Chapter 5
Ancient Ferrous Metallurgy: Historical and Social Perspective

Luis Arturo Reyes and Oscar Zapata-Hernández

Introduction

The term "archaeometallurgy" was coined in 1970s by Beno Rothenberg, since its emergence, it was pointed away from only describing the artifact formation. The study provided more information to archaeologists by exploring the archaeological record of the process left. The final objective was pointed to a more complete vision of the development technology for a particular culture in a defined period. Archaeometallurgy has provided helpful information to archaeologists and anthropologists in the pursuit of a more complete understanding of the role of metals in the structure, organization, and development of societies [1, 2]. The metal production and usage of items can be divided into two branches. The first deals with the metal technology and manufacturing. The second part covers the social features of metal usage of a particular society.

In this context, archaeometallurgical studies can provide information regarding trade networks, interchange interactions, sources, physical characteristics, and the uses and disposal of the objects. The mixture of these two aspects agglutinates the most significant information about implementation of metals in a particular culture [2].

The iron technology developed gradually. Iron substituted other metals in the development of tools or weapons only after various centuries of continuous progress. The evolution from the Bronze Age to the Iron Age took place in Near East around 1200 BCE, where iron smelting began to displace copper alloys and the practice spread out. In early iron production, one of the limiting factors was the availability of wood for charcoal. However, iron ores were in quantities enough for ancient production levels. The earliest produced iron is from Tell Asmar in Mesopotamia and Tall Chagar Bazaar in North Syria [1].

L. A. Reyes (✉) · O. Zapata-Hernández (✉)
Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica,
San Nicolás de los Garza, Nuevo León, Mexico

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The ancient Anatolian people known as Hittites developed skills of iron smelting creating efficient tools and weapons. After their empire fall about 1200 BC, the Hittites workers split into different cities allowing two centuries later their arrival to Europe [3]. Tribes in Africa used iron at least as early as 800 CE, showing well-advanced techniques [4].

The crucible steel in India, also known as Wootz, can be traced back to the third century BCE [5]. Cast iron in China extends even further, possibly to the sixth century BCE [6]. Iron casting in China has led archaeologists to visualize iron technology in that region as a source of inspiration for European iron casting development. In Han China, malleable cast iron generated most agricultural implements, while during that time Romans made artifacts from wrought iron [7]. The trading of Romans involved exchange of iron with India and China, as Pliny the Elder noted that the best iron was sent by the Chinese [8]. These events are a clear demonstration of how technologies have great influence on the course of history. The accessibility of iron silicate, a by-product of copper metallurgy, was perceived as the reason for the emergence of the iron industry and the steel. Although copper was more abundant than iron ores, the resources of early population were not enough to achieve the required temperatures.

In Asia, during the early medieval period, the Altay represented a major area of iron and ironworking production. Altay in the 600–1000 CE was closely linked to the history of inner Asian nomadic tribes such as Altayans, Tuvinians, Khakas, and Shori tribes. Turkic-speaking tribes played major roles in the process of early state formation among these ancient nomads. The first large Turkic state, the Turkic Khaganate, emerged in 552 CE comprising Altay tribes. The Turki dominated a vast part, from western Manchuria to Iraq and Byzantium. But many years of war with China and fratricidal conflicts led to the downfall of this state in 744 CE. During that time, the Turkic Khaganates were concerned with becoming a supplier of iron by gaining the vast ore resources of Altay region.

The progression from the production of bronze artifacts to those of iron began during the fifth to third centuries BCE. The analysis of iron ore, metallurgical furnaces, fuel, and slags shows that in the medieval epoch, iron was extracted exclusively by the blooming technique. This represented a direct chemical reduction of iron from iron ore. As a result of chemical reactions, one part of the oxides was reduced to metallic iron. This iron was formed in separate grains that fused together into a friable iron sponge (bloom) that contained a certain quantity of slag in its interstices. Another part of the iron oxide reduced to ferrous oxide (FeO), combined with oxides compounded in the iron ore, to form an easily melted iron-rich slag that flowed down in the blooming furnace.

The most important condition of the blooming process is the creation of a temperature exceeding 1000 °C throughout the entire working space of the furnace. However, the great demand for iron caused the Altay metallurgists to search for ways to increase metal production by increasing furnace volume. The investigation of bloom slags shows that iron smelting took place at a sufficiently high temperature (1300–1600 °C). Attaining such a temperature required a great expenditure of physical energy and enormous experience in managing the blooming process. The smelting of metal was conducted with a single technology in furnaces of a unique type. The blacksmiths of Altay had great influence in the standardization of products that facilitated the lifestyle of the people that in turn benefited the growth of the economy [9].

