

# Fire and the art of metals

## A short history of pyrometallurgy

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The first documentary evidence for the use of fire to extract a metal was furnished by the wall paintings of the ancient Egyptians showing workers using the blowpipe and bellows to increase the temperature to melt gold in a crucible. Furnaces grew in size and complexity, coke replaced charcoal in the blast furnace, and the Industrial Revolution took place in England that gradually spread worldwide. More metals became known and new techniques were introduced for their extraction. Among these, metallothermic reactions became prominent in the nineteenth century immediately after the discovery of the electric current and its use to liberate the alkali metals from their salts. Once these metals became available, they were used to produce aluminium from alumina that resisted all other methods of attack. Aluminium, now available on a large scale, was used to decompose the most stable compounds and liberate more metals that became the basis of modern civilization.

### Introduction

*Pura* is a Greek word for fire, and pyrometallurgy is the art and science of extracting metals by thermal methods. Pyrometallurgy is as ancient as our civilization. The use of fire made it possible for ancient people to produce gold articles by melting and casting tiny particles found in rocks, or loose in the ground. Pyrometallurgy is most suitable for the reduction of high grade oxide ores. However, due to the absence of other technology, thermal methods were also applied for the treatment of massive sulphides. Even when the sulphides did not yield a metal directly on smelting as in the case of copper and lead sulphides, roasting was invented to transform the sulphide to oxide, which was then reduced to metal.

Furnaces grew in size and complexity, and pyrometallurgical plants became bulky, high capital investments, and in many cases highly polluting. Of the seven metals of antiquity, tin, lead, and mercury are still produced in the same way as during Roman times. Iron production, on the other hand, has undergone tremendous changes: from a primitive furnace producing a kilogram of metal per day to a complex structure producing 10 000 tons/day. Steel, once a rare and expensive alloy, became a material of construction for ships, bridges, and skyscrapers. Together with the steam engine, pyrometallurgy is the origin of the Industrial Revolution. However, the introduction of new pyrometallurgical techniques at the end of the twentieth century is gradually displacing some of the polluting or energy intensive pyrometallurgical processes.

### The shaft furnace

The oldest metallurgical operations were so crude that only the highestgrade material could be treated. As a reducing agent charcoal made by partial burning of timber was exclusively used. There is no account of metal production

by the ancient Egyptians, but several wall-paintings from the Old Empire of Memphis suggest how metals were melted (Figure 1).

Furnaces used by the ancient people for the production of a metal from an ore might have been built each time a metal had to be produced. Alternate layers of charcoal and ore were added and fire made and kept burning for 3–4 days. The charcoal was made by carbonization of timber in heaps. When the metal produced from the ore had run into the cavity at the bottom of the hearth, the fire was raked off, and the lump of metal—probably 1 kg—was collected. The process was repeated each time an ore was reduced.

In order to obtain a clean metal, the cavity in the hearth was often lined with clay. Later on, as the demand for metals increased, furnaces were built to be used over and over when metal production was desired (Figure 2). In the case of reduction of iron ores, the metal obtained was a solid mass contaminated by slag, because of its high melting point. It was known as a bloom; it was partially freed from slag by heating and repeated hammering to squeeze the slag.

### Air blast

It must have been noticed at an early date that blowing the fire with breath or exposure to powerful wind resulted in its intensification. This observation might have been the reason for improving furnace operation by using blowpipes and later bellows. Blowpipes had the advantage that they could direct a jet of air to the fire to increase the temperature of the charcoal. This is more effective than the random currents of air blown in by the wind. Egyptian wall-paintings show blowpipes in use with small furnaces as early as the Fifth Dynasty (2690–2420 BC) (Figure 3).

