NIPPON STEEL TECHNICAL REPORT No. 125 DECEMBER 2020

UDC 666 . 763 /. 764

Technical Review

Progress and Future Prospects of Refractory Technology of Nippon Steel Corporation

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Abstract

Refractory technology is one of the key technologies in the steel industry and was developed with advances in iron and steelmaking technology that often required rigorous operating conditions such as high temperatures, severe corrosion, and prolonged processing. Refractory technology comprises a very wide range of technologies, from the study of durable or low-cost materials to the setting or design of refractory linings that contribute to low-cost, stable and high-quality steel production. In recent years, the development of refractories has been expanded to fields such as inspection and diagnostic technology for stabilizing the life of refractories, recycling of used refractories as an environmentally conscious system, and automation of furnace construction work to improve the working environment. This paper provides an overview of the environment surrounding refractory technology of the 2000s, an overview of the technology development, and an outlook for the future.

1. Introduction

Refractories hold a very important position in the steel industry because of their significant influences on the manufacturing costs and product quality. As a result of diversifying user demands for higher product quality, refractory technology has been improved along with the development of steel manufacturing processes to endure harsh plant operating environments. It has developed in terms of furnace life extension to meet the needs for higher productivity and cost reduction. The technology has also advanced to improve the diagnosis technique of internal furnace conditions and to effectively repair the damaged walls in the old furnaces or ovens. The required qualities of refractory ceramics in the furnace wall are becoming much higher than before in a wide range of processes; many coke ovens have become super-aged, the size of blast furnaces has been increased, the hot metal refining requirements are becoming increasingly stringent in each of the divided processes, such as desiliconization, desulfurization, dephosphorization and decarburization, the ratio of secondary refining of molten steel has been increasing, and the productivity of continuous casters has been raised (higher casting speed and working ratio).

On the other hand, the rapid generational change caused by the mass retirement of the experienced baby boomers from the plant floor was a major change over the last few years. Smooth technical traditions between generations and skill-free plant operation that do not rely heavily on experienced labor were promoted, with the aid of developments of inspection and diagnosis technologies and standardizations for plant operating procedures.

In the meantime, from environmental viewpoints, minimizing the refractory waste generated from the works, ideally to zero amounts (zero emission), became necessary, which motivated the recycling of used refractories.

Moreover, considering the falling birthrate and the aging population, efforts have been exerted to improve the work efficiencies by means of partial mechanization to overall robotization for saving of furnace construction work, which is sometimes viewed as dusty toil.

It has been 12 years since the last special issue of Shinnittetsu Giho (No. 388 in 2008), and in this present issue we look back at the refractory technology of Nippon Steel Corporation.[1] This paper describes the progress of refractory technology after 2000, focusing mainly on the events in the recent 12-year period, and attempts to prospect future challenges. As for the details of specific technologies of different refractory products, the readers are kindly invited to refer to the other articles and reports of this issue.

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2. Change in Environment Surrounding Refractories for Steel Industry in and after 2000s

2.1 Production and import of refractories

Figure 1 shows the total production of refractories in Japan for all industrial sectors.[2] The refractory production of the country fell in the 1990s, but it was compensated by the increase in imports as seen in **Fig. 2**.[3] At present, the domestic refractory production remains at 1.0 to 1.1 million tons per year (Mtpy, unless otherwise specified, all the units herein are metric).

The imported refractories for the steel industry use are mainly fired bricks for general applications, non-fired magnesia-graphite (MgO-C) bricks of intermediate and low grades. Most of the silica bricks and chamotte bricks for construction of coke ovens, hot blast stoves, etc. are also imported from abroad. On the other hand, high-functionality refractory products such as the nozzles for continuous casting, which greatly influence steel quality, monolithic refractory, which is produced in Japan at high productivity and is competitive with the imported products, and some high-grade firebricks of high durability are still manufactured in Japan.

