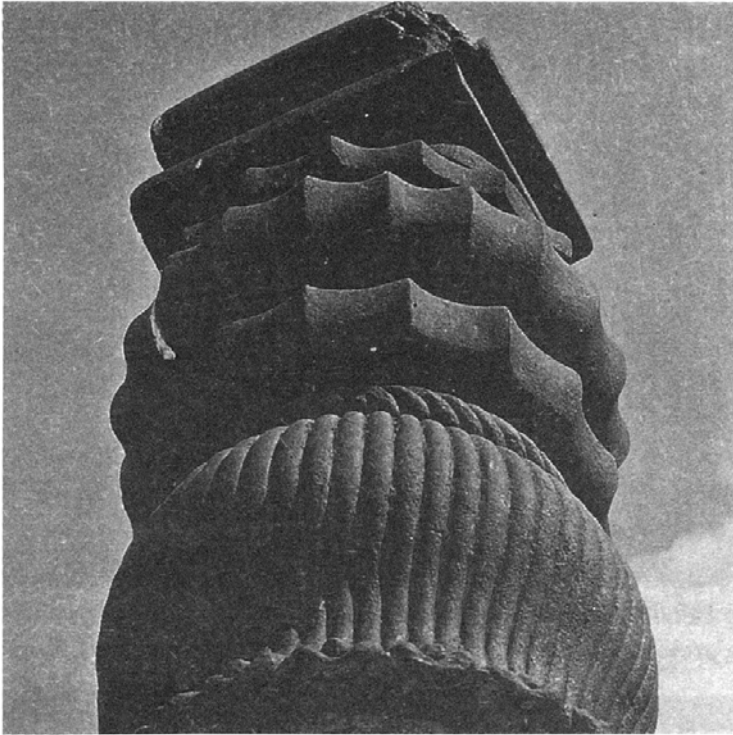


Figure 14: Decorative bell capital of the Delhi Iron Pillar.

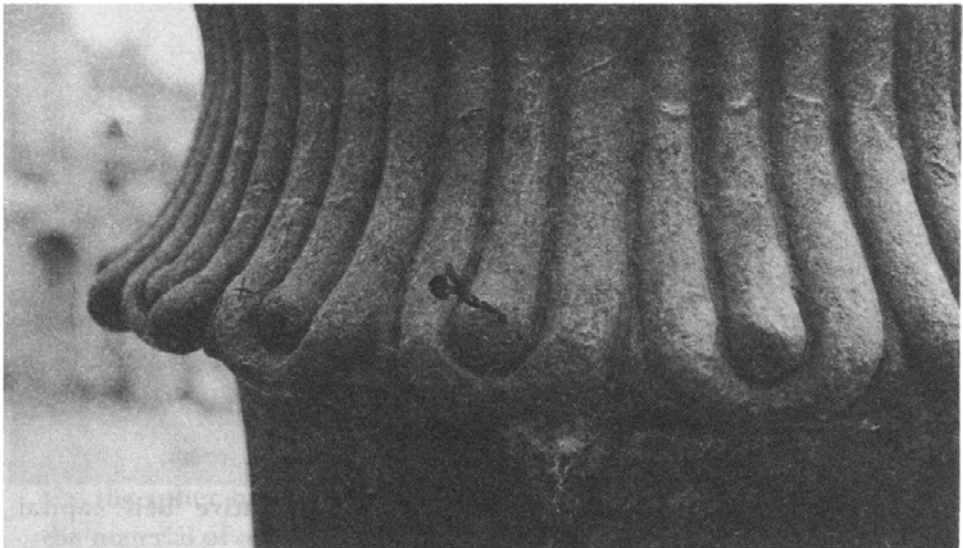


Figure 15: Details of the bottom region of the reeded-bell component of the decorative capital. Notice the presence of a cross mark on one of the rods of this component.

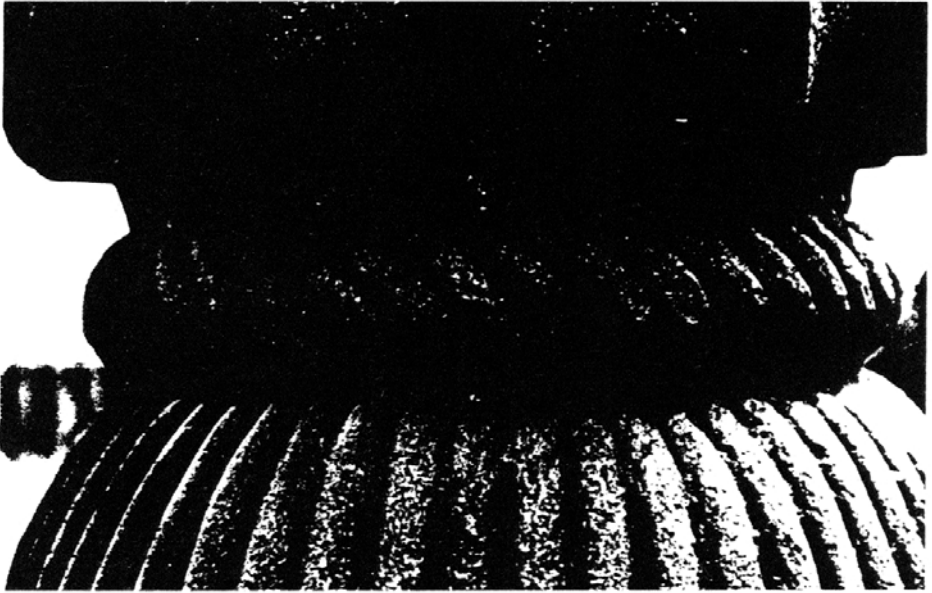


Figure 16: Details of the slanted rod structure above the reeded bell structure. Notice the presence of a black filling inbetween the joints.