It has been reported that iron artifacts until fourteenth to fifteenth centuries CE were made of two-stage process [10], such as extraction of iron from ore by smelting process and smithing process [10]. The blacksmith was considered to be the principal contributor to the creation of earliest conceptions of materials and understanding their behavior [11]. Its origin is believed to be around 1500 BCE [2].

In the premodern times, wrought iron was believed to be probably made in open hearths in locations with strong winds. As a result, a mixed iron and liquid slag in a mushy condition was obtained since the maximum temperature at that time was about 1000–1200 °C. Then, the final product was obtained by hammering [11]. At that time blacksmithing involved heating iron until a certain color was seen. Then, strength of iron was characterized based on hardness (scratching) and bending at ambient temperature. Some magnetic qualities were measured using lodestone [11]. A large number of products made during medieval blacksmithing includes swords, lances, arrowheads, siege weapons, armor, shield, tools, nails, doors (for church and castles), ornaments, knives, etc. [12]. One of the limitations of forging iron blooms is that during forging, slag inclusions open up resulting in cracks in the materials. To solve this problem, forge welding was applied [13]. An example of forge welding is the fabrication of large iron cannons like the one found at Thanjavur, India (Fig. 5.1) [14].

Since the beginning, the metal practice was implemented for the creation of armaments. Different analyzes conducted on weapons from the second millennium BCE belonging to ancient civilizations (Vikings, Persians, Assyrians among others) revealed the implementation forging strategies to achieve the perfect point for the ideal weapon all from iron and alloys. They mainly sought to have hardness and a good persistent edge but without reaching the point that the weapon becomes fragile

Fig. 5.1 Seventeenth-century forge-welded iron cannon [14]

with fissures and failures. These failures were reduced thanks to the implementation of coal and iron mixtures and derivatives. Furthermore, new forging methods were implemented allowing the reduction of impurities generated. Earliest blades hardened by heat treatment were produced to be tough and shock resistant; the hardness property improves the cutting ability and wear capability. Tough cores and hard sharp edges provide a balance of desired properties.

However, the control of carburization and quenching process was a difficult task. The hardness growth in quenching process was due to martensite creation, a metastable structure that develops in steels on rapid cooling, and embrittlement was avoided by carburization on cutting edges [15].

Iron smelting in the Roman Empire consisted of extracting molten slag from the bloomery furnace. Within the furnace, an iron bloom was to be collected in the solid state. After meltdown, the bloom would be withdrawn, and the furnace, if necessary, could be repaired or relined and reutilized [16]. Germanic iron smelting with high phosphorous iron ores was smelted in furnaces where the collected slag was placed below the furnace shaft.

The solid matter of a pit is thought to characterize the slag deposit from a single smelting period. A new pit would be dug for each following smelting [16]. High-carbon steel used in toolmaking could be obtained from solid state process such as the Roman iron punch found in Heeten, which was manufactured from extensively forged iron thin strips of metal that were then carburized and welded together [16].

Iron smelting in India must have started sometime during the second millennium BCE. The thermo-mechanical process for forging Wootz steel and its heat treatment were known only to Indian blacksmiths [17]. They gained experience about the effect of carbon on the physical properties of iron and developed the process of carburization and hardening treatment. This process has been known as “steeling” and it has been widely used for making arrowheads, knives, swords, etc., having very sharp and strong cutting edge.

The surgical knives used by Susruta (500 BCE) were probably prepared from carburized iron. The famous Iron Pillar at Delhi is the earliest heavy iron forging existing on record dating back to 400 CE. The pillar, weighing approximately six tones, had been most probably made by forge welding large number of refined iron blooms to first make massive cylindrical blocks and then joining them using iron inserts [17].