The refractory import began to increase rapidly in the latter half of the 1990s to reach 388 000 t in 2008, but decreased rapidly in 2009 and thereafter, and the amount of imports in 2016 was 177 000 t, less than a half of the peak amount in 2008. The reasons for this trend can be attributed to the following: the plants of the raw materials in China were closed or their transport was restricted because of intensified environmental regulations for the Olympic Games in Beijing in 2008; the price level of refractories from China rose as a result of the wage increase in the country and the change in currency exchange rate, and some Japanese products recovered their price competitiveness; the Chinese government tightened the environmental regulations in 2017; and the excavation of natural magnesia and the operation of brick firing furnaces were restricted in various stages, leading to unstable supply. However, the supply of refractories and their raw materials from China still accounts for a large portion of the consumption in Japan, and risk diversification is an important issue in their procurement.

2.2 Change in steel production and sale of refractories for steel industry

Figure 3 shows the steel production of the world and Japan.[4] The world steel production, which was 720 Mtpy in 1992, grew gradually, and it exhibited a steep increase in the 2000s as a result of the economic growth of the BRICS countries, especially that of China, to exceed 1 000 Mtpy in 2004. Although it decreased temporarily owing to Lehman's fall in 2008, it resumed growth thereafter to surpass 1 800 Mtpy in 2018. The steel production in Japan, on the other hand, after reaching a past peak of 110 Mtpy in 2010, remained at the same level, and has been decreasing slightly over the last few years.

Figure 4 shows the sale of refractory products for Japan's steel industry:[2] the trend is nearly the same as that of the steel production, but in 2016 to 2018, the refractory sale increased in spite of substantially stable steel production.