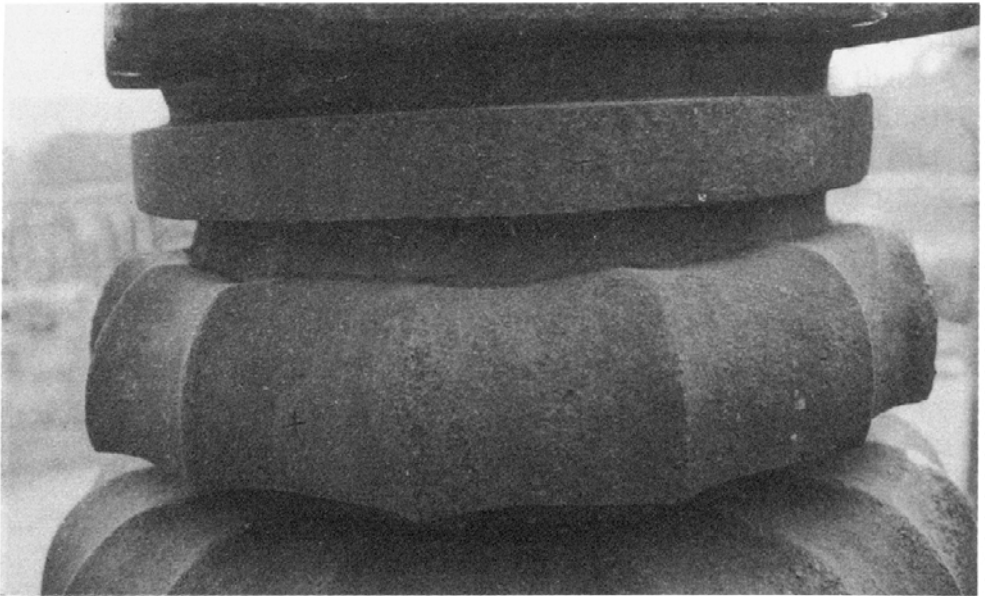


Figure 17: Half-rounded component of the decorative bell capital. Notice the presence of a cross mark on this component.

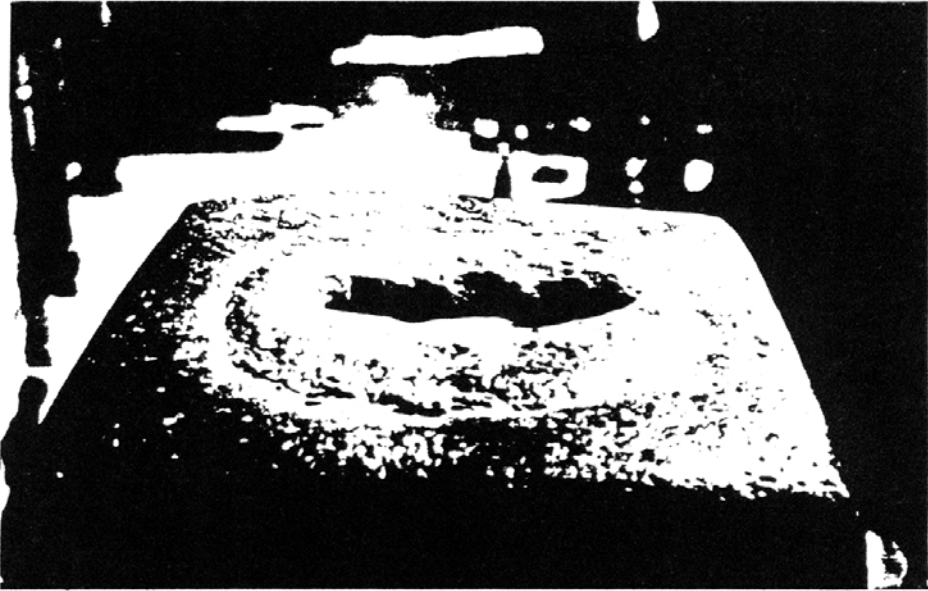


Figure 18: The top of the pillar presently contains a hollow slot in which an idol of Garuda must have been originally present.<sup>12</sup>

## CORROSION RESISTANCE

### REVIEW OF CORROSION RESISTANCE THEORIES

All the theories that have been proposed to explain the pillar's superior corrosion resistance can be broadly classified into two categories: the environmental and material theories. These theories have been critically reviewed by Balasubramaniam.<sup>27,28</sup> The proponents of the environment theory state that the mild climate of Delhi is responsible for the corrosion resistance of the Delhi Iron Pillar as the relative humidity at Delhi does not exceed 70% for significant periods of time in the year, which therefore results in very mild corrosion of the pillar. It is known 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<sup>2</sup> were collected over a period of 30 years between 1930 and 1960. On the other hand, several investigators have stressed the importance of the material of construction as the primary cause for its corrosion resistance.