Ancient Chinese skilled people developed iron casting techniques in the Spring and Autumn time (770–473 BCE). About 2000 years ago, during Warring States Period (476–221 BCE), craftsmen had already found out the way to make iron more strong and tough. The cast iron is a product of melting iron (pig iron) in a blast furnace, with quantities of iron, limestone, and coke, and taking several steps to remove undesirable contaminants. Carbon and silicon content are adjusted to the desired levels. Other elements can be added to the melt before the final form is produced by casting. The principal advantages of cast iron are its fluidity, lower amount of shrinkage when cooling from the molten state, and the very different properties that are conferred upon it. Its disadvantages are its weakness and lack of ductility and malleability. In cast iron, graphite is the largest portion and one of the most important constituents. The carbon that does not precipitate as graphite forms first as austenite, which later decomposes into ferrite and cementite. In short, all the carbon in cast iron will ultimately be found partly in the form of graphite and partly in the form of cementite. White cast iron presents a carbon content often of 3 or 4%, in the form of cementite; white cast iron will possess largely the properties of cementite. It is very hard and brittle, being machined only with the greatest difficulty, and it has great wear-resistance capacity. Gray cast iron castings usually contain 2%, or more, of graphite. The nature and constitution of gray cast iron is far more difficult to understand than that of steel, and even greater is the difficulty of predicting the effect of any change in composition or in constituents [18].

Cast iron tools were widely used in China around 1000 years of the beginning of the Warring States Period (476–221 BC). The introduction of cast iron artillery was a great contributor to cast iron application. By the middle of the fifteenth century cast iron guns are commonplace, as evidenced by both textual and artifactual evidence. Iron cores were used in iron mold casting; metal mold casting was mostly used to produce agriculture tools, hand tools, and chariot fittings [19].

In China, blast furnace iron production was practiced earlier than in Europe. The technology of cast iron was transferred from China to Europe. The earlies travelers observed a flourishing iron industry in the south of the Caspian Sea close to the silk route. Therefore, the use of technology derived from China is conceivable [19].

The largest blast furnaces were developed in Sichuan, China, a hilly region surrounded by high mountain ranges. Figure 5.2 presents a diagram of a blast furnace utilized in the early 1930s for iron smelting. Luo Mian recorded the process [7].

Sichuan smelted iron formed in the blast furnace was transformed to wrought iron in a puddling furnace. The diagram reproduced here as Fig. 5.3 depicts the

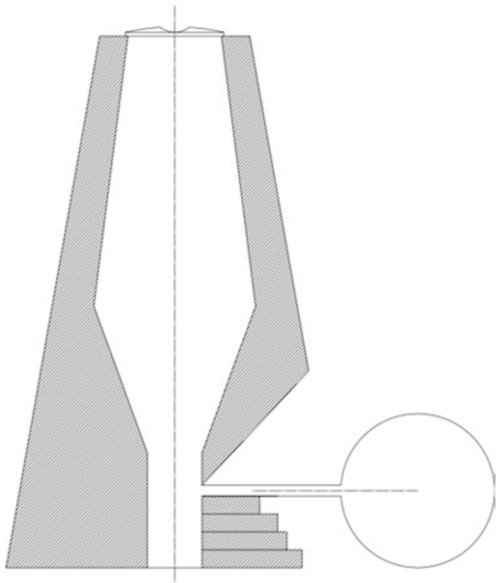

Fig. 5.2 Sichuan blast furnace iron smelting modified from Luo Mian (1936: pp. 19–21) [7]

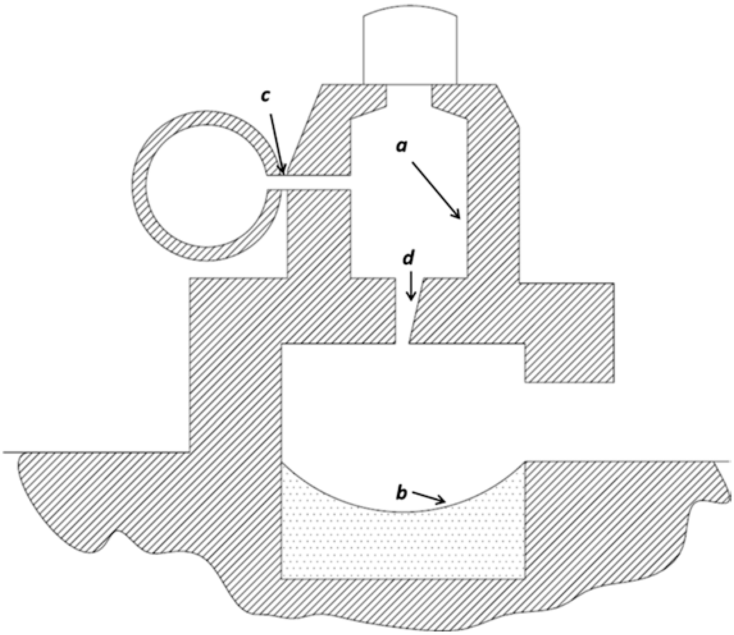

Fig. 5.3 Puddling furnace built entirely of a refractory sandstone. In the closed firebox, charcoal is burned. (**a**) Firebox. (**b**) Puddling bed. (**c**) Blast pipe. (**d**) Flame channel [7]

