RECENT TRENDS IN REFRACTORY PRACTICE IN THE NON-FERROUS INDUSTRY

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REFRACTORIES play a very important role in all high-temperature metallurgical operations. Most of the improvements in metallurgical processes have been effected through improvements in the field of refractories, because in the past refractories often formed the limiting factor, hindering further advances in metallurgical operations. Refractory technology does not follow rule of thumb methods any longer. Scientific resources of petrography, spectroscopy, X-rays, etc., have been applied in improving the quality of refractories, with the result that in all well-advanced countries refractories to suit any particular set of conditions are being supplied to meet the exacting demands of metallurgy. A metallurgist should know the service requirements of his furnace and the refractories that would give maximum service. Judicious application of the most suitable type of refractory for each and every part of the furnace is wanted before it can give maximum life, resulting in higher production, better quality and less cost.

The latest developments in the field of refractories and their application in some of the typical non-ferrous smelting and refining furnaces for copper, zinc, lead and aluminium are dealt with here.

In roasting the copper ore concentrates abrasion by the movement of ore and a scouring action due to the fine particles are the main destructive agencies in an ore roaster. Fireclay bricks are used for the shell and hearth lining, but for the rabble blades, which have to withstand abrasion, silicon carbide is replacing firebrick as it withstands abrasion and corrosion at elevated temperatures and has superior hot strength. The present trend is, however, to omit the roaster altogether and feed the wet concentrate directly into the reverberatory furnace.

The temperature in the reverberatory furnace for copper smelting ranges from 1350° to 1550°C. The lining is subjected to abrasion, erosion and corrosion through chemical action of the slag, fluxes and gases such as chlorine, sulphur dioxide and superheated steam. The fluxes are mainly the oxides of iron and copper, although oxides of calcium and magnesium may also be present in appreciable amounts. The slag is mainly ferrous silicate, but varies in composition depending upon the composition of the charge. Such a slag is capable of corroding both acid and basic refractories. Due to the outstanding characteristic of magnesite refractories of being able to take a considerable proportion of ferrous oxide into solid solution without liquefaction or disintegration, magnesite refractories are less corroded than silica. While it has been observed that cuprous oxide corrodes silica brick considerably more than the basic bricks, if a copper ore is of a siliceous nature, it has been found that silica may perform as well as, if not better than, magnesite. Therefore the choice of suitable refractories for the copper reverberatory furnace depends largely upon the type of copper ore, the operating conditions and the cost of the refractory.

The bottom must be dense to prevent penetration of matte and also strong enough to bear the full load of the molten matte and slag. Silica sand is sintered in place and then heated with successive thin charges of either crushed slag or calcined ore, which is absorbed to form a bonded bottom.

The side walls used to be constructed with silica brick because of its cheapness, but the modern trend is towards metal-clad magnesite. The basic brick withstands slag action better and the metal case decreases its spalling tendency. The oxidized steel plates unite with the basic brick forming a tightly bonded monolithic mass. Silica brick is still retained in the side walls of some furnaces employing side charging, as it is cheaper and as considerable protection of the wall is obtained.

A sprung-arch silica roof was the common practice formerly, but it has given place to a suspended basic roof. Chemically bonded chrome-magnesite has been found to be the best because of its better resistance to spalling than ordinary magnesite brick. Another type of brick which is finding favour as a roof brick for copper reverberatory furnaces is forsterite ($2MgO.SiO_2$). Unless the ferrous oxide is very high, the amount of liquid formed at 1500°C. is very small and hence forsterite brick gives satisfactory performance in copper smelting furnaces.

With the increase in the production rate of copper reverberatory furnaces, the life of silica roof became as short as 90 to 100 days. With the introduction of the suspended basic roof, especially chemically bonded chrome-magnesite, the roof life has improved considerably. The life of chrome-magnesite roof is 2-3·5 times that of silica roof. It is claimed that the well-known Radex brand brick gives a roof life of almost 2 years.

Another recent development in roof construction is the so-called Zebra roof with alternate courses of silica and chrome-magnesite. This is said to retain the advantages of both types, while compensating the defects of each. Though this type of construction has been tried more in steel melting furnaces, some measure of success is reported in copper smelting furnaces also.

In a copper converter, ferrous silicate slag mixed with magnetite and ferric oxide is produced by the oxidation of sulphur and iron when air is blown through the molten copper matte at 1230°-1316°C. As silica flux is added to the furnace, the silica content of the slag is under control and hence a magnesite lining is preferable. With the introduction of Pierce Smith basic converter, the acid converter has become obsolete.

The operation in the converter is periodic and the temperature falls from 1300° to 800°C. during skimming and re-charging. The major refractory maintenance is in the tuyere section. The lining is exposed to maximum abrasion, slag attack and thermal shock. The conventional burned magnesite brick was the first successful basic lining. In addition to its resistance to the oxides of iron and copper, it has the ability to acquire and hold on a coating of magnetite. This magnetite coating takes the brunt of the slag and abrasion attack and protects the brick from alternate heating and cooling. The life of the converter is usually 5-10 years.

While burned magnesite has become the universally established practice for copper converters, trials have been made with chemically bonded magnesite with a good measure of success. This type of brick has better resistance to thermal shock and is cheaper. Chrome-magnesite bricks have not been successful to the same extent because of the tendency of chrome to increase in volume by absorbing iron oxide. Another recent development is to use periclase brick or monolithic ramming for the tuyere zone of the converter. This consists of a purer form of magnesite with more than 90 per cent MgO and decidedly better physical properties than conventional burned magnesite. The tuyere section has generally only 25 per cent life as compared to the rest of the lining. By using special bricks like periclase, etc., the vast difference in the life can be minimized.