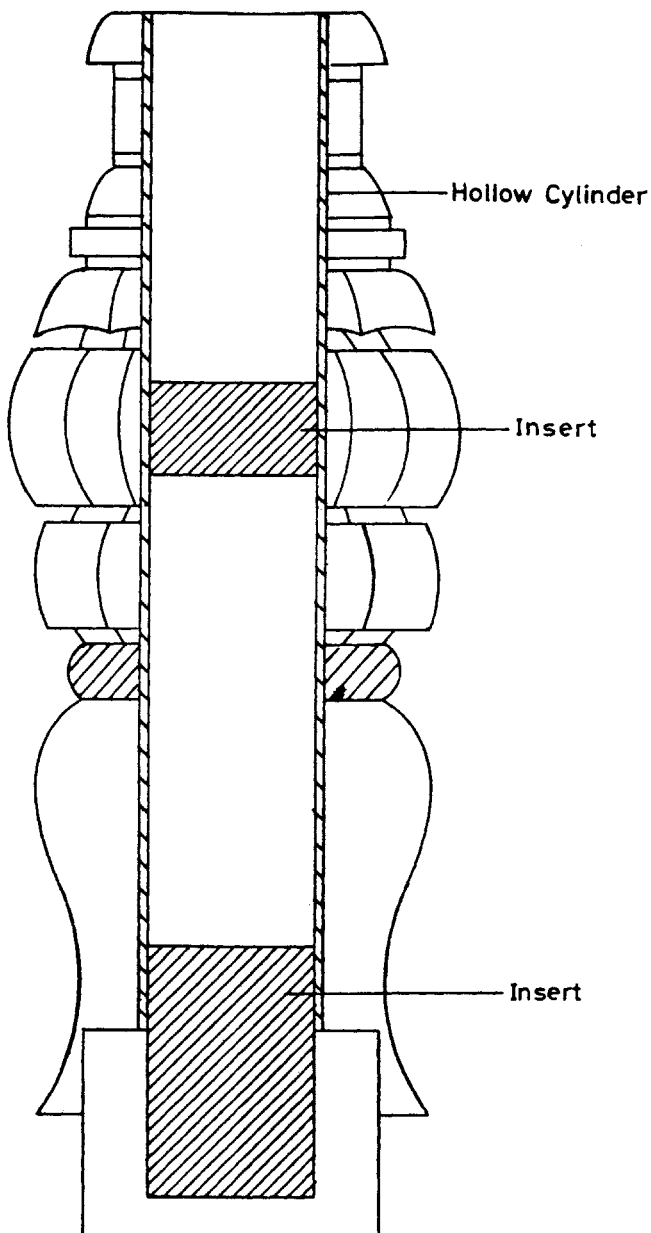


Figure 19: Shrink fitting methodology of the Delhi Iron Pillar decorative capital round a hollow cylinder. Notice that the decorative bell capital is attached to the pillar main body by means of an insert.

The ideas proposed in this regard are the relatively pure composition of the iron used, presence of phosphorus and absence of S/Mn in the iron, its slag enveloped metal grain structure, passivity enhancement in the presence of slag particles and formation of phosphate film. Other theories to explain the corrosion resistance are also to be found in the literature like the mass metal effect, initial exposure to an alkaline and ammonical environment, residual stresses resulting from the surface finishing (hammering) operation, freedom from sulphur contamination both in the metal and in the air, presence of layers of cinder in the metal thereby not allowing corrosion to proceed beyond the layer (cinder theory) and surface coatings provided to the pillar after manufacture (treating the surface with steam and slag coating) and during use (coating with clarified butter). That the material of construction may be the 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 Sūrya temple at Konark in coastal Orissa and the iron pillar at Mookambika temple at Kollur situated in the Kodachadri Hills on the western coast). It is, therefore, obvious that the ancient Indians, especially from the time of the Guptas (300-500 AD), 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.

#### BENEFICIAL 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<sup>13</sup> 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.

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 corrosion 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.<sup>18</sup> 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

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 analysed using the mixed potential theory.<sup>27,28</sup> The analysis is briefly summarised by considering the Evan's diagram presented in Figure 20. The anodic polarisation behaviour of iron has been shown to exhibit active-passive behaviour as it is well known that rust layer(s) form on atmospheric corrosion of iron. Moreover, the DIP iron contains a relatively larger weight fraction of P (average composition 0.25%) which will aid in inducing passivity in iron.<sup>29</sup> The formation of insoluble phosphates is thermodynamically favoured, even for P contents as low as 0.24 %P. Potentiodynamic polarisation 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 orders of magnitude compared to that for steel without P.<sup>30</sup> Therefore, it is valid to indicate that the DIP iron will exhibit active-passive behaviour on anodic polarisation. 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 polarisation line would have intersected the anodic polarisation curve in the active region. This is reasonable as relatively large currents are needed to induce passivity in iron containing P as the critical current density for passivation is relatively large in iron containing P.<sup>30</sup> However, in the

