Delhi Iron Pillar

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INTRODUCTION

The Delhi Iron Pillar (Fig 1) is testimony to the high level of skill achieved by the ancient Indian ironsmiths in the extraction and processing of iron. It has attracted the attention of archaeologist and corrosion technologists as it has withstood corrosion for the last 1600 years. It is singularly featured on the emblems of several Indian institutions (for example, the National Metallurgical Laboratory, The Indian Institute of Metals), thereby signifying its prime identity as the country's metallurgical pride and heritage. Hadfield[1] undertook the first systematic scientific study of the Delhi iron pillar. 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). The buried underground region of the pillar was examined by archaeological excavation. Moreover, a relatively large iron sample was obtained
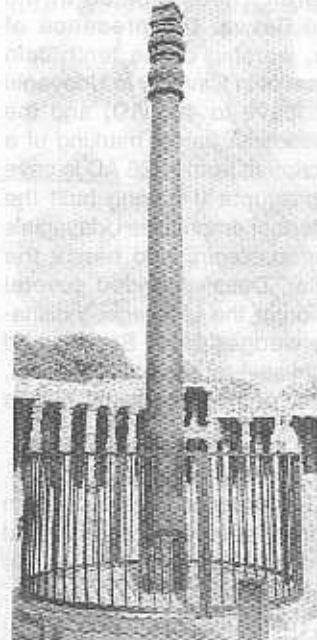

Fig 1 : The Delhi Iron Pillar. Notice the iron grill cage around the Pillar bottom that has been recently constructed.

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 on which future scientific studies of the pillar were based. A review of the pillar's corrosion resistance appeared later in 1970[2] and recently, Prof Anantharaman[3] has published the known scientific facts about the Delhi iron pillar in the form of a book. Balasubramaniam[4] has compiled several new insights on the historical, scientific and technical aspects of the Delhi iron pillar in a recent book. The present review paper will focus attention on the new research insights obtained on the Delhi iron pillar.

HISTORY

Identity of Chandra

Among the several inscriptions on the pillar, the oldest (and also the largest) is a three-stanza six-line Sanskrit inscription

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(Fig 2), at a level of about 7' from the stone platform. This inscription records that the pillar was set up by *Chandra* ('having in faith fixed his mind upon *Vishnu*) as a standard of Vishnu (*Vishnuordhidhvajah*) at a location described as *Vishnupadagiri* (meaning 'Vishnu-foot-hill'). The monarch's conquests have also been poetically described in the inscription. It must be noted that three

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

directions are referred to in the inscription (i e, east, south and west) and also Vishnu's name appears three times in the inscription, although in different contexts. The theories that have been proposed to identify *Chandra* have been critically reviewed elsewhere[5]. Based on the nature of the Brahmi 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 (320AD-600AD). The important imperial Gupta monarchs were Chandragupta I, Samudragupta, Chandragupta II, Kumaragupta I and Skandagupta.

In order to identify *Chandra,* numismatic evidence would be presented. The inscription specifically mentions that the king's name was *Chandra* and this is the most important clue to determine his identity. There are several gold coin-types in which Chandragupta II Vikramaditya's short name of *Chandra* 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 *Chandra* 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 depict the king with a bow and a short name of the issuing king (Fig 3). The most interesting aspect about the archer coin type is that the 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 Chandragupta II Vikramaditya, the short name of the king is inscribed as *Chandra* while the king's complete title and name is provided in the circular legend. Therefore, it is amply clear that Chandragupta II Vikramaditya was called in short as *Chandra* and this is attested firmly by his most popular coin-type. In the archer coins of Kumaragupta I, the king's name provided in the obverse field is *Kumara* or *Ku* or absent in some, but appearing as *Kumaragupta* in the circular legend.

Fig 3 : Archer-type gold coin of Chandragupta II Vikramaditya. In the obverse, the short name *(Chandra)* of the king is provided below his left arm while his full name appears in the circular legend. Photograph courtesy : Ellen M. Raven.

Kumaragupta'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[5]. 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*. The rebellious son of Kumaragupta I, Ghatotkachagupta issued an archer type coin with his name *Ghato* on the obverse field. Skandagupta was succeeded by Narasimhagupta I Baladitya with his short name was provided as *Nara* and then he was followed by Kumaragupta II Kramaditya (with the short name *Ku* and the legend *Kramaditya* ("progress-sun") in the reverse. He was succeded by Budhagupta Vikramaditya whose archer coin type spells his name as *Budha*. Vainyagupta Dvadasaditya succeeded Budhagupta and his archer coins have his name *Va(in)ya*. The last known imperial Gupta ruler was Vishnugupta Chandraditya whose archer type gold coins provides his name as *Vishnu* in the obverse field. Therefore, analysis of the archer coin type of the imperial Guptas provides **conclusive evidence that *Chandra* was the short name for Chandragupta II Vikramaditya[5]. Therefore, the age of the pillar is at least 1600 years.**

Location of *Vishnupadagiri*

The Delhi iron pillar is currently located in the courtyard of the Quwwat-ul-Islam mosque in New Delhi. However, this was not the original erection site of the pillar. The original location of the pillar, *Vishnupadagiri*, has been identified as modern Udayagiri[4,6], in the close vicinity of Besnagar, Vidisha and Sanchi. These towns are located about 50 km east of Bhopal,

in central India. Literary, archaeological, numismatic and geographic evidences for the identification of modern Udayagiri as ancient *Vishnupadagiri* have been discussed in detail elsewhere[4,6]. If there was one location that Chandragupta II Vikramaditya was personally associated with, it must have been Udayagiri because it is here that we find two datable inscriptions specifically mentioning Chandragupta II, and, moreover, 19 of the 20 cave temples at this location are from his reign. The antiquity of *pada* (i e, foot) worship is well established in the region near Udayagiri as indicated by several evidences[6]: worship of inscribed *Vishnupada* (feet of Vishnu) at a place called *Charan Thirth* situated at the confluence of rivers Bes and Betwa, the presence of Heliodorous pillar at Besnagar, worship of the tenth Jain *Thirthankara* Sheetalnath's footmarks in Cave 20 in Udayagiri (dated by an inscription in this cave to 426 AD) and the discovery of a Kushan-period brick with partial marking of a foot at Udayagiri. A later-day inscription from 1036 AD in cave 19 specifically identifies Chandragupta II having built the temples at Udayagiri[6]. In order to further emphasize Udayagiri's positive identification as *Vishnupadagiri*, and hence the original location of the iron pillar, Dass[6] provided several evidences for iron-making tradition in the Udayagiri-Vidisha-Besnagar-Sanchi region (iron wedges from Sanchi and Heliodorous pillars, iron slags from several sites near Vidisha, remains of iron-making furnaces, names of nearby places like Lohangi and Lohapura, etc).