2.3 Change in unit refractory consumption of Japan's steel industry

Figure 5 shows the change in the unit refractory consumption of

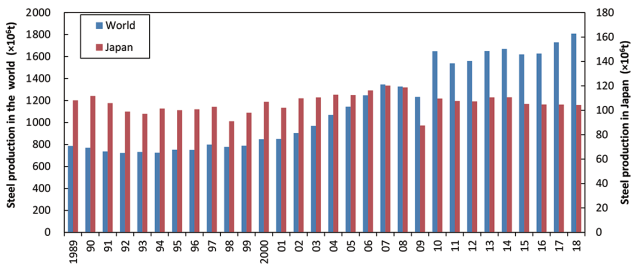

Fig. 3 Change in steel production

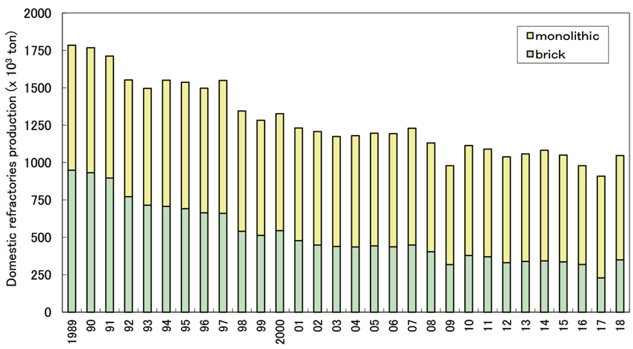

Fig. 1 Domestic refractory production

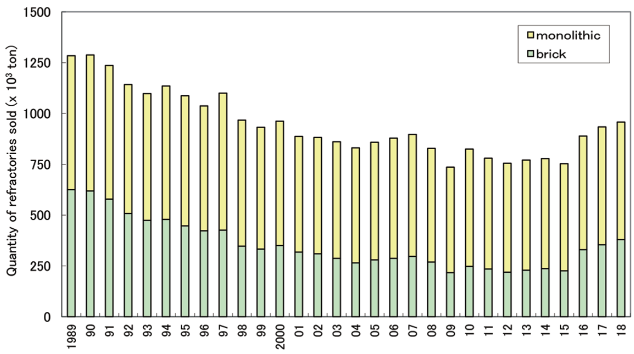

Fig. 4 Change in refractory sale to steel industry

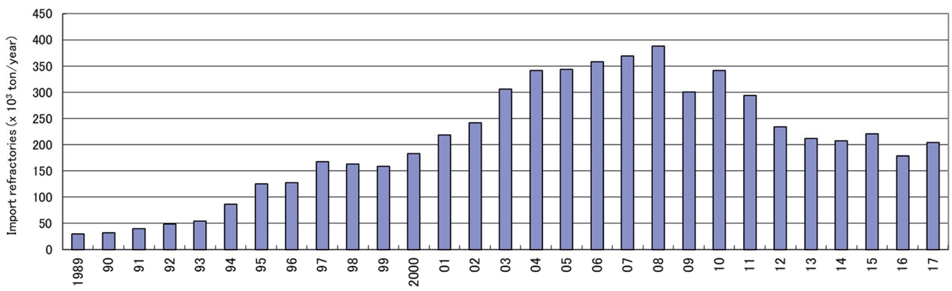

Fig. 2 Change in refractory import

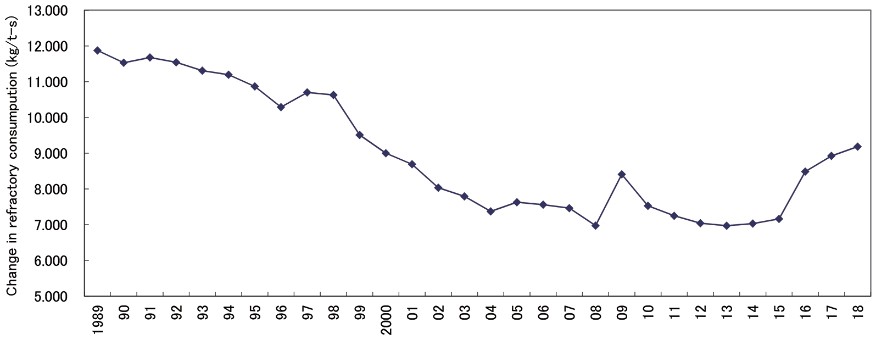

Fig. 5 Change in unit refractory consumption

Japan's steel industry, which is calculated by dividing the amount of the refractory sold to the industry by steel production. The unit refractory consumption has decreased smoothly thanks to the measures such as extension of refractory life and improved repair practice. Although it rose temporarily after Lehman's fall in 2008, it continued to decrease after that, recording a minimum consumption of 7.0 kg/t-steel in 2014. However, it began to increase rapidly in and after 2016. A factor of this change is the rapid increase in the sale of formed refractories, or bricks, which resulted from an increase in the demand for bricks for construction of new furnaces and ovens for renewal of aged ones. Another factor is presumably that steel production fell in this period owing to the equipment problems of some steelmakers, and a safety-oriented plant operation mode (larger safety margin for furnace life, excessive repair, etc.) was widely adopted.

2.4 Research and development in Japan and abroad

Outside Japan, the R&D activities of refractory technology are actively promoted especially in Europe and China.

In Europe, universities, public research institutes and refractory makers of various countries work together in a wide network and in close cooperation with the European Center of Refractories in Germany. The universities and the public institutes undertake fundamental researches and development of human resources, and the manufacturers specialize in application researches and product development; steelmakers and other refractory users do not seem to be much involved. In addition to the above, the Federation for International Refractory Research and Education (FIRE) operates mainly in Europe.[5)] It is a global network organization comprising 10 universities and public institutes and 12 makers from Europe and outside (Nagoya Institute of Technology is a member from Japan), and fosters young refractory engineers through a program whereby the member companies dispatch their employees to the universities. The Federation also develops activities for organizing an international consortium of research and industry.