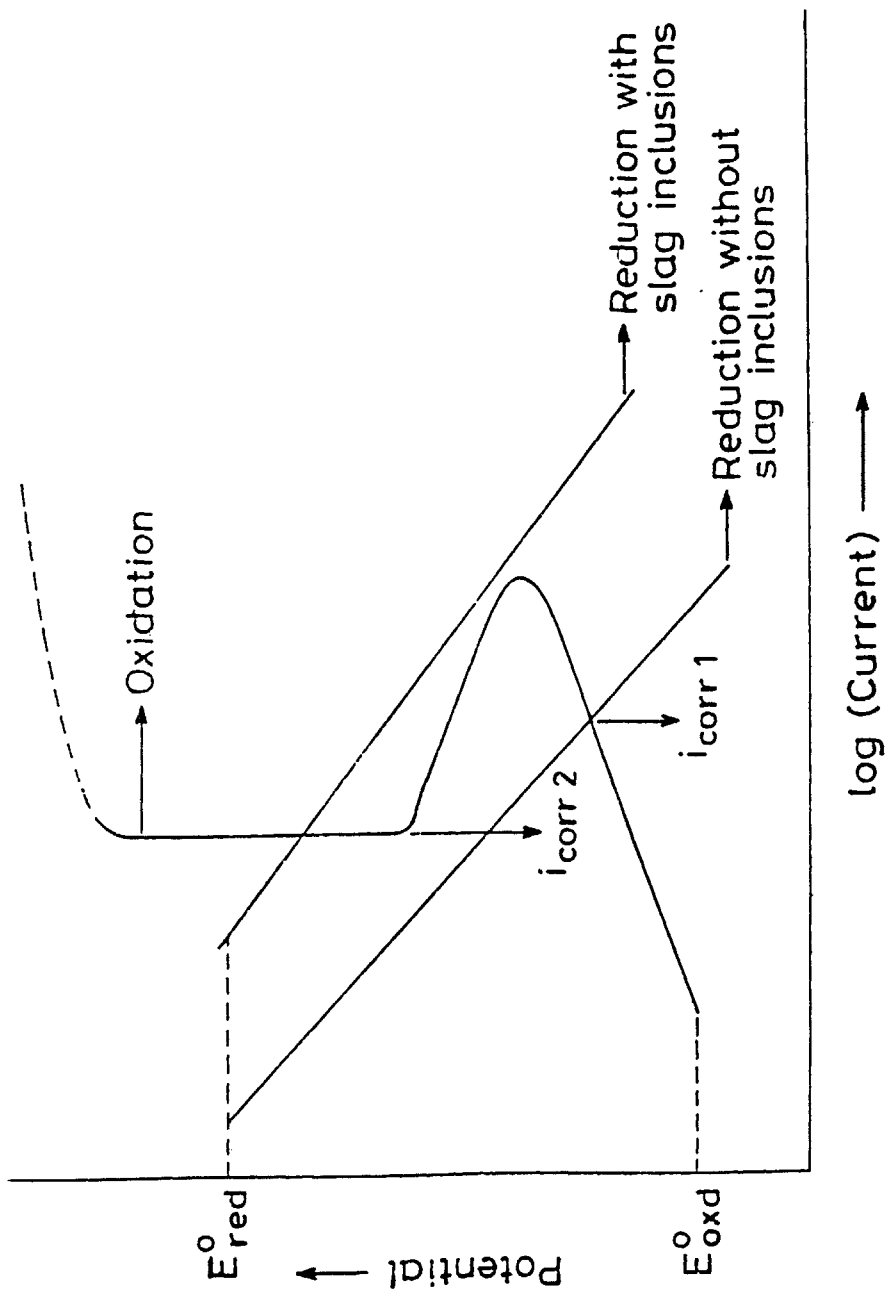


Figure 20: Mixed potential theory analysis for passivity induction in the presence of slag inclusions in the Delhi Pillar iron.<sup>28,29</sup>

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 polarisation line would shift to the right as shown in Figure 20. 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. Therefore, in the presence of second phase particles, the higher current demand of the cathodic reaction(s) will demand a higher corrosion current and in the 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 low rates. 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 polarisation studies using ancient Indian iron of different slag contents.<sup>27,28</sup> 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 Delhi Iron Pillar, 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 formation of the protective film at the metal-metaloxide interface. In case iron with such second phase particles (slags and oxides) is exposed to a more severe environment, for example complete immersion in acidic or alkaline solution, rapid localised 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.<sup>18</sup> In the case of DIP iron, the importance of alternate wetting and drying



conditions for its corrosion resistance can be gleaned by analysing the available corrosion rate data. Wranglen<sup>2</sup> utilised the weight loss data to estimate the thickness of protective film that forms on the surface of the DIP. Assuming parabolic growth kinetics, he predicted the thickness of the scale to be 200  $\mu\text{m}$  after about 1600 years of growth. The excellent match of the estimated thickness with that experimentally estimated by Bardgett and Stanners,<sup>16</sup> using a permanent-magnet type thickness gauge, was indicated as 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%  $\text{SO}_2$  solutions were 6 mg/sq dm/day (mdd) and 54 mdd, respectively.<sup>13</sup> Utilising 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.

#### DELHI IRON PILLAR RUST CHARACTERIZATION

Rust samples were characterised by XRD,<sup>31</sup> Fourier Transform Infrared (FTIR) spectroscopy<sup>32</sup> and Mössbauer spectroscopy.<sup>33</sup> The salient results of the characterisation studies are summarised below. It must be again emphasised that the rust samples were obtained from the region just below the decorative bell capital and therefore, this must be the oldest 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 (Figure 21). The FTIR spectroscopic study of the DIP rust clearly established that, in addition to iron hydrogen phosphate hydrate, the scale also consisted of  $\gamma\text{-FeOOH}$  (lepidocrocite),  $\alpha\text{-FeOOH}$  (goethite),  $\delta\text{-FeOOH}$  (misawite), magnetite and phosphates (Figure 22). 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