The astronomical significance and importance of Udayagiri, i e, *Vishnupadagiri* during the Gupta period, has also been established, for the first time, from several archaeological evidences by Dass[6]. The most significant aspect of the location of Udayagiri is that it is situated at 23°31' latitude, almost on the Tropic of Cancer. There are several evidences to show that Udayagiri was an important center for astronomical observations during the Gupta period[7]. The complete layout of Udayagiri is provided in **Fig 4a**. The general observation of the overall hill site is that it is shaped like a
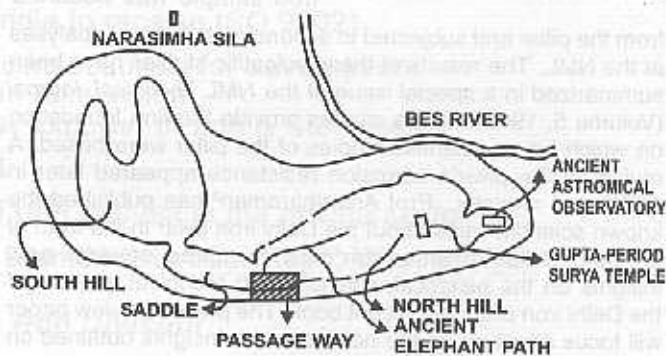

Fig 4a : The layout of Udayagiri hill.

foot. A saddle connects the northern and southern hills. A specially cut passageway is located at the place where the northern hill meets the saddle. The Gupta period embellishment, modification and construction at Udayagiri were concentrated around this passage (shown hatched in

12

Fig. 4a). The passage is very important because it is the only path leading to the west of the hill and it is the main approach to the temple on the northern hilltop and remains en-route to it. The discovery of an ancient elephant path (see Fig 4a) further reinforces the importance of the passageway. Most of the cave temples are located around the passageway. The locations of the cave temples around the passage are provided in **Fig 4b**, which is the detailed map of the hatched
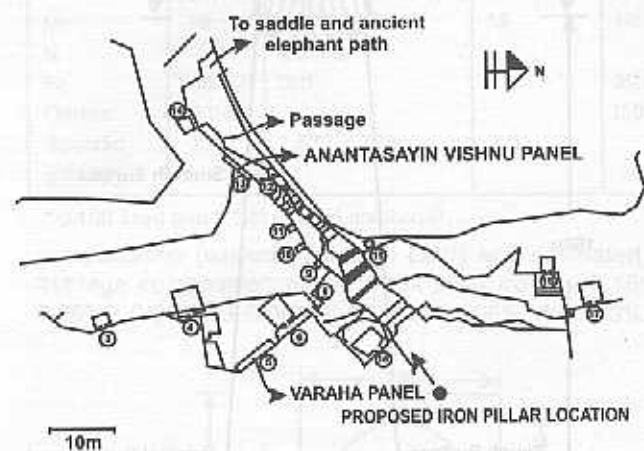

Fig 4b : The layout of the important caves around the passageway.

region in Fig 4a. All the carvings and the caves are cut into the south wall of this passage and also on the east face abutting it (Fig 4b). In this figure, the cave temples have been numbered within circles as per the existing classification system and the most important ones are the *Varaha* panel in cave 5 and *Anantasayin Vishnu* panel in cave 13. The astronomical aspects of the iconography of images that appear at Udayagiri have been addressed and analysed in detail elsewhere[7].

As the Udayagiri site was astronomically significant, the iron pillar must have been located at a calculated position with respect to the important caves. It has been shown elsewhere[6] that the decorative bell capital of the Delhi iron pillar was originally topped with a *chakra* image (**Fig 5**). The iron pillar, therefore, alluded to the weapons of Vishnu, namely the *gada* (i e, mace) and *chakra* (i e, discus). The main body of the pillar symbolically represented *gada* while the *chakra* emblem, the discus. This is also in tune with the iron pillar inscription that the pillar was meant to be the standard of Vishnu (*Vishnuordhidhvajah*). Interestingly, the image of the Delhi iron pillar capital's
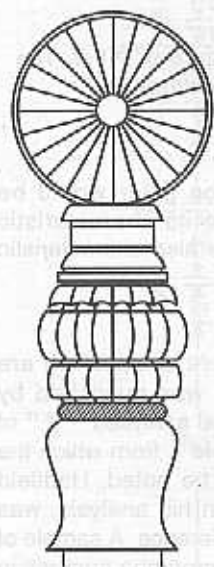

Fig 5 : Reconstruction of Delhi Iron Pillar capital with the *Chakra* image atop the capital.

box pedestal along with the *chakra* image is depicted in one of the Vishnu panels in cave 6 at Udayagiri itself (**Fig 6**) and this is the most forceful argument for the *chakra* image atop the Delhi iron pillar capital. The circular disc is also in tune with the cut that is seen on the top surface of the capital and this will be addressed later.

Fig 6 : High magnification view of the *chakra* of Vishnu of cave 6 at Udayagiri. Photograph courtesy : Ellen M. Raven.

The astronomical aspect of the iron pillar's erection site needs to be addressed in detail. Based on the hierarchy of inscriptions at Udayagiri, it was concluded that the pillar was located in front of cave 7 in front of the passage[7]. The original location of the pillar has been tentatively marked with a dot in Fig. 4b. The pillar must have been oriented such that the Sanskrit inscription faced east because this is the entrance direction to the complex in Udayagiri. If the iron pillar was located in front of cave 7, then several facts regarding the shadow of the pillar during early morning sunlight on significant astronomical periods in the year can be deduced based on detailed solar observations at Udayagiri[8]. The summer solstice is significant because the sun rises in direct alignment with the passageway[7]. Therefore, the early morning iron pillar shadow fell on the *Anantasayin* Vishnu panel in cave 13 only in the time preceding and following the summer solstice. The significance of the solstice and its further relevance to the Udayagiri site have been elaborated elsewhere[7]. Therefore, the positioning of the iron pillar additionally served to highlight the astronomical intelligence, knowledge and advancements prevalent during Chandragupta II Vikramaditya's time.

Later History

The Delhi iron pillar was re-located to its current location in New Delhi in the courtyard of the Quwwat-ul-Islam mosque (near the Qutub Minar) around **1233 AD by Iltutmish**[8]. The history of movement of the iron pillar from its original erection site at Udayagiri to its current location has been discussed in detail elsewhere[3].

ENGINEERING DESIGN OF THE PILLAR

The current burial level of the pillar was not the original burial level of the pillar when it was erected at Udayagiri. Hammer-marked cavities that are still visible on the surface of the pillar in the rough region just below the smooth surface-finish region
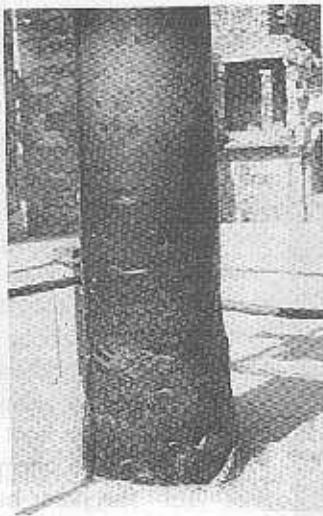
Fig 7 : Bottom region of the Iron Pillar. The rough portion was originally buried in the ground.