process. The furnace is constructed fully of refractory sandstone, and charcoal is burned in the firebox. Blast is blown into the firebox, while the flame moves downward into the puddling bed.

Henry Cort patented the puddling process in 1784. This process was in essence very similar to Sichuan process. Henry Cort's innovation has a great advantage compared with the previous process since it allows to single-out the fuel from the iron and consequently makes possible the use of coal in transforming cast iron to wrought iron. A key change in the industry was the usage of mineral coal rather than charcoal in iron smelting process. In 1937, with the start of full-scale hostilities with Japan, Sichuan took a new path where government and most of China's universities and scientific institutes moved there [7].

In the late eighteenth century, there was a great demand for pig iron to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulfur, and very low carbon content. This puddled iron was also very variable in its properties. It was more consistent than the irons produced previously and with the method it lends itself to the production of much larger quantities. Figure 5.4 shows a microstructure of historical forged iron bridge (1898) from Mendoza, Argentina.

The Iron Bridge in Shropshire, England, was the first cast iron bridge built during 1770s by Abraham Darby III. The application of the steam engine to power blast bellows, starting in 1743 in Britain, was a key factor in increasing the production of

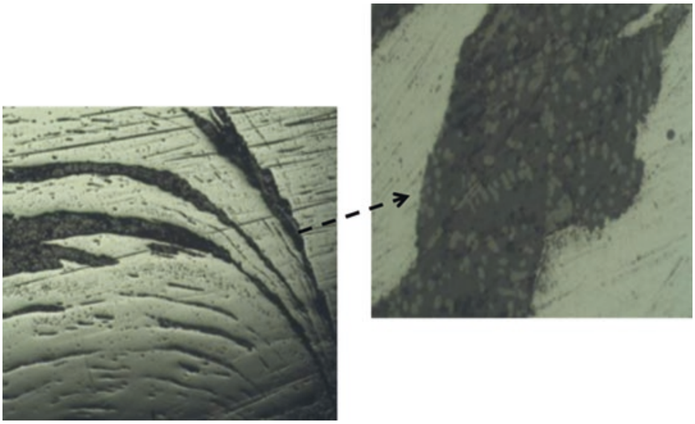

Fig. 5.4 Microstructure of historical forged iron bridge (1898). Equiaxed ferrite grains with a certain amount of inclusions of the silicates, sulfides, phosphates, and iron oxides present in dendritic form. (See Chap. 12: Case Studies of Reverse Engineering on Ancient Metals: Archaeometallurgical and Heritage Study on the Iron Bridge Over the Mendoza River)

cast iron. These took production to an increasing level in the 1750s. Cast iron bridges became commonplace as the Industrial Revolution surged. The best way of using cast iron for bridge construction was by using arches, so that all the material are in compression. Cast iron typically is very strong in compression and comparatively brittle in tension. It was cheaper than wrought iron and thus more common for building artifacts. Cast iron bridges were replaced in England by steel equivalents by 1900 owing to the widespread concern about cast iron under bridges on the rail network in Britain. The replacement bridge was built with wrought iron and steel [20].

Mesoamerican expertise in the creation of metal artifacts had evidently been incorporated by diverse ethnics in early Classic period (CE 300–900) and by diverse groups of Mesoamericans during the Postclassic time (CE 900–1521) [21]. Over the course of several centuries, the spread of metallurgical technology between South and Central America probably occurred. Since the beginning, metal objects engaged spiritual and sacred connotations for Mesoamerican people; however, ferrous technologies were not developed by the pre-Columbian people.