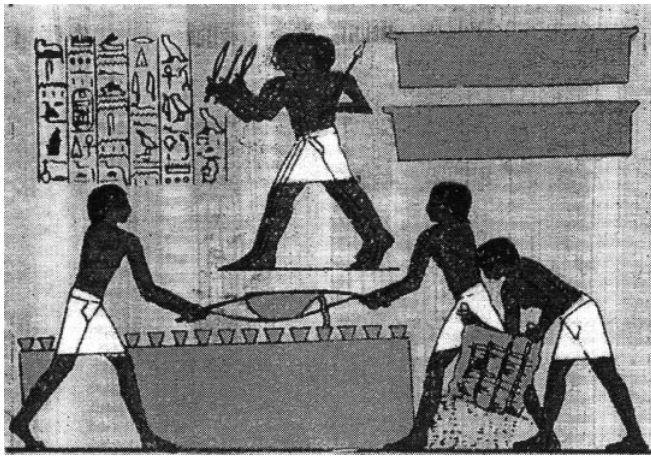


Figure 1. Egyptian wall-paintings showing workers melting and casting gold

Gradually, furnaces enlarged and work became more complicated; the smith found the blowpipe not enough for his purpose. This led to the invention of bellows made of goatskin with a tube leading to the fire. Egyptian wall-paintings show the workmen standing with each foot on a bellow (Figure 4). By resting his weight on one foot, he drives the air from the bellows into the fire, while by lifting the other bellow with a cord he causes it to be filled with air. After a time, two bellows were needed, each smith operating a pair. Larger bellows were later used and these were mechanically driven by horses.

The water-wheel became an important part of a smelter (Figure 5). Water power became more important than the availability of ore when choosing the location for smelters. Thus, the preferred smelter location changed from the mountains, with proximity to ore and wood, to the river valleys, with their availability of flowing water. The blast produced by very large water-driven bellows (Figure 5) resulted in the following improvements in iron production:

- The intense heat generated resulted in the melting of the 'blooms.' Once iron was molten, it dissolved appreciable amounts of carbon, and the solidified product became fragile and necessitated further treatment to remove the carbon. The knowledge that carbon dissolved in iron and was responsible for its brittleness was discovered in the eighteenth century.
- The dissolved carbon also resulted in lowering the melting point of iron. The liquid iron was directly cast into finished products such as furnace plates and cannon



Figure 2. Primitive furnace for melting ores. In the background to the left is a heap used to make charcoal from timber



Figure 3. Ancient Egyptian wall-painting showing the use of the blowpipes to increase the temperature of fire

balls, or bars for sale or for further processing in the finery.

- The furnaces could be charged without interrupting the process (Figure 6).
- This in turn enabled relatively larger furnaces to be operated and hence increased productivity.

#### The use of coke

In the early iron ore smelting processes, charcoal made from forest timber was used. Later on, mined coal was introduced, but it was soon realized that it softened in the furnace and spoiled the metallurgical processes. This factor, together with the mining difficulties such as coal-gas explosions in mines, ventilation and drainage, as well as the laws prohibiting the destruction of forest, contributed to the increased price of timber. This problem was solved when in 1607 coal was first converted into coke (Figure 7). This simple step revolutionized the iron industry, for coke being hard and porous is able to withstand a far greater burden without crushing, thereby making possible the construction of much larger furnaces, with a resultant increase in output.

#### The finery

The finery was the workshop where the crushed pig iron was melted in a hearth and decarburized under an oxidizing slag. Steel blooms were formed from the molten metal as it

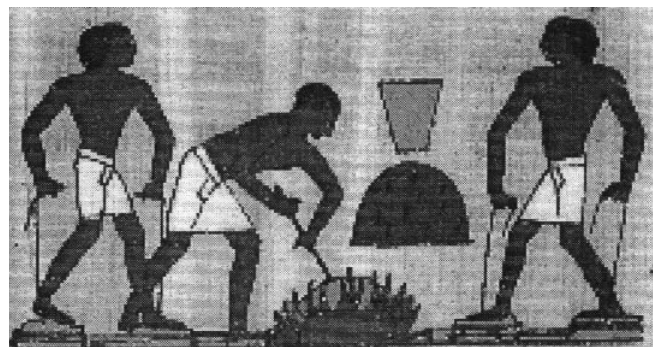


Figure 4. Ancient Egyptian wall-painting showing the use of bellows to blow air into a fire

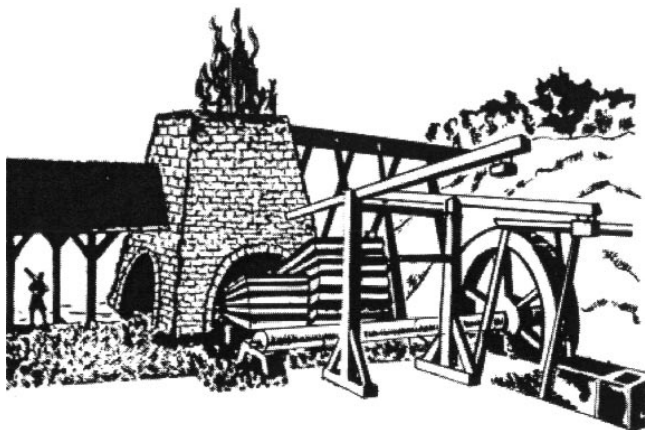


Figure 5. An eighteenth-century water-wheel operating bellows to blow air into a blast furnace

thickened, and these were then hammer-forged into semi-finished products. The furnace workers were able in some degree to control the properties of the product, but their empirical knowledge was limited.