(Fig 7). The rough portion of the pillar was originally buried in the ground 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[a]. Sketches[10] and earlier published photographs of the pillar taken before[11,12] (for example, Fig 8[11]) 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[13]. 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 **Fig 9**. The rough surface occupies one-fourth (60U) and the smooth surface three-fourths (180U) of the pillar's main body length, excluding the decorative top. The burial of the pillar body to one-fourth of its height would
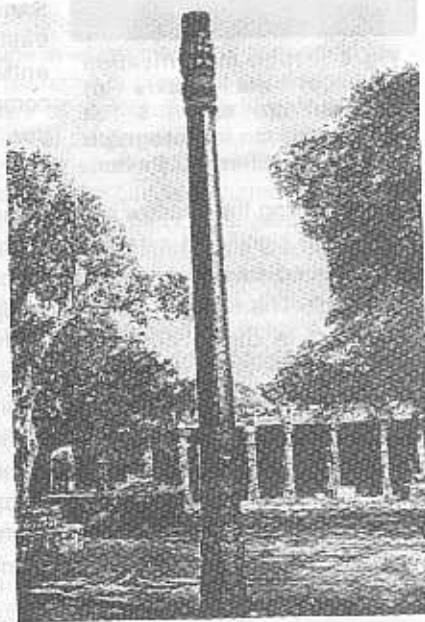

Fig 8 : One of the oldest published photographs of the Delhi Iron Pillar[11]. Notice the absence of the stone platform around the base of the pillar.

have provided the necessary stability to the structure. The decorative bell capital[14] is again a symmetrical object and its relative dimensions are provided in **Fig 10**. The *chakra* image atop the capital 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 is equal to 1 inch (1 *angulam*).
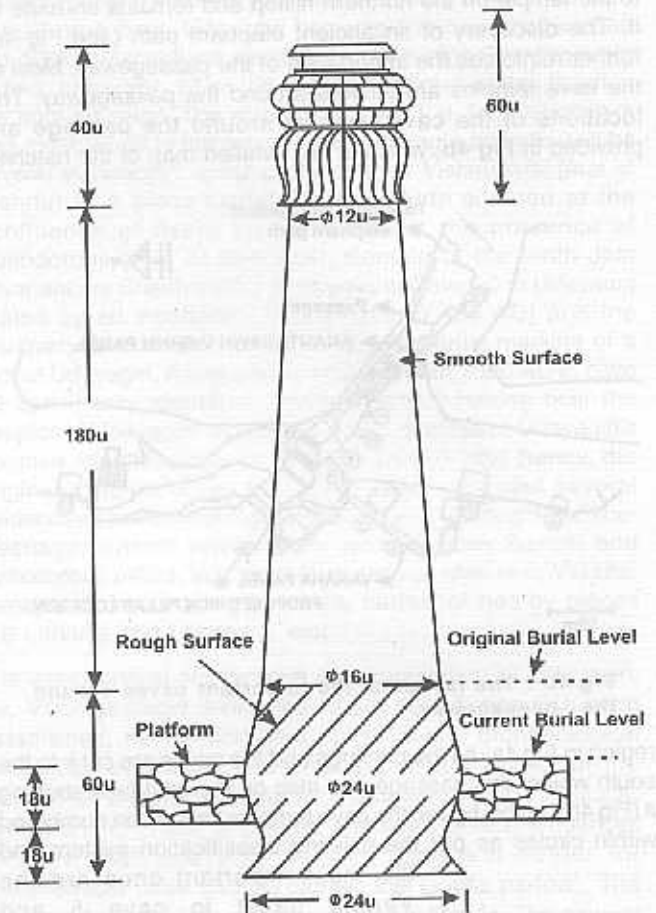

Fig 9 : Relative dimensions of the Delhi Iron Pillar. The unit U measures 1" and is equal to 1 *angulam*.

IRON OF THE 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 irons.

Composition

Several analyses of the Delhi pillar iron's composition are available ever since the first analysis was published by Hadfield[1] in 1912. The published chemical analyses[1,15,16,17] of the Delhi pillar iron are presented in **Table 1** from which the variation in the 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 Delhi pillar 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[19]. Wranglen[2] utilised the available

Table 1 : Published Composition Analyses of DIP Iron

Components	Hadfield[1] (1912)	Ghosh[15] (1963) Above	(1963) Under	Lahiri et al[16] (1963)	Lal[7] (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

compositions (excluding that of Lal[17]) and estimated the average composition of the Delhi pillar iron as 0.15%C, 0.25%P, 0.005% S, 0.05%Si, 0.02% N, 0.05% Mn, 0.03% Cu,
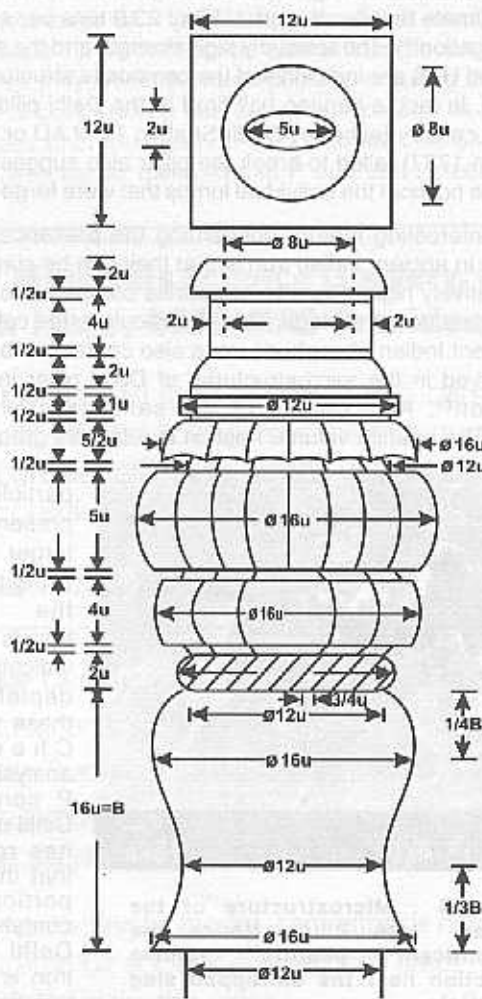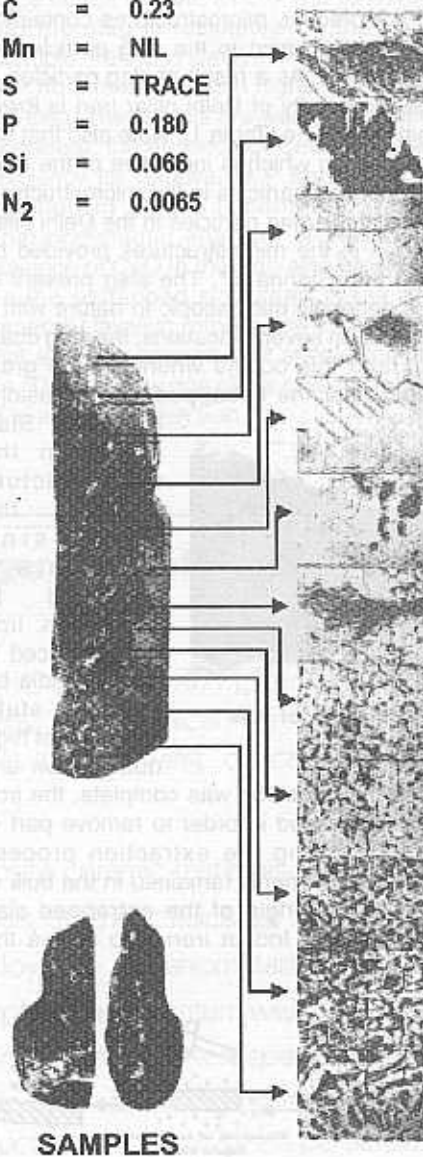

Fig 10 : Relative dimensions of the decorative bell capital of the Delhi Iron Pillar.