In China, the R&D activities of refractory technology are concentrated to universities. Nine universities have research laboratories specialized in refractories; the total number of undergraduates is 1 500, and that of graduates 200, approximately. These laboratories constitute the world's largest source of new human resources in the field of refractory technology. Those universities also have organizations such as high-temperature material laboratories and engineering research centers for furnace lining; they are viewed as priority research facilities under government auspices.

In Japan, in contrast, the private sector is mainly responsible for the refractory R&D activities. The framework is characterized by cooperation between refractory manufacturers and users such as steelmakers. The public institutes engaged in refractory R&D are limited to those such as Kyoto Institute of Technology, Nagoya Institute of Technology and Okayama Prefecture Industrial Promotion Foundation. Thus the refractory R&D system in Japan is very insufficient in the aspects of fundamental researches and fostering and supply of human resources.

3. History of Nippon Steel's Steel Manufacturing Processes and Refractory Use

3.1 Ironmaking processes

As seen in **Fig. 6**, Nippon Steel has enlarged the inner volumes of blast furnaces at every occasion of relining: of the 12 blast furnaces in operation as of April 2020, nine have inner volumes larger than 4 000 m^3, and seven of them more than 5 000 m^3. Against this background, the company has developed refractory products that support the operation of large blast furnaces at high productivity coefficients (t-hot metal/m^3/day) such as carbon blocks for the hearth. As for hot-blast stoves, some of them have been in operation for more than 40 years, and early renewal is required. While various life extension measures are applied and their renewal is being studied, advanced methods for their diagnosis and repair are being devised and put into practice.

Figure 7 shows the age distribution of coke oven batteries. Aged batteries have been replaced one after another with newly constructed ones since 2008, and at present, of the 28 batteries in operation, 11 are less than 12 years old. On the other hand, as many as 16 batteries are older than 40 years, and the renewal of aged oven batteries has to be continued.

Against this background, the development project of SCOPE21 was brought forward aiming at commercial operation to meet the urge for oven renewal. Eventually, a new SCOPE21 battery was built and commissioned at Oita Works in 2008, and another at Na-

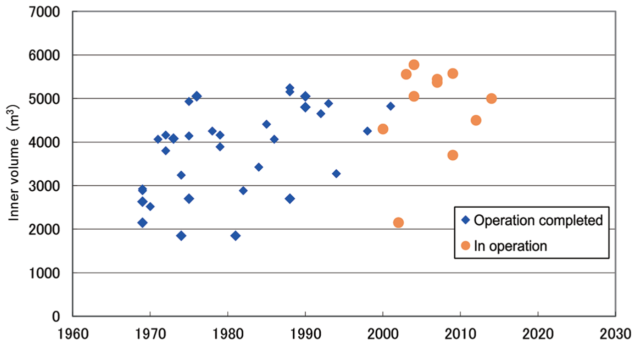

Fig. 6 Change in inner volume of Nippon Steel's blast furnaces

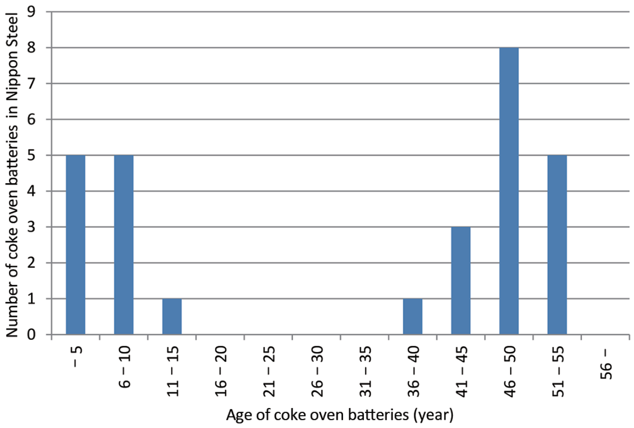

Fig. 7 Age of Nippon steel's coke oven batteries

goya Works in 2013.[6] As a measure to extend the life of aged ovens, besides brick relaying in hot conditions, the doctor of coke ovens (DOC), a machine system to examine and diagnose the condition of oven walls in high precision and repair their damage in hot conditions, has been developed. It was first introduced to Oita Works in 2003, and then spread to the other works.[7]