### The phlogiston theory

In the seventeenth century, attempts were made to understand the nature of fire and the smelting process. It was once believed that when coal was burnt, phlogiston which in Greek means flame, was released and a calx, that is, ash remained. If an ore or an oxide was heated with coal it took up the escaping phlogiston in the fire to form the metal, that is:

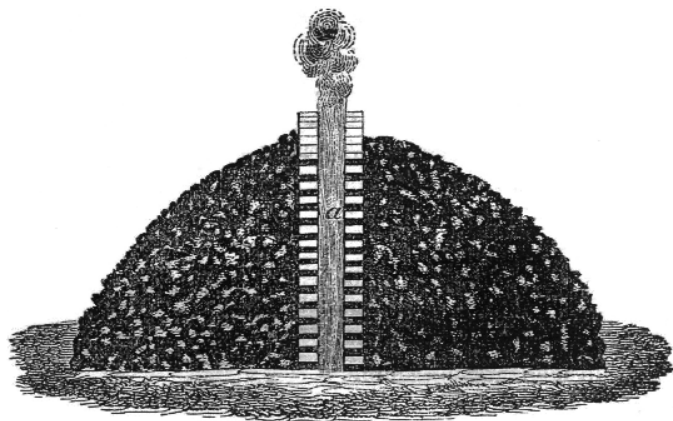


Figure 7. Making coke from coal in heaps similar to those used for making charcoal from timber. a = brick chimney



(oxide) (from coal)

[1]

It was the French chemist Lavoisier (Figure 8) who, in 1777, finally directed the fatal blow to the theory, when a few years earlier oxygen was discovered, and he interpreted the phenomenon of combustion as an oxidation process, i.e., a reaction of oxygen with the substance in question.

### Fire assaying

Control of the purity of gold and silver, and the prevention of counterfeiting of coins were always of primary

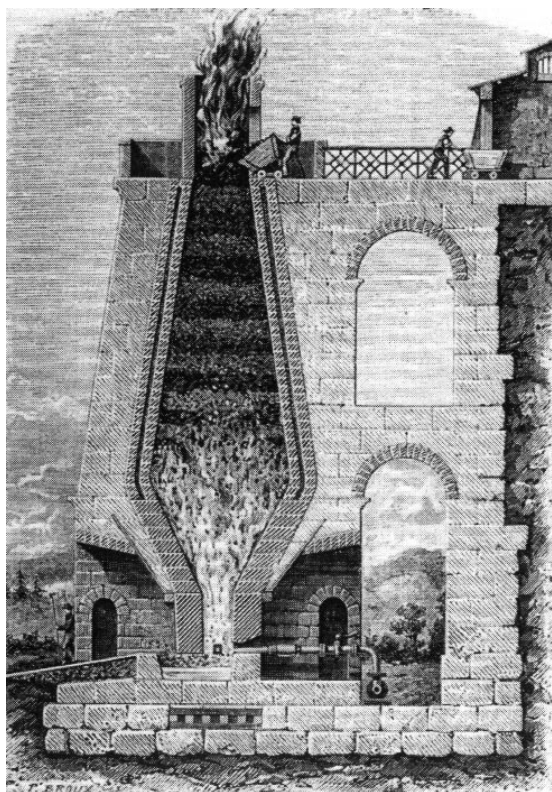


Figure 6. A shaft furnace from the eighteenth century showing continuous charging at the top



Figure 8. Antoine Laurent Lavoisier (1743–1794) was the first to explain the phenomenon of combustion as an oxidation process



**Figure 9. Roasting of sulphide ores in heaps at Copper Cliff, Ontario, in 1887**

importance to the administrators of the early communities. It is not surprising, therefore, that methods for analysing gold and silver were developed. The earliest known procedure, which is still in use today, is known as fire assaying. In summary, the material is melted with fluxes, litharge (PbO), and a reducing agent such as flour. The fluxes contained such ingredients as silica glass, salt, and borax. The gold and silver are collected in the lead formed by the reduction of litharge. The lead is then removed as oxide under oxidizing conditions in another step known as 'cupellation' by absorption in the material of the cupel, and there remains a bead of gold and silver, to be weighed. The same principle was applied on a large scale for the recovery of precious metals from lead ores.