0.05% Ni and balance Fe. The high P content of the Delhi pillar iron must be noted.

Microstructure

Some important aspects of the underlying microstructure of the Delhi pillar 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[15,16] (Fig 11). 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[15]. Many slip bands were seen in the surface ferrite grains. Elongated slag particles and oxide particles were also seen in the deformed structure in the near surface regions. Lahiri et al[16] also conducted metallographic examination of the Delhi pillar iron and the irregular distribution of pearlite was also noted. The absence of a uniform distribution of pearlite is indicative of segregation

C	=	0.23
Mn	=	NIL
S	=	TRACE
P	=	0.180
Si	=	0.066
N_2	=	0.0065

SAMPLES

Fig 11 : Microstructure of the Delhi Iron Pillar (after Ghosh[15]).

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[15,18]. Therefore, a wide variation in structure is exhibited by the Delhi pillar 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 Delhi pillar iron's composition as determined by several investigators (Table 1).

The Delhi pillar iron was characterized by a relatively high proportion of slag inclusions and the microstructure near the slags showed wide variations (including normalised and annealed structures)[15]. 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 Delhi pillar iron is lower than that for the purest form of Fe (Table 1). Note also that the specific gravity is not uniform which is indicative of the non-uniform distribution of the slag particles in the microstructure. The non-uniform nature of the slag particles in the Delhi pillar iron can be clearly seen in the microstructures provided by Ghosh[15], and Bardget and Stanners[18]. The slag present in the Delhi Iron Pillar is generally microscopic in nature with a few of them in larger sizes. In several locations, the slag coats the grain boundaries and this occurs whenever the grain bounda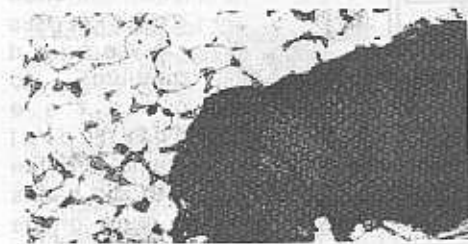ries are located near the entrapped slag inclusions (Fig 12). Slag results in the microstructure due to the processing method employed to obtain iron. Iron was produced in ancient India by solid state reduction of high quality iron ore

Fig 12 : Microstructure of the Delhi Iron Pillar[18]

using charcoal[19]. 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 (Fig 13). 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
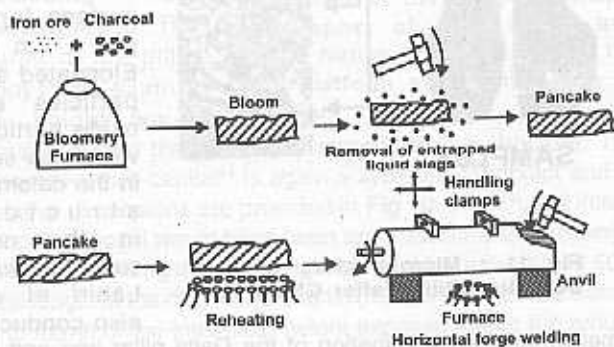

Fig 13 : Iron extraction in ancient bloomery furnaces.

presence of a small amount of unreduced iron oxides. Generally, silica impurities in the ore combined with unreduced iron oxide result in the slag fayalite Fe_2SiO_4. The ancient Indian ironmakers specifically selected silica-containing ores because of the need to maintain liquid fayalitic slags at the relatively low operating temperatures ($1100^\circ C$ to $1300^\circ C$) in the ancient bloomery furnaces[4]. Microstructural investigations on iron produced during the Gupta period showed that fayalite and iron oxides were present in the entrapped slag inclusions in iron[20,21]. Some of the iron oxides also contained carbon, presumably due to charcoal used in iron extraction[20]. The presence of carbon in these unreduced oxides would render these oxides cathodic in nature with respect to the surrounding matrix.

It must be also noticed that the slag particles in the Delhi pillar 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[23] 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[18]). 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 pillar iron 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 can be surrounded by a relatively higher fraction of pearlite compared to regions far removed from the slags. This is particularly the case when the ancient Indian phosphoric irons also contain carbon. This is observed in the microstructures of Delhi pillar iron[15] and Eran iron[20]. An example of the same is provided in Fig 1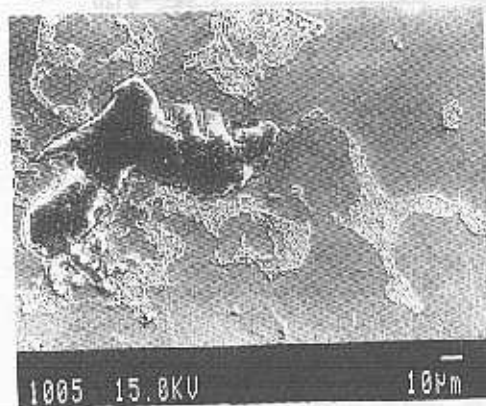4. The pearlite volume fraction is relatively greater near the slag particles. The presence of a larger amount of pearlite near the slag inclusions is indicative of P depletion in these regions. Chemical analysis of the P content in Delhi pillar iron has revealed that the major portion of P content in the Delhi pillar iron is in solid solution while a smaller

Fig 14 : Microstructure of the Dhar Iron Pillar. Notice the significant pearlite volume fraction near the entrapped slag particle.

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[15]. The presence of P was also confirmed, by electron microprobe analysis, in the entrapped slags of the Gupta period iron[21,32]. 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 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 Delhi iron pillar. As the Delhi pillar 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 large 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 cold working due to segregation of P at the grain boundaries (the phenomenon being termed cold shortness). While it was earlier believed that P in ancient steels comes from slag inclusions[24], 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 fayalitic slags (i e, consisting of iron orthosilicates Fe_2SiO_4). This is also corroborated by available compositions of ancient iron-making slags from archaeological excavation sites[17]. The slags do not contain lime[17]. 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[25]. Therefore, the absence of CaO in the slags leads to a lower efficiency for removal of P from the metal, which invariably 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[26]. As the entrapped slag seen in the ancient Indian iron is generally fayalitic 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.