3.2 Steelmaking processes

Torpedo cars, pig iron ladles and converters are used as the reaction vessels for the hot metal pretreatment and the primary refining of steelmaking. The present processing practice of desiliconizing, desulfurizing and then dephosphorizing hot metal before decarburizing in a top- and bottom-blowing converter was mostly established by the 1980s. To further enhance the refining efficiency, the desulfurization by the KR process, an injection process using the Kambara Reactor, has been separated from the other processes, and then, the LD-optimized refining process (LD-ORP) and the multi-refining converter process (MURC) have been put into daily practice, separating the dephosphorization from decarburization. On the other hand, the quality of iron ore and coal has lowered over the last few years, and the consequent increase in the silicon concentration in hot iron has increased the loads on the desiliconization process. As the refractories suitable for these processes, Nippon Steel has improved the quality of non-burned bricks of the materials such as MgO-C and alumina-silicon carbide-graphite (ASG). In addition to the above, slag splash coating (SSC) has been commercially applied as a measure to protect converter refractory on line, and the best slag composition and temperature range for the purpose have been specified to maximize the effects.

In the secondary refining processes, on the other hand, in addition to the conventional dehydrogenation process for heavy plates, the demands for decarburizing increased rapidly as the production of interstitial-free (IF) and other high-grade steels increased. By continuous processing of vacuum degassers (RH, etc.), it is possible to keep the vessel temperature high, reduce the refractory costs, and lower the steel temperature at the tapping from the converters. In consideration of these points, the application of light RH treatment has been expanded to cover steel grades for general applications, and hot refractory repair facilities have been introduced to some of the works to allow RH treatment of all converter heats. As the number of the steel grades that undergo the RH treatment increases, selection of the refractory materials for the degassing vessel according to the operation condition and their development is becoming increasingly important.

In continuous casting, the casting speed has been increased, as has the cast section area, and the number of consecutive has been increased to raise productivity, and measures to decrease non-metallic inclusions, internal defects and center segregation have been introduced to enhance product quality. Higher reliability and enhanced performance of such basic functions as the flow control of molten steel, suppression of oxidation and contamination and prevention of splash and leakage are required for the refractories. By tundish dry coating, for example, water is not used for application of the lining, and it is highly effective at preventing hydrogen pick up. By this method, in addition, the coating layer does not overly adhere to the base refractory by burning, it can be removed after use within a short time, and the damage to the base layer is reduced.

3.3 Rolling processes

For the reheating furnaces for hot rolling, regenerative burners have been introduced for energy saving, and use of ceramic fiber for heat insulation has expanded. When the damage to the ceramic fiber by iron oxide scales flying inside the furnace is significant, however, a heat insulating monolithic material of calcium aluminate[8] highly resistant to scale is used, or sometimes, a high-performance heat insulating material is used behind conventional refractory lining.

Heat-insulating refractory bricks were used for the inner lining of continuous annealing furnaces for cold-rolled sheets, but to prevent the processed sheets from being hit by falling bricks and save energy, the inner lining has been replaced, one after another, with ceramic fiber wrapped in stainless steel sheets. However, the furnace temperature has been rising over the last few years owing to increased production of high-strength steel sheets, and as a consequence, the stainless steel sheets deteriorate more quickly than expected, and countermeasures are being sought.

4. Advance in Refractory Technology of Nippon Steel and Future Prospects

The principal challenges of the refractory technology that have to be tackled in response to the changes in the surrounding conditions and steel manufacturing facilities mentioned above are summarized as follows:

(1) To improve durability to withstand increasingly tougher operating conditions of steel manufacturing facilities;
(2) To sophisticate diagnosis methods for stable plant operation and maintenance;
(3) To develop new methods of furnace construction and repair that do not heavily rely on manual labor and their mechanization; and
(4) To stop discharging waste refractories to outside works premises.