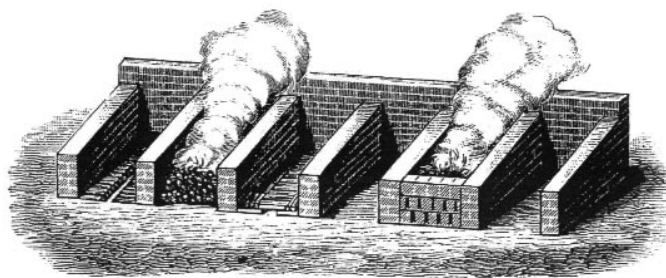
### The blowpipe

The blowpipe was essential for chemical analysis in the eighteenth and nineteenth centuries. With its help, the qualitative composition of most minerals was ascertained and the metals Co, Ni, Mn, Mo, W, Te, Ti, Nb, Ta, Ce, Cd, V, and In were discovered. The blowpipe is essentially a narrow tube with which air can be blown into the flame. By mixing suitable fluxes with the sample and using an oxidizing or reducing flame, the mineral samples were fused and from the colour and appearance of the fused material it was possible to draw conclusions about its composition. This useful tool was abandoned only after the invention of spectral analysis.

### Roasting

The early smelter operator was mainly concerned with the treatment of oxide ores. When he attempted to treat sulphides, problems started. He had some success in getting metallic lead from galena in a small hearth furnace. The ore was mixed with fuel, which floated on a bath of molten lead in a cast-iron dish set in masonry. Air was supplied by a side blast. The reduced lead trickled through the charge into the bath and overflowed down a sloping plate into an iron pot outside the furnace. The lumps of slag were picked out and removed as they were formed, and fresh quantities of ore and fuel added. However, the productivity was very small. With copper sulphides the material melted without forming the metal.

Gradually, the smelter operator learned that the sulphide ores could be heated under certain conditions to get a calcined product (an oxide) that can be smelted to metal



**Figure 10. Vertical kilns, also known as 'stalls'**

when heated with charcoal in a second operation. The first step was characterized by the emission of irritating sulphurous gases (SO<sub>2</sub>). The process of transformation of sulphide to a calcined product without melting, became known as 'dead roasting'. It underwent numerous stages of development, and became an important pyrometallurgical unit operation — oxidation of a solid phase.

### Roasting in heaps

This was the earliest method for the oxidation of sulphides, exactly the same way charcoal was made from timber or coke made from coal (Figure 9). The method was in extensive use during the nineteenth century for the treatment of copper ores. The ore, about 50 mm pieces, was piled over a framework of wood into heaps, enough wood being incorporated to ignite the sulphides. Transverse channels were left in the heap to facilitate combustion. Heaps 2–3 m high and piled on an area 15 × 30 m were in common use. The contents of such heaps would be about 2000 tons. The wood was ignited and enough heat was generated to cause the sulphides to ignite. Sulphur dioxide was simply emitted into the atmosphere.

The ore must contain at least 12% sulphur to sustain the combustion. On the other hand, if the sulphide content was high, great care was necessary in regulating air supply to prevent fusion. For this reason, high sulphur content ores were sometimes diluted with low-grade ores to have the proper sulphur content for the heap. Also, the height of the heap was a function of the sulphur content of the ore. An ore containing 15% S was piled about 2.4 m high, while an ore containing 35% S or more was piled only to 1.5 m. A heap may burn for a few weeks up to few months depending on its size, the nature of the ore, and the amount of sulphur desired in the oxidation product.

When the operation came to an end, the product was charged on wagons for transportation to the next operation. Usually during this step much dusting occurred, thus causing losses and adding to the pollution of the environment. The process was very inefficient because the product was never uniformly oxidized. Parts of the heap would be completely oxidized, other parts would melt to a matte, and still other parts would contain unoxidized ore. Further, SO<sub>2</sub> was fatal to vegetation over very wide areas. The process became obsolete at the beginning of the twentieth century.

### Vertical kilns

The heaps were superseded by small vertical kilns made of bricks known as 'stalls' (Figure 10). The stalls were about 2.5 × 3 m and 1.8 m high and had capacities of 25–30 tons each. They were charged and emptied manually. Sulphur

dioxide was emitted high up in the atmosphere. The process was better than the heaps but was still very inefficient.