(To be continued in the next issue)

Delhi Iron Pillar

(Continued from April 2004 issue)

R. Balasubramaniam

MANUFACTURING METHODOLOGY

The manufacturing methodology of the main body of the pillar will be addressed initially[23] and later the decorative bell capital's design[14] 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 iron 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 is 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[23]. 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 15)**. The addition of metal would have been sideways
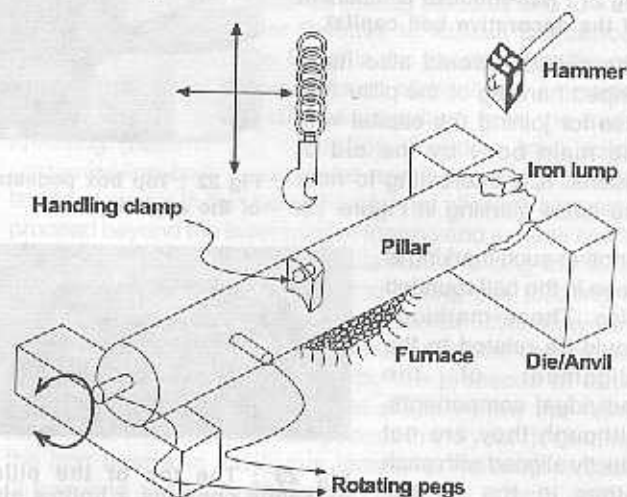

Fig 15 : Horizontal forge welding technique for manufacturing the pillar's main body

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 16)**. 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 is provided in Figure 8 in Balasubramaniam[23]. This insert (originally containing the holding clamp) appears to have been inserted onto the surface of the pillar and this is indicated by the presence of cracks emanating from the insert periphery onto 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 17)**. Close observation of this region reveals that this rectangular slot is exactly of
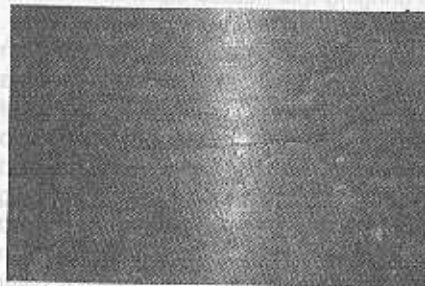

Fig 16 : Evidence for a rectangular insert (arrowed) in the previously brightly polished region of the pillar. A close-up view of the same, when the region appeared brightly polished, has been provided in Figure 8 in Balasubramaniam[23].
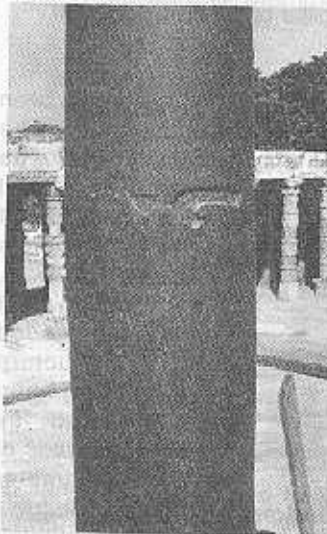
appeared brightly polished,

Fig 17 : Missing clamp located at a vertical distance of about 6 feet above the insert seen in Figure 16

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 was manufactured, the handling of the pillar must have become 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 was probably 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 smoothened by chiseling and burnishing the surface of the pillar and, thereby, providing it a smooth tapered cylindrical appearance. Finally, the Sanskrit inscriptions were inscribed onto the surface of the pillar. Cold dies must have been used for inscribing the writings on the metal surface, possibly after local heating before inscribing. The decorative bell capital must have been finally fitted onto the top portion of the Delhi iron pillar and then the whole pillar erected at Udayagiri.

Decorative Bell Capital

The decorative bell capital of the Delhi iron pillar has been described in great detail by Balasubramaniam[14]. The main features of the capital will be summarized. The decorative bell capital consists of seven distinct parts (Figures 18a & b). The bottom-most part is the reeded bell structure which has been manufactured by utilizing iron rods of uniform diameter (Figure 19). Atop this comes the slanted
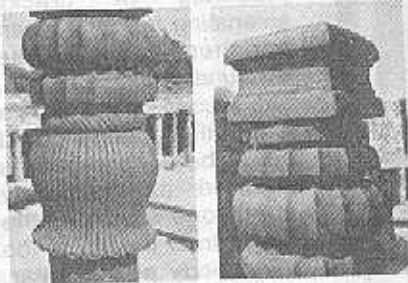

Fig 18 : Decorative bell capital of the Delhi iron pillar : (a) bottom and (b) top

rod structure (Figure 20). 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[27,28]. The next three members are rounded structures, with the top one being only

Fig 19 : Details of the bottom region of the reeded-bell component of the decorative capital
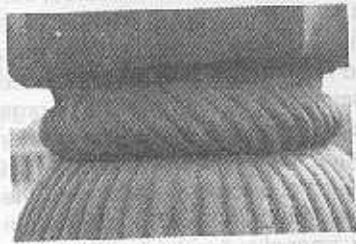

Fig 20 : Details of the slanted rod structure above the reeded-bell structure. Notice the presence of a black filling in between the joints.
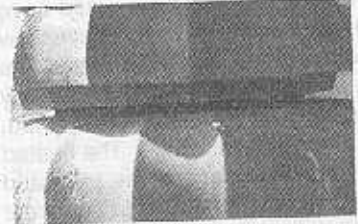
Fig 21 : Half-rounded component of the decorative bell capital

The cylinder would also have helped handing 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 marking in Figure 19. Another such marking is seen in the half rounded disc. 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.

half rounded (Figure 21) because when the pillar is viewed from the bottom, this part would appear curved when viewed in perspective from the bottom. A round disc comes above this and finally the box pedestal is placed on the top of the capital (Figure 22). The box capital contains holes that are empty at the four corners[14] and these could have been originally utilized for holding different animal figures, depending upon the season of the year[8]. The top of the pillar presently contains a hollow slot (Figure 23) in which the chakra image must have been originally fitted. The fitting methodology of the various components is illustrated in Figure 24, where the individual components are shown shrunk fit around a hollow cylinder. Evidence for this kind of fitting method has been presented earlier[14].

Fig 22 : Top box pedestal of the capital

Fig 23 : The top of the pillar presently contains a hollow slot in which an image of Chakra must have been originally present[8].

CORROSION RESISTANCE

Review of Corrosion Resistance Theories

Several 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[29,30]. 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[2] 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. 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 ammoniacal 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 Surya temple at Konarak 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
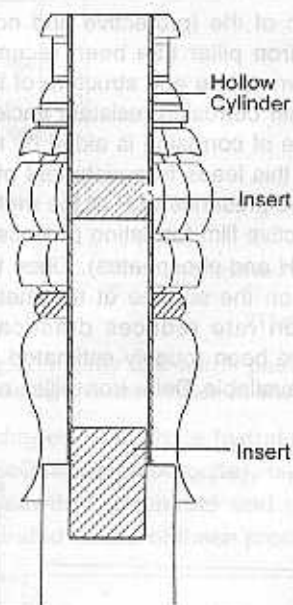
Fig 24 : Shrink fitting methodology of the Delhi iron pillar decorative capital round a hollow cylinder. Notice that the decorative bell capital is attached to the pillar's main body by means of an insert.

the time of the Guptas (300-500AD), produced iron that was capable of withstanding corrosion. **This is primarily due to the high P content of the iron produced during ancient times.**

Beneficial Role of Slag Particles in the Passivation Process

The method of extraction of iron lumps used in constructing the Delhi iron pillar 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[15]) 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[20]. Therefore, it is anticipated that the two-phase structure of the Delhi pillar iron should corrode at a faster rate as compared to iron of similar composition, as the Delhi pillar iron is essentially a composite structure.