Conditions in the copper refining furnaces are more or less similar to those of reverberatory furnace. The bottom is built of silica brick with silica sand fritted in place. Monolithic sintered magnesite bottoms also have been tried with success. For the side walls chemically bonded magnesite-chrome brick has given a life of 16 months in place of 12 months with conventional magnesite brick.

With a silica roof the life of the side walls is very much reduced. The chief cause of failure of the roof and side walls is due to splashing about of copper during air blowing and poling. The copper splashes are oxidized and react with the brick to form copper silicate. Suspended chemically bonded magnesite is replacing sprung-arch silica roof.

Spinel-bonded magnesite-chrome and spinel-bonded forsterite are among the latest developments in the field of basic refractories. With their high strength at intermediate as well as high temperatures and high resistance to wetting by cupric oxide at working temperatures, they should give good service in copper melting furnaces.

In indirect arc and induction furnaces for melting alloys of copper, nickel and chromium, etc., fireclay brick and low-alumina ramming mixes are giving place to high-alumina and mullite brick and ramming mixes. These have better resistance to slag as well as thermal shock.

In India, although there is an abundant supply of good quality ceramic raw materials, a variety of refractories, with properties to meet specific purposes, is not being manufactured at present. An exception is the case of kyanite; we have some of the best deposits of kyanite in the world and good quality kyanite bricks are being produced in this country. Hence metallurgists have to be either satisfied with what is available in the market or else import to meet special requirements. With a view to obviate this deficiency, development work has been undertaken in the National Metallurgical Laboratory on production of the best quality magnesite, chromite and chrome-magnesite bricks from Mysore and Salem magnesites and chromites, and also of forsterite refractories from dunite, saxonite and serpentine rocks. The bauxite deposits of North India are generally high in titania content and are not quite suitable for the manufacture of high-alumina brick with optimum properties. An attempt is, therefore, also being made in the National Metallurgical Laboratory to develop the best quality high-alumina brick using low-titania bauxites from Shevaroy Hills in the South.

The essential requirements of refractories for zinc distillation are rigidity and strength at high temperatures and resistance to slag action, especially under reducing conditions. In addition, low permeability, good thermal conductivity and thermal shock resistance are desirable. Though fireclay retorts were being used in the past, the life was very short — of the order of 35-40 days. This is understandable from the fact that a firebrick composition containing 5 per cent zinc oxide will have about 18 per cent melt at 1400°C. Hence at the working temperature, there will be considerable slagging of the fireclay retorts.

Silicon carbide is gradually replacing fireclay for making zinc retorts. It meets all the essential requirements mentioned above. Both in vertical and horizontal retorts, silicon carbide stands more severe firing conditions and can withstand a higher amount of detrimental impurities. Due to the high conductivity of silicon carbide compared to fireclay, there is a considerable saving of fuel and the recovery of zinc is also higher. The life of the retort is trebled. Silicon carbide has good resistance to stresses at high temperature, but it has a tendency towards growth between 1000° and 1100°C. under oxidizing conditions. To counteract this defect, silicon carbide grains are generally protected by a glaze coating.

At present silicon carbide refractories are not manufactured in India. The manufacture of silicon carbide in India may be economical when cheap electric power is available in plenty from our multipurpose river projects. A beginning has been made in the National Metallurgical Laboratory to produce silicon carbide refractories, with imported silicon carbide grains and indigenous bonding materials.

In the lead smelting and refining industry moderately severe demands on refractory linings are encountered only in furnaces for the recovery of lead from dross resulting from the kettle operation. In these furnaces the temperature is about 1100°C. and the slag is corrosive. High-heat duty fireclay brick for the bottom and high-alumina brick for the side walls with a few courses of magnesite brick at and below the slag line are used. The roof and uptakes are usually lined with high-alumina brick because of its superior resistance to thermal shock.

In aluminium remelting furnaces, though the temperature is low, fireclay refractories do not stand up well. Disintegration of the brick occurs due to alumino-thermic reaction, especially in the presence of iron oxide. Zircon brick is found to be quite suitable for the hearths of such furnaces, as aluminium does not wet the surface or penetrate the brick. Further, as the specific gravity of fireclay brick is very close to that of aluminium, small bits of spalled refractory remain suspended in the molten metal and cause inclusions in the castings. But with zircon brick — the specific gravity being 4·16 — spalled pieces will sink to the bottom and will not cause inclusions. Hearths built of zircon offer the following advantages:

(1) cleaner metal; (2) increased output per furnace through uninterrupted production; (3) longer hearth life; (4) lower refractory cost per ton of metal produced; and (5) immunity from attack in oxidizing or reducing atmospheres.

India has some of the best deposits of zircon in the world, but no one here is manufacturing zircon refractories. It is expected that the projected expansion of the aluminium and glass industry will involve a need for zircon bricks in considerable quantities. In the National Metallurgical Laboratory it has been possible to produce good quality zircon bricks from the domestic raw materials which compare well with the imported product.

In conclusion it is worth mentioning that progress in refractory practice in metallurgy can be achieved only by the co-operative effort of the refractory manufacturer, research worker and the consumer. In the Refractories Division of the National Metallurgical Laboratory the staff are ready to devote time and energy towards solving problems in refractories of either long-term or an immediate nature. A symposium on Recent Trends in the Field of Production Practice and Research on Refractories used in Metal Industry is to be held in the coming year.