### Blast roasting

This method was aimed at preparing an agglomerated oxidation product of pyrite that was suitable for charging to blast furnaces. It was found that when an updraught of air was blown through a layer of hot ore, oxidation took place and the product was an agglomerated porous mass. The process was conducted in large cast-iron pots having a false bottom through which air under pressure was admitted. The pots were of hemispherical shape,  $2.5 \times 3$  m diameter at the top and 1.2 to 1.8 m deep, and holding 8 to 10 tons of charge (Figure 11). When a charge was oxidized, the pot was carried by a crane and poured on the floor where the agglomerated cake would be broken up into fragments of a suitable size.

In operation, the false bottom was covered by a layer of burning coal or a red-hot calcine, which would ignite the charge when the blast was turned on. The pots were covered with hoods during combustion. The intense heat generated during oxidation could fuse the feed material and consequently cause stoppage of the airflow. This difficulty was circumvented by diluting the sulphides with  $\text{CaO}$  or  $\text{CaCO}_3$ . The process was not efficient because it was conducted batchwise.

### Reverberatory furnace

Furnaces about 18 m long and 5 m wide with a firebox at one end and door openings in the side walls were used. Ore was fed on the hearth farthest from the firebox and moved along manually by rakes through the doors. The depth of the ore bed was 7–10 cm. Manual operation was replaced by rakes mechanically dragged by chains along the hearth and a variety of other means. However, the method, became cumbersome, inefficient and expensive and became obsolete a few years later.

### Rotary hearth

Instead of a long straight furnace, a circular furnace was introduced, which was heated by burning a fuel. Figure 12 shows a simple design in which the ore was dropped from a hopper on the centre of a rotating hearth slightly raised at the center. Fuel is burned on the firebox on the right. During rotation, the particles of ore undergo oxidation and roll on the hearth until they fall at the discharge end.

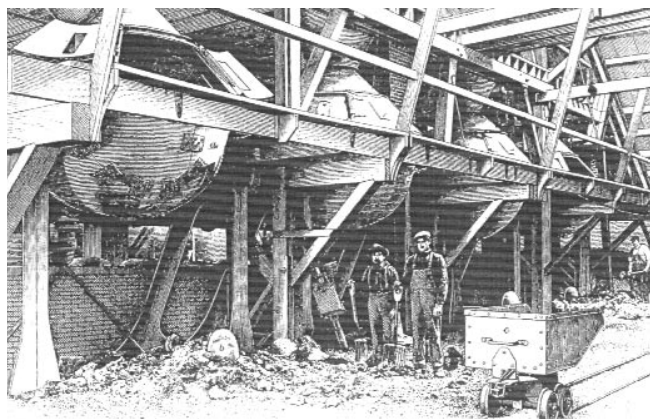


Figure 11. Blast roasting

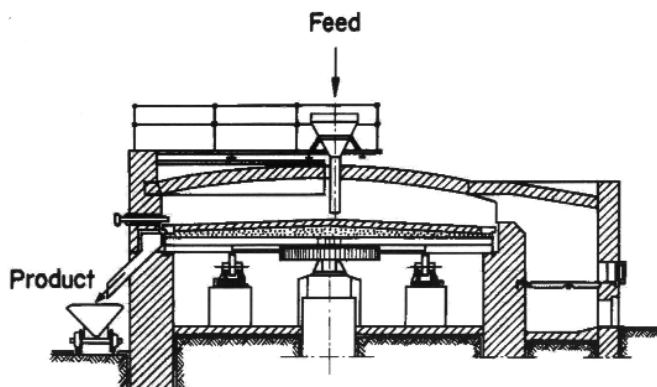


Figure 12. Roasting of sulfide ores on a rotary hearth

### Moving-grate furnace

Oxidation of sulphides in a moving grate furnace is a continuous process and can be completely automated. A machine 1 m wide and 7 m long will roast approximately 140 tons of lead sulphide per day. By installing a hood over the grate and recirculating a part of the exit gas from the second half of the grate it was possible to increase its  $\text{SO}_2$  content. The machine was invented by the American engineers Richard Lloyd (1870–1937) and Arthur Dwight (1864–?) and is known as the Dwight–Lloyd machine.