In order to explain the anomaly of the composite structure of Delhi pillar iron exhibiting excellent corrosion resistance, the oxidation and reduction processes occurring on the Delhi pillar iron were analysed using the mixed potential theory[29,30]. The analysis is briefly summarised by considering the Evan's diagram presented in **Figure 25**. 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
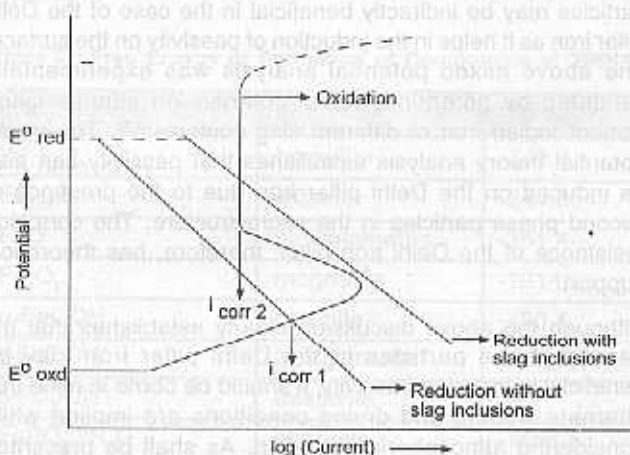

Fig 25 : Mixed potential theory analysis for passivity induction in the presence of slag inclusions in the Delhi pillar iron

atmospheric corrosion of iron. Moreover, the pillar iron contains a relatively larger weight fraction of P (average composition 0.25%) which will aid in inducing passivity in iron[31]. 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 as compared to that for steel without P[32]. Therefore, it is valid to indicate that the Delhi pillar 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 Delhi pillar 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[32]. However, in the presence of slag particles, the exchange current of the cathodic reaction(s) would be higher than in the case when there were no slag particles and the cathodic activation polarisation line would shift to the right as shown in Figure 25. 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 Delhi pillar iron. A similar representation is also employed in Evan's 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 need 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 Delhi pillar 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[29,30]. The mixed potential theory analysis establishes that passivity can also be induced on the Delhi pillar 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 Delhi pillar 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[20,33]. In the case of Delhi pillar iron, the importance of alternate wetting and drying conditions for its corrosion resistance can be gleaned by analysing the available corrosion rate data.

A kinetic model for the growth of the (protective and non-protective) rust on the Delhi iron pillar has been recently proposed[33], based on the known nature and structure of the rust on Delhi iron pillar and other corrosion resistant ancient Indian irons. The initial fast rate of corrosion is aided by the entrapped slag inclusions and this leads to enrichment of P at the metal-scale interface. The presence of P at the metal-scale interface promotes protective film formation processes (catalytic formation of δ-FeOOH and phosphates). Once the protective passive film forms on the surface at the metal-scale interface, the corrosion rate reduces drastically (Figure 26). Growth rates have been roughly estimated for these two regions based on available Delhi iron pillar rust thickness measurements[33].
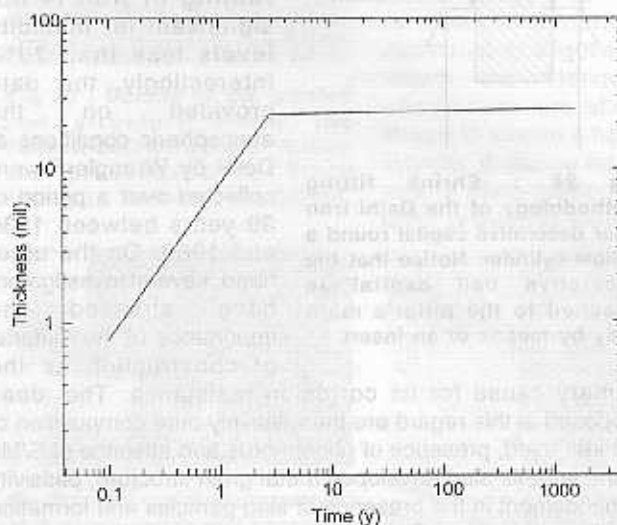

Fig 26 : Proposed kinetics of protective passive film growth on the Delhi iron pillar

Delhi Iron Pillar Rust Characterization

Rust samples were characterised by XRD, Fourier Transform Infrared (FTIR) spectroscopy and Mössbauer spectroscopy[34]. The salient results of the characterisation studies are summarised below. It must again be 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 27). The FTIR spectroscopic study of the DIP rust clearly established that, in addition to iron
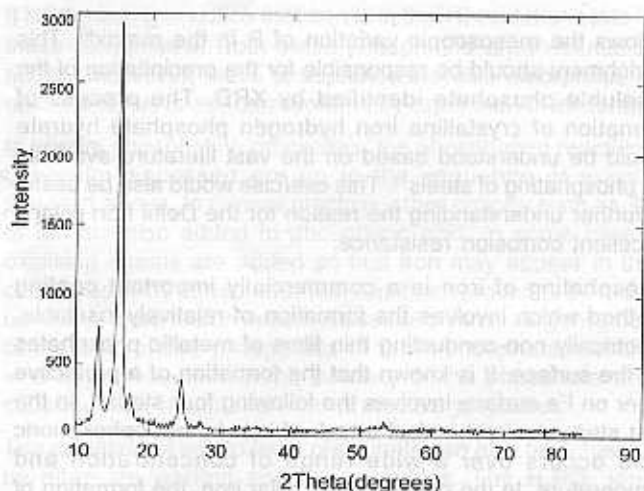
Fig 27 : X-ray diffraction pattern of the Delhi iron pillar rust showing the intensities in the region 2θ = 10° to 80°

hydrogen phosphate hydrate, the scale also consisted of γ-FeOOH (lepidocrocite), α-FeOOH (goethite), δ-FeOOH (misawite), magnetite and phosphates (Figure 28). The hydrated nature of these products was also indicated. It was
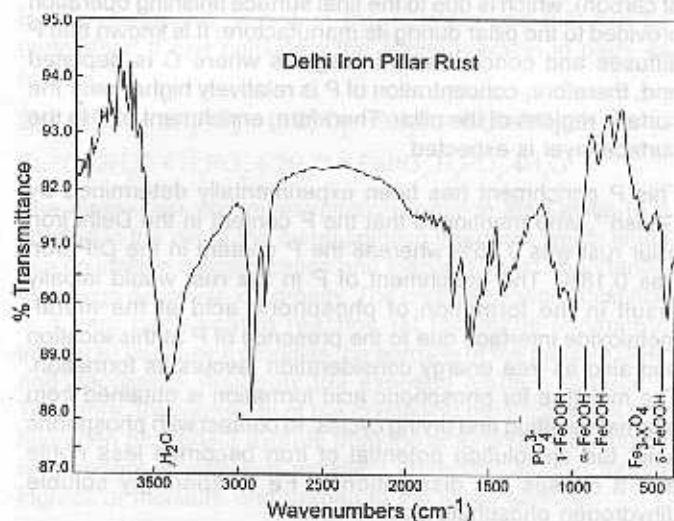