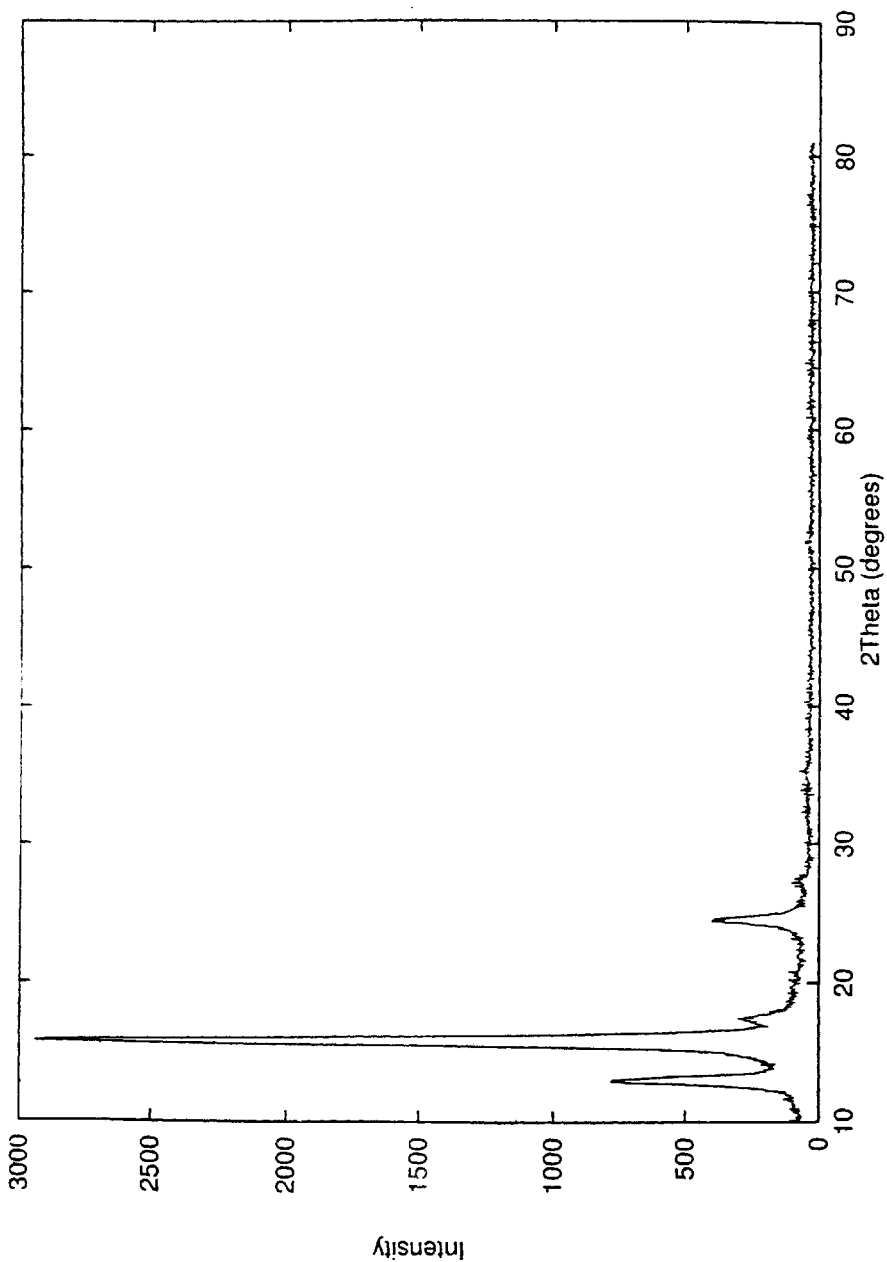


Figure 21: X-ray diffraction pattern of the DIP rust showing the intensities in the region  $2\theta = 10^\circ$  to  $80^\circ$ .

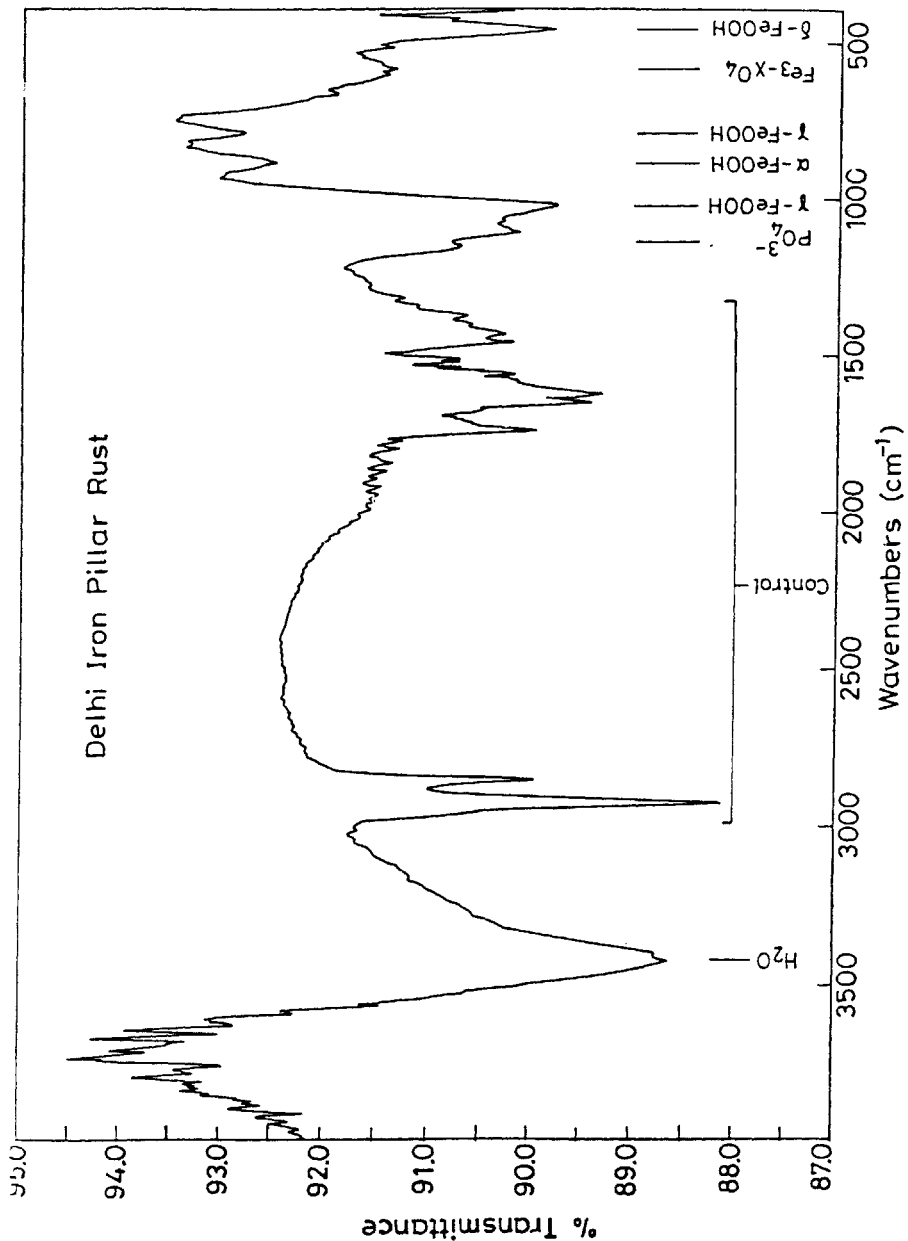


Figure 22: Fourier transform infrared (FTIR) spectrum from the DIP rust.

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 (Figure 23). 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.