### Multiple hearth furnace

The first multiple hearth furnace was constructed in England in 1850 by Parker. It had two superimposed hearths 3 m diameter (Figure 13). An improved design was made in 1883, also in England, by MacDougall. Other designs were developed by John Herreshoff (1851–1932), Wedge, and Huntington-Heberlein. In general it is a cylindrical steel structure, bricklined, and composed of a number of hearths over which rakes act at an angle and attached to a vertical shaft in the centre of the furnace. The shaft is actuated by a bevel gear at the bottom and, when it rotates, the rakes also rotate.

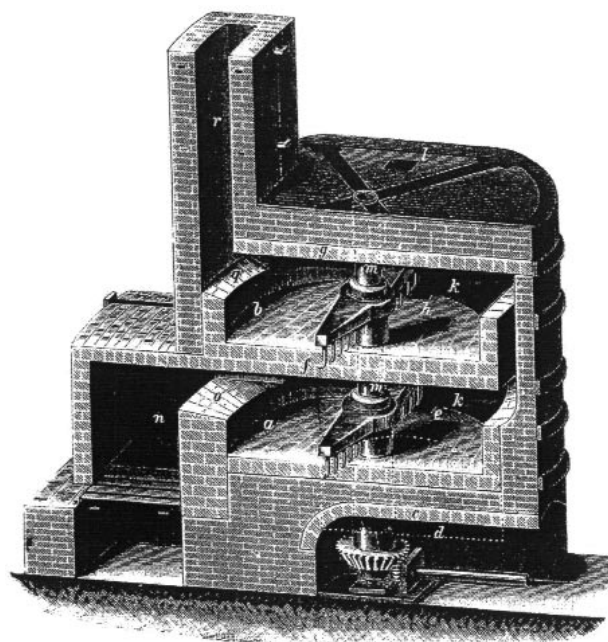


Figure 13. An early design of a multiple hearth furnace



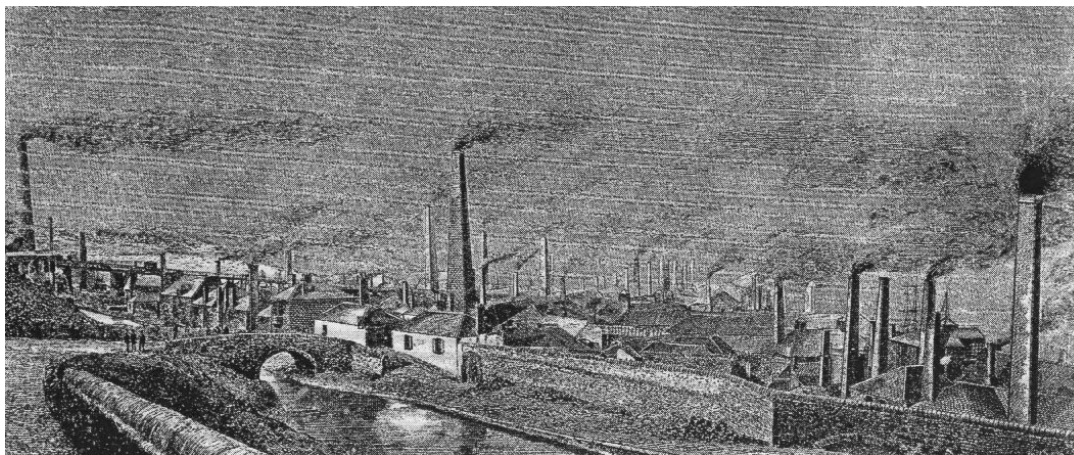


Figure 14. A view of nineteenth century copper smelters in Swansea, Wales

Ore or concentrate fed to the top hearth is raked the full area of the hearth to the centre where it falls through openings to the second hearth. In the second hearth the rakes are set to move the ore to the periphery, and from there it is discharged through openings to the next hearth. Hot gas is introduced at the lowest hearth and comes into contact with the ore in the hearths in a counter-current flow, leaving the furnace at the top.

#### Fluidized-bed furnace

The fluidized-bed roaster was invented by Fritz Winkler (1888–1950) in collaboration with BASF in Germany in 1922 for coal gasification. In 1942, the Standard Oil Development Company placed the first fluid catalytic cracking unit in service to produce aviation gasolines from heavier petroleum products. The rights to this technology were acquired by Dorr-Oliver, and the first fluidized-bed roaster for refractory, gold-bearing arsenopyrite concentrates was installed at the Cochenour Willans mine in Ontario in 1947. A second roaster was delivered to the Golden Cycle mill in Cripple Creek, Colorado in 1952. A few years later it was applied for roasting pyrites for sulphuric acid manufacture and for other sulphides.

