1,600

Thanks to its enduring corrosion resistance, an Indian historical artifact's appearance belies its age.

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A distance of approximately 7,200 miles (11,587 km) may separate Troy, New York, and Delhi, India, but the two cities share an important bond for Professor R. Balasubramaniam.

While earning his doctorate in materials engineering at Troy-based Rensselaer Polytechnic Institute (RPI) in the 1980s, Balasubramaniam attended a seminar given by the eminent corrosion scientist Helmut Kaesche that discussed one of Delhi's most famous archeological landmarks. Having grown up in India, Balasubramaniam was familiar with Delhi's 24-ft (7.3-m)-tall pillar of iron that has remained largely free of rust since it was fabricated in approximately A.D. 400. However, he cites the Kaesche seminar as the source of his fascination with the artifact. Returning to his homeland in 1990 to accept a materials and metallurgical engineering assistant professorship at the Indian Institute of Technology, Kanpur (IIT Kanpur), Balasubramaniam began his investigation of the Delhi Iron Pillar in earnest—apart from his other research activities. Specifically, he sought to determine why the pillar exhibits such remarkable resistance to atmospheric corrosion. After more than a decade of independent, self-funded research, he concludes that the property stems from the formation of a protective passive film on the pillar's surface.[1]

In this recent photo, materials engineer R. Balasubramaniam stands near the Delhi Iron Pillar. A new fence protects the base of the column from the large number of visitors to the site. Photo courtesy of R. Balasubramaniam, IIT Kanpur.

A Major Artifact

Originally fabricated and erected 1,600 years ago at Udayagiri near the present-day city of Bhopal in central India, the pillar was relocated to the Quwwat-ul-Islam mosque in Delhi's Qutub Minar Complex approximately 7 centuries ago. Constructed of rubble from earlier Hindu temples and now designated a World Heritage Site by the United Nations, the Quwwat-ul-Islam mosque is the first mosque built on the Indian subcontinent. The approximately 6-tonne pillar was constructed during the Gupta Period (from A.D. 320 to 600), which is considered the golden age of Indian history.

"The Iron Pillar is considered a major artifact the world over," says Balasubramaniam, now a full professor at IIT Kanpur. "Historians and archeologists consider the pillar to be a very important object of Indian history. The oldest Sanskrit inscription is famous, and its interpretation is still extensively discussed in academic circles."

A Metallurgical Treasure

Balasubramaniam points out that scholarly fascination with the pillar is not limited to students of archeology and history. "Powder metallurgists claim [it] is a living example of an object manufactured by the powder metallurgical route," he says. "Corrosion scientists are aware of the remarkable corrosion resistance of the pillar."

Years Young

The 1,600-year-old Delhi Iron Pillar exhibits very good corrosion resistance despite its age. Photo courtesy of R. Balasubramaniam, IIT Kanpur.

Since the first such analysis in 1912,[2] researchers have estimated that the pillar's average composition is 0.15% carbon, 0.25% phosphorus, 0.005% sulfur, 0.05% silicon, 0.02% nitrogen, 0.05% manganese, 0.03% copper, 0.05% nickel, and the balance iron.[3] "Interestingly, a sample of Delhi pillar iron was subjected to microprobe analysis in order to determine the composition of the elements manganese, chromium, copper, and nickel in the near-surface regions," says Balasubramaniam. "It was found that the composition of copper [0.05%], nickel [0.05%], manganese [0.07%], and chromium [nil] was uniform through several millimeters into the sample from the surface." [4]

Balasubramaniam says that the pillar's high phosphorus content has kept it from rusting on a widespread basis. "The presence of phosphorus is crucial to the corrosion resistance," he notes, explaining that the phosphorus content is high because limestone was not used as a flux when the iron was extracted. "The absence of calcium oxide [CaO] in slags leads to a lower efficiency for removal of phosphorus from the metal, which invariably resulted in higher phosphorus content. Archeological evidence indicates that the ore for extracting the iron must have been carefully chosen so that a relatively high amount of phosphorus would result in the extracted metal."