Table 1 lists the refractory technologies that Nippon Steel has developed in relation to these challenges. Emphasis has been placed on aspects such as construction and repair practice, recycling, evaluation and analysis. Various measures to extend the service life of individual production facilities have arisen from different works; many of such measures comprehensively cover the fields of refractory material engineering, lining structure, equipment operation, new construction and repair methods, and measurement and diagnosis technology.

4.1 Higher durability of refractories to cope with increasingly tougher plant operation conditions

The operation conditions of various steel manufacturing facilities have become increasingly tough for reasons mainly such as increasing use of raw materials of poorer quality, increased production

Table 1 Changes of refractory technology of Nippon Steel

	2000–2005	2006–2010	2011–2015	2016–2018
Material	• Applying of plasma spray gunning technique to ZrO_2-C • Low thermal conductivity for MgO-C • Nano-technology MgO-C • Carbon block with TiC for blast furnace • Insulating refractories for reheating furnace	• Chrome-free brick for second refining process • MgO-C brick with excellent thermal fatigue resistance • Improvement of shotcrete material for torpedo car	• Coating material for ceramic fiber blanket • Foaming thermal insulation castable • Anti-clogging Immersion nozzle (AI nozzle)	• Control of peeling slag protection layer at MgO-C brick
Construction of brick lining	• Monolithic lining technique for upper part of RH degassing	• Improvement of brick lining of for corn of BOF		• Reinforcement of the support structure for ceramic fiber blocks in reheating furnace • Structural stabilization by improving the bottom lining in electric furnace • Improvement of the lance injection port refractory for desiliconization of molten iron in torpedo car
Mechanization of brick work	• Microwave drying I for monolithic refractories • Microwave drying for of RH	• Microwave drying II for monolithic refractories		
Repair and diagnosing technique	• Rotary shot repair method	• Repair and diagnosing technique for coke-oven chamber • Shortening the time required to change the converter tap hole non-destructive diagnostic technology for refractories using radiation	• Hot Quick Mixing Injection and Mist Injection (H-QMI) • Dry coating technology for tundish • Quick Mixing Shotcrete (QMS)	• Improvement of hot injection process • Application of mist injection shot technology to tundish coating material
Demolish and recycle technique	• Recycle technique for refractories in NSC • Auto-ripping machine for refractory maintenance	• Recycle technique for refractories in Nagoya, Oita, Yawata and Kimitsu Works	• Technology for applying recycled refractories to reheating furnace	
Evaluation method	• Application of stepwise heating method to MgO-C brick • X-ray photography method for slag penetration in magnesia brick • Mechanical characteristics with coarse-grained to monolithic refractory • The design of Al_2O_3-C ladle shroud suitable for long-time use and reuse • Analysis of brick structure using the rigid bodies-spring model • Basic study of alkali resistance in reduction atmosphere	• Evaluation of cyclic thermal treatment for corrosion resistance of MgO-C brick • Evaluation of characteristic image of Al_2O_3-C by TEM • Evaluation method for corrosion resistance of refractories for degasser	• Microstructural analysis of refractories for blast furnace main through • Technology to control the adhesion of inclusions to submerged nozzles	• Acoustic emission evaluation of cracks generated during bending fracture of MgO-C brick

of high-end and difficult-to-manufacture steel grades, and process changes aiming at improving product quality and productivity. This problem has been solved by the development of refractory materials of better durability and new repair methods.