The technology behind metal items in particular manufacturing techniques is based on research and understand of metallurgical concepts. Archaeological metal research extended to consider the furnace design and efficiency in addition to raw materials from the smelt process. The railroads have been of great importance for the growth and prosperity of South American region. The vast quantity of iron needed for construction of railway networks across Argentina's territory was supplied by the British Empire. An enormous variety of products could be made of cast iron, not only for railway lines and stations but also for every product needed in urban constructions [20]. An important example of cast iron work is the threaded bolt of Buenos Aires to the Pacific Railroad, in which through metallographic

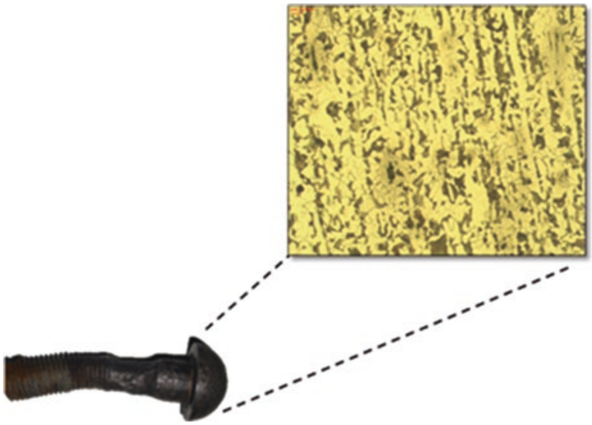

Fig. 5.5 Threaded bolt of Buenos Aires to the Pacific Railroad; a metallography was taken at ×100. (See Chap. 12: Cases Studies of Reverse Engineering on Ancient Metals: Archaeometallurgical Study of Pieces from Buenos Aires to Pacific Railway, BA&P, in Mendoza, Argentina)

analysis of two pieces it was evaluated the probable manufacturing techniques of the parts. In addition, this information allows to compare techniques and materials from that era with the current one and see how much it has varied. Figure 5.5 presents a metallography of the bolt's head, where a ferrite-perlite structure is observed. There seems to be a decrease in grain size due to machining work. During this investigation, it was determined that the pieces would be made of metals that would resemble some steels that are also used today to withstand large loads. Numerous metal installations in the twenty-first century with which our grandparents, great-grandparents, and parents grew up, and even we, are already part of archaeometallurgy. Cases such as Monterrey foundry is part of industrial evolution of México.

It is worth mentioning the influence of British in South America, developing, and raising Paraguay iron industry and technology around the years 1850–1870. Important events occurred during this period such as the triple alliance war (1864–1870), a war between Paraguay and triple alliance of Argentina, Brazil, and Uruguay. The war caused: a significant decline in the prosperity of the economic and metallurgical development of Paraguay, important demographic disaster, and considerable loss of their territories. In addition to the loss of their land, they were forced to pay financially after the acceptance of the free navigability of their rivers. Their lands, factories, and services were privatized. Furthermore, the destruction of blast furnaces by explosives, isolation of weapons, and the demolition of fortifications [22, 23]. Paraguayan political model was an independent system which consisted in a monopoly for wood trade and blast furnaces, this regime facilitated the foundation of the national steel industry. Paraguayan mining was noted for its iron resource, allowing the construction of ships in their own shipyards, railroads, and telegraphs.

The installation of the blast furnaces of Ibicuy for the purpose of weapons production and the hiring of the first English technician Henry Godwin in the year 1848 had a transcendental role in Paraguay industry and the expansion of plants through the Mbuyapey area. The blast furnace of Ibicuy was the first foundry, which was a breakthrough in the country of Paraguay. The foundry of Ibicuy was composed of vast buildings, workshops, and sheds, mainly highlighting its blast furnace that admits a load of 5000 pounds of ore and consumes an equal weight of charcoal.

The principle of operation of this furnace includes a series of processes, which are scorification, decarburization, and recarburization while the contents rotate [24].

Already at the end of the eighteenth century there was a demand for pig iron (an impure form of iron), to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulfur, and very low carbon content. Henry Bessemer patented in 1855 the first cheap process for the manufacture of steel. Henry Bessemer was a British inventor who was inspired by the situations of war, in which his country needed abundant steel production. This event inspired him to develop a better process. In Thomas-Bessemer converter, the rotating furnace (Bessemer oven) lined with refractory bricks inside throws hot air over the iron–carbon mixture. The principal phases of the Bessemer process are: scorching, decarburization, and recarburization. Some of the modifications Bessemer made in the steel process took reference four elements that are essential to the modification. These are: shape of the converter, nature of lining, composition of metallic charge, and composition of blast [25].