Fig 28 : Fourier transform infrared (FTIR) spectrum from the Delhi iron pillar rust

also seen in the XRD pattern that there was a very small amount of iron oxide/oxyhydroxides present in the crystalline form. The identification of the oxide/oxyhydroxides of iron by FTIR clearly established that they are present in the amorphous form. The FTIR study also provided that phosphate ions were present in the rust, confirming the results of XRD. The Mössbauer spectroscopic study of the Delhi iron pillar 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 29). In summary, while XRD analysis proved the existence of crystalline iron hydrogen phosphate hydrate, FTIR
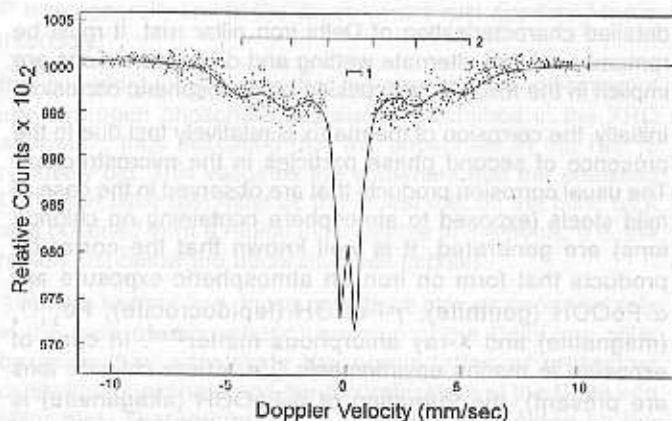

Fig 29 : Mössbauer spectrum obtained from the second Delhi iron pillar rust sample

and Mössbauer spectroscopy proved the presence of magnetite and several oxyhydroxides in the amorphous form. Results of rust characterization of the 950-year-old Dhar iron pillar are also available[35].

In order to understand the presence of the identified corrosion products in the Delhi iron pillar 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[36]. 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 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.

Table 2 : Free Energy of Formation of Compounds at 298K[36]

Compound Formula	Compound Name	DG (kJ/mol)
γ-Fe_2O_3	hematite	-742.4
$Fe_{0.95}O$	wüstite	-244.3
FeO	stoichiometric	-251.4
Fe_3O_4	magnetite	-1014.2
α-FeOOH	goethite	-490.4
γ-FeOOH	lepidocrocite	-471.4
δ-FeOOH	misawite	-
$FePO_4.2H_2O$	strongite	-1657.5
H_3PO_4 (aqueous)		-1142.6
(crystalline)		-1119.2
(liquid)		-1111.7

Process of Protective Rust Formation

The process of protective film formation on the exposed surface of the Delhi iron pillar can be outlined, based on the

9

detailed characterization of Delhi iron pillar 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 α-FeOOH (goethite), γ-FeOOH (lepidocrocite), $Fe_{3-x}O_4$ (magnetite) and X-ray amorphous matter[37,38]. In case of exposure in marine environments (i e, where chloride ions are present), the formation of β-FeOOH (akaganeite) is favoured. In the case of Delhi pillar 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[15]. It is also likely that the sample analysed by them could have contained amorphous δ-FeOOH as the formation of this phase during the initial corrosion of iron has been shown by Misawa and co-workers[37,39] 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 δ-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 $H_2PO_4^-$ ions prevent crystal growth of the corrosion products. The formation of amorphous δ-FeOOH confers the initial corrosion resistance to the DIP iron. The δ-FeOOH phase forms in a discontinuous manner in normal mild steels 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 δ-FeOOH layer next to the metal surface, which is also enriched with the element(s) added to provide weathering resistance (i e, Cu and P). Conversion of amorphous δ-FeOOH to nanocrystalline goethite is indicated on longer exposure times[38]. While the α-FeOOH and γ-FeOOH could be identified by X-ray diffraction, it is generally not possible to identify the δ-FeOOH phase by this characterisation technique.

It is important to note that the oxyhydroxides and magnetite present in the old Delhi iron pillar rust are nanocyrstalline/amorphous in nature and not crystalline. As it is known that the initial oxide and oxyhydroxides that form on the Delhi pillar iron are crystalline in nature[16], 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[37].

The enrichment of P in the δ-FeOOH layer continues with prolonged exposure and this has been observed in P-containing weathering steels[37,28]. Enrichment of P has also been determined in the rust of ancient Indian iron and this

follows the mesoscopic variation of P in the matrix[40]. 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[41]. 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[41]. In the first step, electrochemical attack of iron by orthophosphoric acid occurs over a wide range of concentration and temperature. In the case of Delhi pillar 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 Delhi pillar iron than in the bulk[15]. It was earlier noted that the surface regions of Delhi iron pillar 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 surface layer is expected.

This P enrichment has been experimentally determined by Ghosh[16], who mentioned that the P content in the Delhi iron pillar 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 favours its formation. The moisture for phosphoric acid formation is obtained from 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

$$2H_3PO_4 + Fe \rightarrow Fe(H_2PO_4)_2 + H_2$$

The transient oxides of iron (in which Fe is in the +2 oxidation state) will also be corroded by phosphoric acid to provide $Fe(H_2PO_4)_2$ according to

$$2H_3PO_4 + FeO \rightarrow Fe(H_2PO_4)_2 + H_2O$$
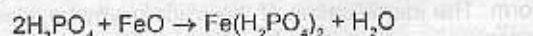
Among the above two reactions, the first one mainly occurs[41].

In the second stage, the contact of the metal shifts the equilibrium in such a way that massive precipitation of monohydrogen phosphate $FeHPO_4$ and tribasic iron phosphate $Fe_3(PO_4)_2$ occurs. The precipitation reactions are

$$3Fe(H_2PO_4)_2 \rightarrow Fe_3(PO_4)_2 + 4H_3PO_4$$

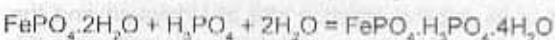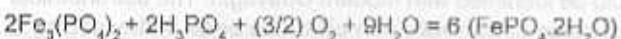$$Fe(H_2PO_4)_2 \rightarrow FeHPO_4 + H_3PO_4$$
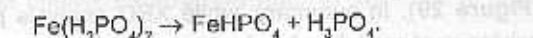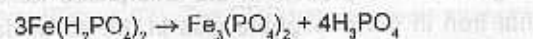
It is interesting to notice that iron is in the +2 oxidation state in these phosphates. Both these phosphates are insoluble in nature. Moreover, these phosphates are also amorphous in nature and this is well corroborated by experimental evidence.