#### The horizontal furnace

The horizontal furnace was extensively used for glass manufacture in which a batch of sand, soda, and crushed limestone was melted together to form glass. It was adopted by the metallurgical industry when high-grade sulphide ores were exhausted and the metallurgist was obliged to beneficiate low-grade ores by crushing, grinding, and later by flotation, obtaining a fine material not suitable for charging to a shaft furnace. This was mainly applied for copper production to produce a molten matte containing the copper and a molten slag containing the gangue material. When solidified, the matte was crushed and finely ground; half of it was oxidized then mixed thoroughly with the other half and the mixture was melted in another furnace with fluxes so that the 'roast-reaction' between copper oxide and copper sulphide may take place to produce metallic copper, and at the same time iron is eliminated as a slag:



The Welsh metallurgists in Swansea (Figure 14) were skilled in conducting this process, which became known as the 'Welsh Process'. Matte from as far as Butte in Montana and Chuquicamata in Chile was shipped to Swansea for transformation to copper.

#### The converter

Not far from Swansea, Henry Bessemer (1813–1898) (Figure 15) and, independently, William Kelly (1811–1888) in the USA invented his revolutionary process in 1856 to produce steel from pig iron by blowing air through the molten material, thus replacing the old process of exposing the molten material to an oxidizing draft in a horizontal furnace known as the 'Puddling process.' The process became known as 'conversion'. In this process, the time to produce a batch of steel was reduced from a few days to a few minutes and at the same time the need to use fuel for making the transformation was eliminated.

This technique resulted in the tremendous increase in



Figure 15. Henry Bessemer (1813–1898) in England revolutionized metallurgy by introducing the 'converter'



**Figure 16. The Swedish chemist Jöns Jakob Berzelius (1779–1848) isolated in 1824 zirconium and titanium for the first time by metallothermic reaction**

steel production and in displacing the older methods of steelmaking. In 1880, Pierre Manhès in France adapted Bessemer's steelmaking process to the copper industry. He used air blast to oxidize FeS in copper matte and to convert white metal, Cu<sub>2</sub>S, into metallic copper. As a result, the roast reaction was displaced by what became known as the conversion reaction:



overall reaction:



### Metallothermic reactions

Immediately after the discovery of the electric current in 1800 by Volta in Italy, Humphry Davy in England succeeded in isolating the alkali metals sodium and potassium from their compounds using the battery. Chemists of the early nineteenth century used the alkali metals to liberate metals from their compounds—a reaction that became known as the 'metallothermic reaction'. The Swedish chemist Jöns Jakob Berzelius (Figure 16) isolated zirconium and titanium in 1824 for the first time by this method.

The method was developed on an industrial scale in the 1850s by the French chemist Henri Sainte-Claire Deville

(1818–1881), who produced the first aluminium ingot by heating AlCl<sub>3</sub>–NaCl with metallic sodium. Once aluminium became available in large quantities, it was also used to liberate metals from their compounds. The German metallurgist Hans Goldschmidt in 1892 used aluminium powder for preparing carbon-free chromium and manganese. During the Manhattan Project to produce an atomic bomb in USA in World War II, the method was extensively used to prepare metallic uranium by reducing UF<sub>4</sub> by magnesium. In the 1950s the method was used in the USA by the Luxemburg metallurgist Wilhelm Kroll (1889– 1973) to produce the first metallic titanium on a pilot, then on a commercial, scale by reducing TiCl<sub>4</sub> by magnesium.

### Summary

- Fire was first used in metallurgy to melt native gold. Centuries later, it was used to prepare copper and bronze by reducing oxide ores with charcoal.
- Reduction of high-grade lumps of iron oxide ores in primitive shaft furnaces came much later.
- High-grade, massive nonferrous sulphides were also charged to shaft furnaces.
- The use of coke instead of charcoal was a turning point in the history of metallurgy.
- The use of low-grade ores necessitated grinding and flotation and were charged to fossil fuel-fired horizontal reverberatory furnace. Result: pollution, high-energy consumption, and excessive dust formation. Flash smelting was introduced to solve these problems.
- Bessemer's invention in 1856 revolutionized steelmaking and had an important impact on our civilization.

### Suggested readings

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