Table 2 : Free Energy of Formation of Compounds at 298K<sup>31</sup>

Compound Formula	Compound Name	$\Delta G$ (kJ/mol)
$\gamma\text{-Fe}_2\text{O}_3$	hematite	-742.4
$\text{Fe}_{0.95}\text{O}$	wüstite	-244.3
FeO	stoichiometric	-251.4
$\text{Fe}_3\text{O}_4$	magnetite	-1014.2
$\alpha\text{-FeOOH}$	goethite	-490.4
$\gamma\text{-FeOOH}$	lepidocrocite	-471.4
$\delta\text{-FeOOH}$	misawite	-
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	strongite	-1657.5
$\text{H}_3\text{PO}_4$ (aqueous)		-1142.6
(crystalline)		-1119.2
(liquid)		-1111.7

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.<sup>31</sup> 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 phase diagram of the Fe-P-O phase diagram that the formation of phosphate is favorable even when only 0.24% P is present.

### PROCESS OF PROTECTIVE RUST FORMATION

The process of protective film formation on the exposed surface of the Delhi Iron Pillar can be outlined on the basis of 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),  $\text{Fe}_x\text{O}_y$  (magnetite) and x-ray amorphous matter.<sup>35,36</sup> In case of exposure in marine environments (i.e. where chloride ions are present), the formation of  $\beta$ -FeOOH (akaganeite) is favoured. In the case of DIP iron, the formation of lepidocrocite and goethite was confirmed by XRD analysis of 1.5 year old rust from the Delhi Iron Pillar surface by Lahiri et al.<sup>11</sup> It is also likely that the sample analysed by them could have contained amorphous  $\delta$ -FeOOH (misawite) as the formation of this phase during the initial corrosion of iron has been conclusively proven by Misawa and co-workers<sup>35,36</sup> utilising FTIR spectroscopy.

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  $\delta$ -FeOOH layer next to the metal-metaloxide interface should be favoured like that observed in the case of P-containing weathering steels. Moreover, experiments have shown that  $\text{H}_2\text{PO}_4^-$  ions prevent crystal growth of the corrosion products. The formation of amorphous  $\delta$ -FeOOH confers the initial corrosion resistance to the DIP iron. The  $\delta$ -FeOOH phase forms in a discontinuous manner in normal mild steels while it forms as a compact layer next to the metal-metaloxide interface in the case of P- or Cu-containing weathering steels due to catalytic action. The superior corrosion resistance of P- and Cu-containing weathering steels has been attributed to this compact  $\delta$ -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.<sup>37</sup> While the  $\alpha$ -FeOOH and  $\gamma$ -FeOOH could be identified by X-ray diffraction, it is generally not possible to identify the  $\delta$ -FeOOH phase by this characterisation technique.

It is important to note that the oxyhydroxides and magnetite present in the old DIP rust are nanocrystalline/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,<sup>11</sup> 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 due to process of alternate wetting and drying, as has been shown in P-containing weathering steel.<sup>35</sup>

The enrichment of P in the  $\delta$ -FeOOH layer continues with prolonged exposure and this has been observed in P-containing weathering steels.<sup>35,36</sup> 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 vast literature available on phosphating of steels.<sup>38</sup> This exercise would also be useful in further understanding the reason for the Delhi Iron Pillar's excellent corrosion resistance.

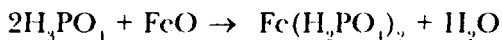
Phosphating of iron is a commercially important coating method which involves the formation of relatively insoluble, electrically non-conducting thin films of metallic phosphates on the surface. It is known that the formation of a protective layer on Fe surface involves the following four steps.<sup>38</sup> 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. However, it is also important to note that the concentration of P is relatively higher near the surface regions of the DIP iron than in the bulk.<sup>13</sup> It was earlier noted that the surface regions of DIP contain a higher amount of ferrite (i.e. depleted

of carbon) which is due to the final surface finishing operation provided to the pillar during its manufacture. It is known that P diffuses and concentrates in regions where C is depleted 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<sup>13</sup> 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 consideration favor its formation. The moisture for phosphoric acid formation obtains 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

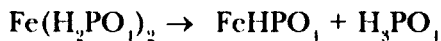
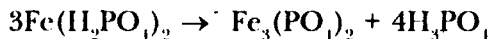


The transient oxides of iron (in which Fe is in the +2 oxidation state) will also be corroded by phosphoric acid to provide  $\text{Fe}(\text{H}_2\text{PO}_4)_2$  according to



Among the above two reactions, the first one mainly occurs.<sup>38</sup>

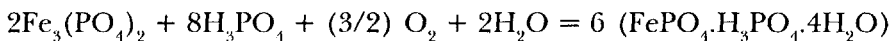
In the second stage, the contact of the metal shifts the equilibrium in such a way that massive precipitation of monohydrogen phosphate  $\text{FeHPO}_4$  and tribasic iron phosphate  $\text{Fe}_3(\text{PO}_4)_2$  occurs. The precipitation reactions are



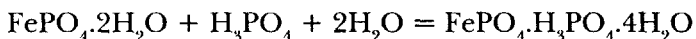
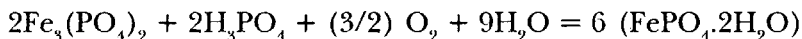
The interesting thing to notice is that iron is in the +2 oxidation state in these phosphates. Both these phosphates are insoluble in nature. Moreover, these phosphates are also amorphous in nature and this is well corroborated by experimental evidence.

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, oxidising agents are added so that iron may appear in the coating as ferric phosphate. This has been proved to be more beneficial to corrosion resistance as the crystal reorganisation of the amorphous phosphates to ferric phosphates results in a large reduction in the porosity of the phosphate and subsequently, much improved protective properties.