Typical of ancient Indian irons, the microstructure of the pillar shows a wide variety of structures, says Balasubramaniam. He adds that the structures also prove the iron was obtained by the direct reduction process rather than casting. "The pillar is a solid body with good mechanical strength," notes Balasubramaniam. He points out that the yield strength is 23.5 tons (21,319 kg)/in.^{2} (645 mm^2), the ultimate tensile strength 23.9 tons (21,682 kg)/in.^{2}, and elongation 5%.

Forge welding was the process used to manufacture the pillar. Balasubramaniam says that approximately 40- to 50-lb (18- to 23-kg) lumps of iron served as the raw materials. "Forge welding is an operation in which iron lumps were joined together by forging them in the hot state such that fusion is obtained between them," he explains. "Research has indicated that the pillar was manufactured with the pillar in the horizontal position, and the addition of lumps was from the side," he says. "The decorative bell capital is truly a marvelous example of blacksmithy and consists of seven distinct parts. These individual components were shrunk-fit around a hollow cylinder, which was joined to the main body by the aid of an insert."

Environment or Materials?

Balasubramaniam says that two general schools of thought exist to explain why the pillar exhibits superior corrosion resistance: the environment and materials theories. "The proponents of the environment theory state that the mild climate of Delhi is responsible for

These photos show the upper and lower sections of the decorative bell capital atop the Delhi Iron Pillar. The different components were shrunk-fit around a hollow cylinder. Photos courtesy of R. Balasubramaniam, IIT Kanpur.

the corrosion resistance," he says, pointing out that the city's relative humidity (RH) does not exceed 70% for significant periods of time in a given year. "It is known that atmospheric rusting of iron is not significant for humidity levels less than 70%."

Advocates of the materials theory, to which Balasubramaniam subscribes, stress the construction material's role in determining corrosion resistance. "The ideas proposed in this regard are the relatively pure composition of the iron used, presence of phosphorus, and absence of sulfur [and] manganese in the iron, its slag particles, and formation of a protective passive film," he says. The passive film component of the theory stems from Balasubramaniam's research. "The large mass of the pillar also plays a contributory role," he adds.

Although the environment and materials camps comprise the two predominant sides of the debate, Balasubramaniam adds that the literature does feature other, less-widely held theories about the pillar's corrosion resistance. These suppositions include: initial exposure to an alkaline and ammoniacal environment; residual stresses resulting from the surface finishing (hammering) operation; freedom from sulfur contamination both in the metal and in the air; the "cinder theory," which holds that layers of cinder in the metal stop corrosion from advancing; and that surface treatments of steam and slag and coatings of clarified butter were applied to the pillar after manufacture and during use, respectively. "The use of surface coatings is readily discounted because a freshly exposed surface attains the color of the rest of the pillar in about 3 years' time,"[5] says Balasubramaniam.

Balasubramaniam asserts that the low incidence of corrosion on ancient iron artifacts in more humid parts of India supports the materials theory. "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 RH is high for significant periods of the year," he says. The Surya temple at Konarak, located near the Bay of Bengal, and the Mookambika temple in the Kodachadri Hills, which rise near the Arabian Sea, reportedly are two such locations. Balasubramaniam says that ancient iron beams at the Surya temple and an iron pillar at the Mookambika temple all are in very good shape despite their proximity to coastlines.

Protective Passive Film

Balasubramaniam cautions that the Delhi Iron Pillar does rust, but he adds that the passive rust is so protective and thin that it keeps the occurrence—and appearance—of corrosion at a minimum. Because the region just below the decorative bell capital is inaccessible to the public, rust from this location is the oldest undisturbed rust on the pillar. Consequently, Balasubramaniam and a colleague collected rust from this region and characterized it by x-ray diffraction, Fourier Transform Infrared spectroscopy, and Mössbauer spectroscopy.[6] Balasubramaniam says the inspections revealed that the rust contains amorphous iron oxyhydroxides (lepidocrocite [gamma-FeOOH], goethite [alpha-FeOOH], and delta-FeOOH) and magnetite. It also contains crystalline phosphates, including iron hydrogen phosphate hydrate ($FePO_4 \cdot H_3PO_4 \cdot 4H_2O$).