Carbon blocks for blast furnace hearths are a typical example. Different types of carbon blocks of improved durability have been developed for large blast furnaces operated at increasingly higher productivity. **Figure 8** shows the development history. Resistance to molten iron has been improved, hot iron prevented from penetrating into the blocks by decreasing the size of pores, the thermal conductivity raised to lower the hot face temperature, and finally, a new type of carbon block has been developed having the function of increasing the viscosity of molten iron near the hot face to lower corrosion.[9, 10)]

Another example is MgO-C bricks for converters. As new operating methods such as the LD-ORP and the MURC processes were put into commercial practice, longer service life of refractories has been sought to raise the converter working ratio. MgO-C bricks are worn owing to structural degradation due to oxidation of graphite and reduction of MgO, which is termed as the MgO-C reaction. A measure has been developed to suppress the MgO-C reaction by applying a graphite decreasing method utilizing fine carbon material

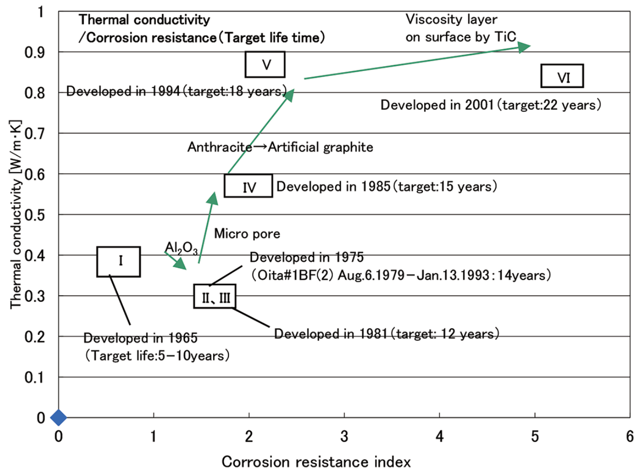

Fig. 8 Development of carbon blocks

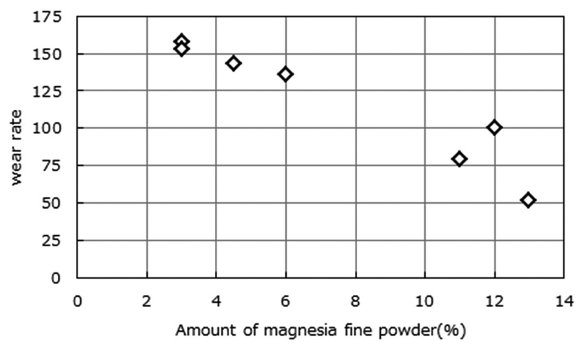

Fig. 9 Relationship between amount of MgO fine powder and wear rate of MgO-C bricks

of a nanometer size,[11] and decreasing the mixing amount of MgO fine (see **Fig. 9**).[12]

Other developments include a high-density alumina-magnesia moldable material for casting use wherein water addition is markedly decreased by using a high-performance dispersant, and a stick-proof nozzle using autogenic materials.[13, 14]

Dry spraying methods, whereby material in powder is pneumatically pumped to a nozzle tip and mixed with water before being sprayed, are predominant for hot repair of refractories. By these methods, however, the mixing of the powder and water tends to be insufficient, the water mixing amount excessive, and the deposits obtained tend to be highly porous and inhomogeneous. To solve the problem, a method of hot quick mixing & mist injection (H-QMI) has been developed and practically applied;[15, 16] by this method, thanks to a newly developed continuous quick kneader, it is possible to form high-density and high-durability deposits with low moisture contents. **Figure 10** schematically shows the equipment configuration for the H-QMI. High-durability spray methods (rotary shot[17] and quick mixing shotcrete (QMS)[18, 19]) have been developed exclusively for cold repair, and actually employed; these methods are characterized by the formation of high-quality deposits by eliminating pneumatic or pressure pumping of the refractory material and thus decreasing water addition.