The oxidation of iron to ferric phosphate can also be achieved by alternate wetting and drying cycles. The  $\text{H}_2\text{PO}_4^-$  ions accelerate the air oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  under alternate wetting and drying cycles and also prevent the crystal growth of the corrosion products. Over time,  $\text{Fe}_3(\text{PO}_4)_2$  is oxidised by atmospheric oxygen and  $\text{H}_3\text{PO}_4$  to iron hydrogen phosphate hydrate according to:



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



The dissolution and reprecipitation reaction also leads to a change in the pH of the metal-solution interface, which leads to a crystalline reorganisation and is followed, most importantly, by a large decrease in porosity. The crystalline reorganisation 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.<sup>38</sup> 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-metaloxide interface) is, therefore, responsible for the superior corrosion resistance of the Delhi Iron Pillar. Ghosh anticipated



this mechanism in his excellent study of the DIP iron. 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 exposure surface of ordinary irons.” 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 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 also to note that the crystalline modification of iron hydrogen phosphate hydrate was obtained in the XRD analysis,<sup>31</sup> thus indicating that the phosphate in the rust is relatively old. This validates the statement that the analysed 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  $H_2PO_4^-$  ions. The iron pillar’s weight is estimated to be approximately 7 tonnes and therefore, the large mass of the metal plays a contributory role in aiding the alternate wetting and drying process. Sanyal and Preston<sup>39</sup> and, later, Bardgett and Stanners<sup>16</sup> proposed that the large mass of the pillar implies a large heat capacity for the iron and therefore, the pillar will heat up faster or cool down faster than the surroundings. This provides the right conditions of alternate wetting and drying of the iron pillar surface. The intensity 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<sup>13</sup> and elaborated in detail later by Balasubramaniam<sup>27-29</sup> is valid, with the

minor difference being that it is the crystalline (and not amorphous as originally proposed by Balasubramanian<sup>27,28</sup>) iron hydrogen phosphate hydrate layer that is responsible for the corrosion resistance of the Delhi Iron Pillar. The conclusion drawn is unambiguous as it has strong experimental support from actual Delhi Iron Pillar rust characterization.

#### DIFFERENCE WITH CORROSION OF STEEL AND WEATHERING STEELS

The protective passive film that forms on the DIP would be contrasted with the films forming on mild and weathering steel 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 oxidised from Fe(II) complexes.<sup>35</sup> 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  $\gamma$ -FeOOH. After this forms, a part of it begins to transform to another allotropic modification ( $\alpha$ -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. There is also debate on the exact nature of the magnetic oxide that forms on exposure of the iron to the environment. This is because the diffraction peaks of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  occur at the same location. However, Mössbauer studies of rust formed on steel exposed to the environment does indicate that  $\text{Fe}_3\text{O}_4$  (more precisely to be called  $\text{Fe}_{3-x}\text{O}_4$ ) forms first and this is later converted to  $\gamma\text{-Fe}_2\text{O}_3$ . 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  $\alpha$ - and  $\gamma$ -FeOOH, there can be another

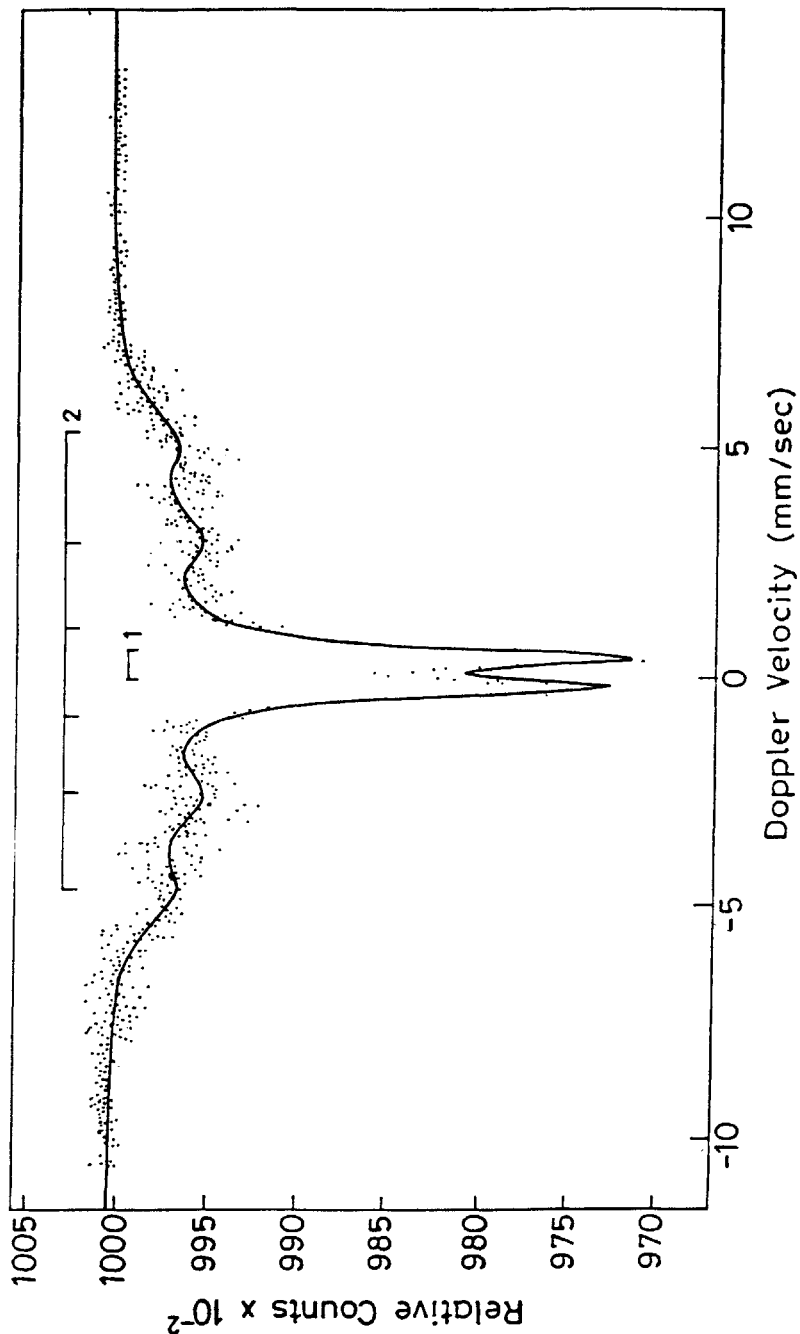
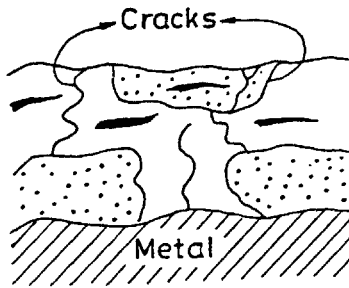
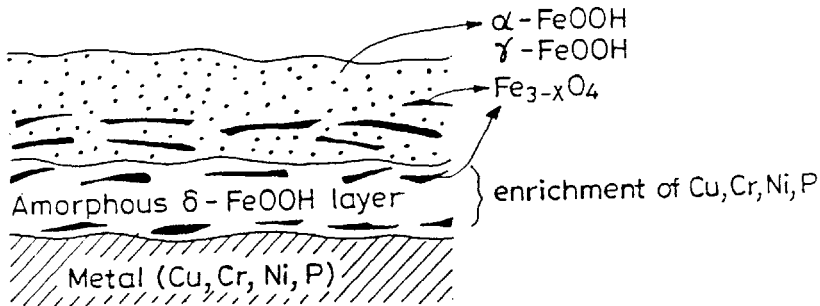