In México, the arrival of blast furnace technology was during 1807 through the Guadalupe ironworks created by Andrés Manuel del Rio in Michoacán, with a reverberatory furnace and a blast furnace. At that time, New Spanish mining faced serious obstacles such as the insufficient supply and shortage of iron used in the elaboration of tools used in the mines, or metal that was brought from Biscay. The ironworks equipment and tools in Michoacán generated bases for the establishment of the blast furnace in Monterrey at the beginning of the 1900s for large-scale production. It should be mentioned that the invention of blast furnaces replaced the old technologies such as the Catalan furnaces.

Steel industrial progress in México gave a high priority to in-house steel production over imports from developed countries. The emphasis on industrial growth in Monterrey was due to several factors such as geographical position, large investment of government, and visionary people focusing on the potential of steel industry. During that time there was a huge demand of steel due to the industrialization of the country motivated by President Porfirio Díaz. The investment allowed the edification of large production foundry that included exploitation of iron ores and coal, smelting, processing, and product sales activities [26].

The blast steel furnace known as "Fundidora Monterrey" started operation in 1903; it was the most important steel industry in Latin America at that time. The foundry started with the blast steel furnace No. 1, which had a capacity to produce 350 tons of pig iron per day and had 32 m of height and a crucible diameter of 3.6 m; each of these had four stoves and 14 steam machines that had a force of 4600 HP that gave power to the air blowers [27]. The existence of mineral deposits of iron and coal in the region as well as abundant water at that time in Monterrey were decisive factors for the start of the steel industry. In the first years, *Fundidora Monterrey* faced serious economic difficulties: the global crisis of 1907, the flood in the city in 1909, and the start of the Mexican Revolution in 1910 [28]. Figure 5.6 shows the facilities of *Fundidora Monterrey*, México [29].

Fundidora Monterrey operated for 86 years. During that period, three blast furnaces were installed and departments were adapted for finished product, foundry and machinery, and structures and transportation. The blast furnace No. 1 ran from

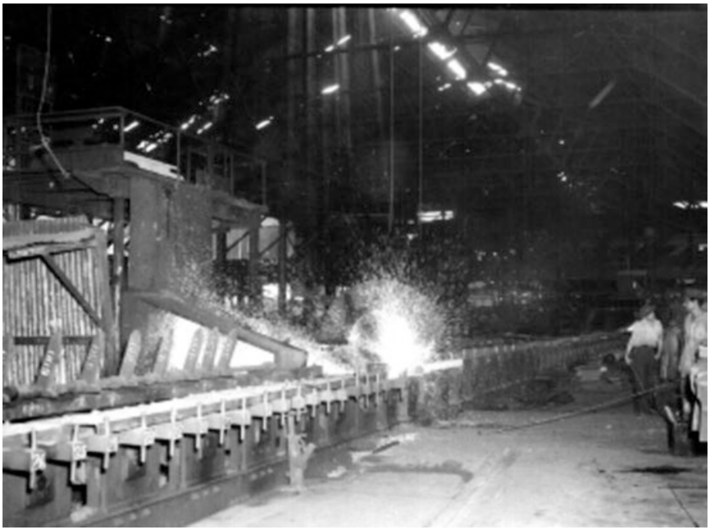

Fig. 5.6 Facilities at Fundidora Monterrey [29]

1903 until the start of 1940s. Operation of blast furnace No. 2 took place early 1940s to meet the demand of the U.S market where steel production began to grow considerably due to the World War II. To accomplish the objective, *Fundidora Monterrey* established various growth strategies to modernize the facilities and increase and adjust the existing ones [26].

The blast furnace No. 2 had a diameter of 4.75 m, height of 51.21 m, and a total volume of 500 m^3. It was designed to produce 500 tons of pig iron per day. The third blast furnace was constructed in the 1960s to meet the demand for steel making. It had a diameter of 8.5 m, automatic charge operation, and a blower of 15,000 HP. It was designed to produce 1500–20,000 tons of pig iron per day, starting operation in 1968 [26]. Monterrey foundry was closed in 1986 by the government; the foundry, for 86 years, had a key place in the steel production of México. Nowadays, after its closing, a steel museum was adapted in the old blast furnace No. 3 structure—a cultural space that commemorates its history and recreates the steel industrial process promoting scientific instruction and technology among the people [30].

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