4.2 Sophisticated diagnosis technology for stable plant operation

The importance of maintaining the stability of the condition of plant facilities and their operation is being strongly felt against the background of harsher plant operation conditions and high ages of

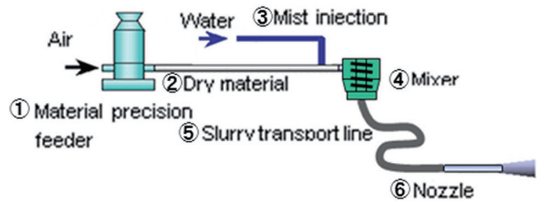

Fig. 10 Schematic diagram of H-QMI

the facilities, and from the viewpoint of refractory technology, sophisticated diagnosis technology is required. A recent example of such technology that brought about positive results is the introduction of an on-line refractory diagnosis system using laser profile meters and thermos-viewers (infrared cameras). Thanks to the advance in information technology, laser profile meters, among others, have become capable of processing a large amount of data at high speeds, and as a result, performing three dimensional measurement quickly using laser scanners has been enabled. Such diagnosis systems have been used at many works of the company.[20, 21] Since they have made it possible to quantify remaining refractory and use it to estimate the lowest limit of thickness, they contribute to stabilizing the equipment condition and its operation, and also refractory cost saving.

In the meantime, new methods of refractory diagnosis are being developed for application to long-operating furnaces of the closed type, with which it is impossible to observe the inside during operation, such as hot blast stoves, reheating furnaces and annealing furnaces. Furthermore, it is necessary to devise a next generation of diagnosis systems that employ advanced information technologies such as artificial intelligence and big data analysis to grasp the progress of refractory wear and damage more precisely, predict wear progress based on operation conditions, and develop repair plans reflecting the degree of degradation.

4.3 Development of furnace construction methods not relying on human labor and work mechanization

Whilst large furnaces and ovens will continue to be relined or newly constructed, the shortage of furnace construction labor in Japan is expected to become more tangible owing to the declining birthrate and aging population. In this situation, it is necessary for smooth equipment renewal to develop simplified furnace construction methods that do not rely on refractory technicians specialized in furnace construction, secure the required workforce thus reduced, improve the work environment, and shorten the work period. Wider use of monolithic refractories has helped labor saving to a certain extent, but most brick installation work is still done by human labor. It is therefore necessary to study how to mechanize and automatize brick constructions. Muscular labor in hot environments such as refractory repair work in hot conditions also has to be mechanized and remote-controlled.

4.4 Zero emission of waste refractories to outside works premises

Nippon Steel has developed recycling technologies to minimize the discharge of waste refractories to outside the works premises, and based on improvement of their handling (fractional recovery, transport, crushing, classification, packing, quality control, etc.), equipment design and the technology for mixing with monolithic refractories, refractory recycling facilities were built and commissioned at Kimitsu, Nagoya, Yawata and Oita Works in the 2000s,[22] contributing to the reduction of refractory costs. Use of low-grade waste containing numerous impurities as the slag forming agent for converters, the material for road beds, etc. was developed, and their disposal by land filling has been greatly decreased. In the future, it is necessary to develop new usages of waste refractories, search for easily recyclable materials to realize true zero emission, expand the use of monolithic refractories and non-fired bricks of low environmental loads and further enhance the thermal insulation of furnaces and ovens to decrease carbon dioxide emission.

5. Closing

The changes in the environment surrounding the refractories for the steel industry, development of refractory technologies and their commercial applications have been outlined hereinabove focusing mainly on the events in and after the 2000s. The last 20-year period has been an era of significant changes: the steel supply and demand in the world changed remarkably with China serving as the pivot; the market competition has become tougher owing to rapidly growing new mills; and a quick change of generations has taken place. The conditions surrounding refractory technology are considered to become increasingly difficult.

Because refractory technology supports stable plant operation at high efficiency, and as such, it is the source of the competitiveness to win the global market, we continue to sharpen the technical edge through close cooperation with the process technology and plant engineering organizations.

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