Balasubramaniam says that the rust layer becomes increasingly protective—and the rate of corrosion decreases—as its composition changes. "In the initial stages, the rust comprises lepidocrocite and goethite,” he says. “These forms of rust do not offer excellent protection and, therefore, the rate of corrosion is still maintained on the high side. Conversion of part of this rust to magnetite does result in lower corrosion rates.” However, he adds that cracks and pores in the rust allow oxygen to diffuse and complementary corrosion reactions to occur. “Moreover, reduction of lepidocrocite also contributes to the corrosion mechanism in atmospheric rusting,” he says.

According to Balasubramaniam, the catalytic formation of delta-FeOOH initiates the Delhi Iron Pillar’s enhanced corrosion resistance. “This phase is amorphous in nature and forms as an adherent compact layer next to the metal-scale interface,” he says. “Its formation is catalyzed by the presence of phosphorus in the iron. Upon its formation, the corrosion resistance enhances significantly because delta-FeOOH forms a barrier between the rust and the metal.” He says a similar mechanism is at work in weathering steels that contain copper and phosphorus.

“In the special case of Delhi pillar iron and in the general case of ancient Indian irons, the presence of significant amounts [greater than 0.1%] of phosphorus in the metal leads to further effects, which have a direct bearing on their corrosion resistance,” says Balasubramaniam. “Due to the initial corrosion of metal, there is enhancement of phosphorus at the metal-scale interface. This phosphorus reacts with moisture, and conditions are created in the rust that are ideal for formation of phosphoric acid [H_3PO_4], which eventually leads to the precipitation of phosphates in the long term.”

Balasubramaniam says that several phosphate formation reactions occur. Exposure conditions dictate the nature and type of these phosphates, which demonstrate an inhibitive nature and thus affect corrosion resistance. “Added benefits accrue when the phosphate forms as a continuous layer next to the metal,” the researcher says. “In the case of alternate wetting and drying cycles [such as those present in atmospheric corrosion], the amorphous phosphates can transform to crystalline modifications, and in this process there is a large reduction in porosity in the phosphate. This transformation results in further excellent corrosion resistance properties.”

Following the ‘Beacon’

When viewed from a nonscientific standpoint, the Delhi Iron Pillar’s ability to resist corrosion has often been called a “mystery.” Balasubramaniam is quick to dismiss this response. “There is nothing mysterious about the iron pillar,” he says. “The resistance to atmospheric corrosion is due to the presence of a relatively high amount of phosphorus in the pillar. The remarkable corrosion resistance can be understood by applying the basic principles of corrosion research.” He adds that the direct reduction technique used to produce the iron is no mystery, either. “The ancient Indian ironmaking technology is well-known,” he says. The established scientific facts notwithstanding, Balasubramaniam concedes that one aspect of the pillar is difficult to explain. “There is one aspect that is not well-understood and this may be called a mystery, in one sense,” he says. “This is the method by which the iron lumps were forge-welded to produce the massive 6-tonne structure.”

The top of the 24-ft-tall Delhi Iron Pillar. Photo courtesy of R. Balasubramaniam, IIT Kanpur.

Mystery or not, the Delhi Iron Pillar serves as a guidepost for metallurgists in the 21st century and beyond, asserts Balasubramaniam. In fact, just as a seminar at RPI inspired him to study the pillar, he hopes that his research will motivate others to explore the potential uses of phosphorus-containing iron. “There are so many wonderful options available with phosphoric irons,” he concludes, adding that the Iron-Phosphorus phase diagram deserves as much attention as the more popular Iron-Carbon phase diagram. “There is an exciting future in developing phosphoric irons, particularly for corrosion scientists and engineers.[7] The beacon of light showing the way to the future is the Delhi Iron Pillar, with its tested proof of corrosion resistance.”

Editor’s note: Balasubramaniam has compiled his entire body of research on different aspects of the Delhi Iron Pillar into a book titled Delhi Iron Pillar: New Insights *(New Delhi, India: Aryan Books International, 2002). A separate paperback version written for a nontechnical audience,* Delhi Iron Pillar: A Metallurgical Marvel *(New Delhi, India: Foundation Books, 2005), will be published soon.*

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