Figure 23: Mössbauer spectrum obtained from the second DIP rust sample.

## MILD STEEL



## WEATHERING STEEL



## DELHI IRON PILLAR

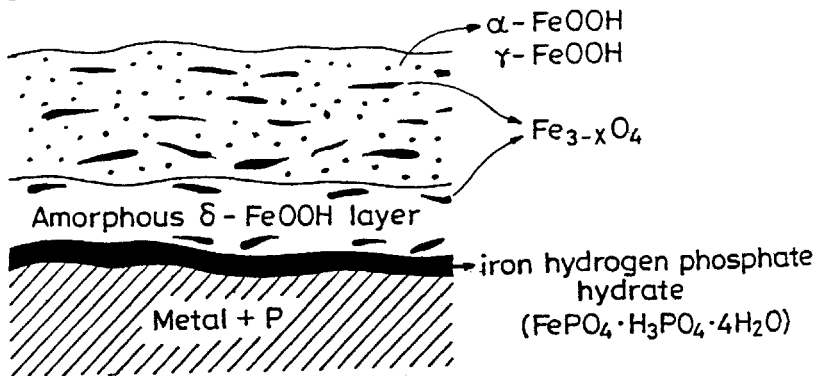


Figure 24: Schematic comparing the rust structure formed on mild steel, weathering steel and Delhi Iron Pillar.

oxyhydroxide of nature  $\delta$ -FeOOH, which can form on atmospheric exposure of iron. It is interesting to note that  $\delta$ -FeOOH is generally amorphous in nature and therefore no diffraction peaks would be observed from this phase.<sup>35</sup> In ordinary mild steels, this phase does not form as a continuous layer but rather in a discontinuous manner (Figure 24) as it results due to dehydration-oxidation of the Fe(II) complexes. Therefore, the  $\delta$ -FeOOH that forms in ordinary mild steels is not protective in nature for these reasons. However, it is possible for this  $\delta$ -FeOOH to form next to the metal surface as a continuous layer in which case the steel obtains corrosion resistance (Figure 24), as the oxyhydroxide is also amorphous in nature. The formation of  $\delta$ -FeOOH as a continuous layer next to the metal surface is catalysed by the presence of P and Cu in the material.<sup>35</sup> Moreover, the  $\delta$ -FeOOH is enriched with P and Cu, elements that are added for improving atmospheric corrosion.<sup>35</sup> The presence of this amorphous layer is the reason for the excellent corrosion resistance of the weathering steels 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.<sup>35,36</sup>

In the case of DIP, the process of protective rust formation has been outlined in great detail earlier. The structure of the passive film on the DIP is schematically also provided in Figure 24 for comparison with the films that form on mild and weathering steels. Cross sectional microstructural analysis of DIP rust confirms the structure of DIP rust presented.<sup>29</sup>

## CONCLUSIONS

New insights on the Delhi iron pillar have been discussed in this communication. The identity of Candra and Viṣṇupadagiri of the oldest Sanskrit inscription on the pillar has been analyzed to show that Candra should be identified with Candragupta II Vikramaditya while Viṣṇupadagiri should be identified with modern Udayagiri. The engineering design of the pillar was next discussed paving the way for understanding of the manufacturing methodology for the main body of the pillar and the

decorative bell capital. The paper also briefly addressed the nature of iron that makes up the DIP and the possible reason for its relatively high P content. 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. The rust was composed of iron hydrogen phosphate hydrate ( $\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ) in the crystalline form in addition to  $\alpha$ -,  $\gamma$ -,  $\delta$ - $\text{FeOOH}$  and magnetite, all in amorphous form. The process of protective rust formation on DIP iron has been outlined based on the rust analysis. The passive film formation on the Delhi Iron Pillar has been contrasted with rusting of normal and weathering steels. The critical factor aiding the superior corrosion resistance of the Delhi Iron Pillar is the formation of crystalline iron hydrogen phosphate hydrate, as a thin layer next 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 the 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 (with 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).

#### ACKNOWLEDGEMENTS

The author gratefully acknowledges the inspiring advice of Professor Anantharaman during various phases of the study and the co-operation of the Archaeological Survey of India.

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