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 H_3PO_4 ions accelerate the air oxidation of Fe^{2+} to Fe^{3+} under alternate wetting and drying cycles and also prevent the crystal growth of the corrosion products. Over time, $Fe_3(PO_4)_2$ is oxidised by atmospheric oxygen and H_3PO_4 to iron hydrogen phosphate hydrate according to:

$$2Fe_3(PO_4)_2 + 8H_3PO_4 + (3/2) O_2 + 2H_2O$$
$$= 6 (FePO_4.H_3PO_4.4H_2O)$$
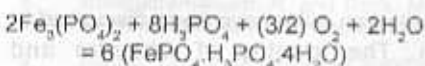
In this compound, iron is in the +3 state and this can be understood if one considers the above reaction in parts as follows:

$$2Fe_3(PO_4)_2 + 2H_3PO_4 + (3/2) O_2 + 9H_2O = 6 (FePO_4.2H_2O)$$

$$FePO_4.2H_2O + H_3PO_4 + 2H_2O = FePO_4.H_3PO_4.4H_2O$$

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 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[41]. Therefore, the formation of the crystalline modification of iron hydrogen phosphate hydrate from the amorphous phosphate is important in providing excellent protection against further ingress of moisture and oxygen to the metal surface.

The 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 Delhi pillar iron[15] 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 to also note that the crystalline modification of iron hydrogen phosphate hydrate was obtained in the XRD analysis[35], thus indicating that the phosphate in the rust is relatively old. This validates the statement that the analysed Delhi iron pillar 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 Delhi iron pillar because they accelerate the precipitation of protective crystalline phosphate and the amorphization of the Delhi iron pillar rust. The amorphization of rust is also aided by the presence of H_3PO_4 ions. The iron pillar's weight is estimated to be approximately 6 tonnes and, therefore, the large mass of the metal plays a contributory role in aiding the alternate wetting and drying process. Sanyal and Preston[42] and, later, Bardgett and Stanners[18] 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 Delhi iron pillar iron because of the large mass of the pillar.

In summary, the protective passive film theory can explain the superior atmospheric 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 formed on the Delhi iron pillar 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[37]. 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 lepidocroite (γ-FeOOH). After this forms, a part of it begins to transform to another allotropic modification goethite (α-FeOOH) and the rust at later times is composed of both these oxyhydroxides. Both these oxyhydroxides are not protective against corrosion and they readily crack allowing for ingress of oxygen and moisture to reach the metal surface and cause further corrosion. However, with time, a part of the FeOOH formed transforms to magnetic oxides of iron, which are much more protective than these oxyhydroxides. There is

also debate on the exact nature of the magnetic oxide that form on exposure of the iron to the environment. This is because the diffraction peaks of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) occur at the same location. However, Mössbauer studies of rust formed on steel exposed to the environment does indicate that Fe_3O_4 (more precisely to be called $Fe_{3-x}O_4$) forms first and this is later converted to γ-Fe_2O_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 α- and γ-FeOOH, there can be another oxyhydroxide of amorphous nature δ-FeOOH, which can form on atmospheric exposure of iron. It is interesting to note that as δ-FeOOH is generally amorphous in nature, no diffraction peaks would be observed from this phase[37]. In ordinary mild steels, this phase does not form as a continuous layer but rather in a discontinuous manner (Figure 30) as it results due to dehydration-oxidation of the Fe(II) complexes. Therefore,
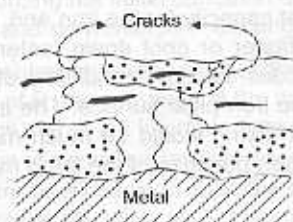
MILD STEEL

WEATHERING STEEL

DELHI IRON PILLAR

Fig 30 : Schematic comparison of the rust structure formed on mild steel, weathering steel and Delhi Iron pillar

the amorphous δ-FeOOH that forms in ordinary mild steels is not protective in nature for these reasons. However, it is possible for this amorphous δ-FeOOH to form next to the metal surface as a continuous layer in which case the steel

obtains corrosion resistance (Figure 30), as the oxyhydroxide is also amorphous in nature. The formation of amorphous δ-FeOOH as a continuous layer next to the metal surface is catalysed by the presence of P and Cu in the material[37]. Moreover, the amorphous δ-FeOOH is enriched with P and Cu elements that are added for improving atmospheric corrosion[37]. 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[37,38].

In the case of Delhi iron pillar, the process of protective rust formation has been outlined in great detail earlier. The structure of the passive film on the Delhi iron pillar is schematically also provided in Figure 30 for comparison with the films that form on mild and weathering steels. Cross sectional microstructural analysis of Delhi iron pillar rust confirms the structure of rust presented[31].
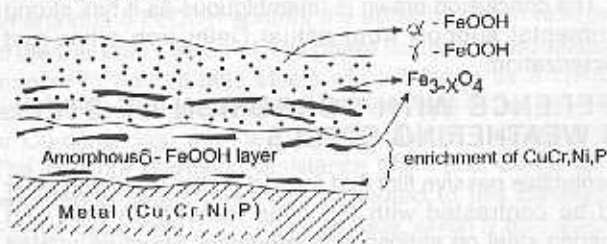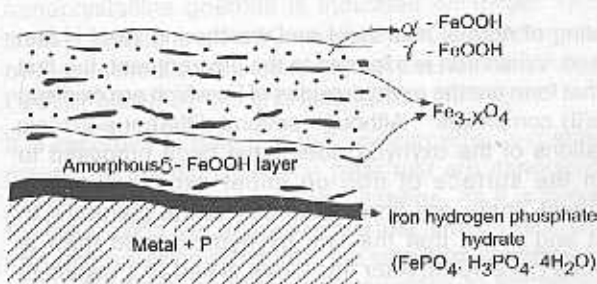
CONCLUSIONS

New insights on the Delhi iron pillar have been discussed in this communication. The identity of *Chandra* and *Vishnupadagiri* of the oldest Sanskrit inscription on the pillar has been analyzed to show that *Chandra* should be identified with Chandragupta II Vikramaditya while *Vishnupadagiri* should be identified with modern Udayagiri. The astronomical significance of the Delhi iron pillar has been addressed by a discussion of its original erection site at Udayagiri and the identification of the *chakra* image that was originally atop the iron pillar capital. The engineering design of the pillar was discussed next, paving the way for understanding of the manufacturing methodology for the main body of the pillar and the decorative bell capital. The nature of Delhi pillar iron and the possible reason for its relatively high P content have been discussed. The nature of the protective passive layer on the corrosion resistant Delhi iron pillar has been addressed based on a detailed characterization of its rust. The rust was composed of iron hydrogen phosphate hydrate ($FePO_4.H_3PO_4.4H_2O$) in the crystalline form in addition to goethite (α-FeOOH), lepidocrocite (γ-FeOOH), δ-FeOOH and magnetite, all in amorphous form. The process of protective rust formation on Delhi pillar 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, which drastically lowers the rate of corrosion. The process of protective passive film formation is aided by alternate wetting and drying cycles, which is an important contribution of the atmosphere to the pillar'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 a protective passive film).**

12

ACKNOWLEDGEMENTS

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