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*Technical Review*

# Development of Refractory Technology

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## 1. Introduction

Refractory technology plays an essential role in the steel industry. Nippon Steel Corporation has strengthened the foundation for steel production by continuously reviewing and improving the development, selection, installation, maintenance and disposal of refractory materials with the perspective of a major user.

As a result of its development of refractory technology (see **Fig. 1**), the unit refractory consumption of the company decreased by about 40% over the last 30 years. This paper presents typical examples of the refractory technology that Nippon Steel has developed.

## 2. Examples of the Refractory Technology Developed by Nippon Steel

### 2.1 Carbon blocks for blast furnace hearths

Nippon Steel began to use carbon blocks as the refractory for blast furnace hearths in 1951. For good corrosion resistance and easy formation of a protective surface layer through cooling, a high thermal conductivity is essential for carbon blocks. Based on the examination of carbon blocks after use, appropriate measures were investigated and adopted to prevent penetration of molten iron into the blocks and to improve their corrosion resistance and thermal conductivity. More recently, attempts have been made to achieve higher corrosion resistance by actively producing a protective layer at the surface of the carbon block through contact with molten iron and slag.

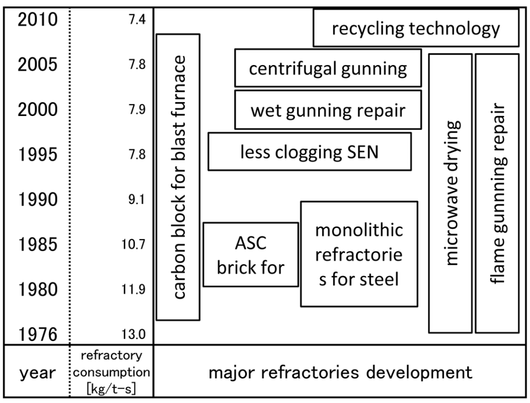


**Fig. 1 Development of refractories technology in Nippon Steel**

As seen in Part (a) of **Fig. 2**, brittle layers often formed in early generation carbon blocks that were designed to combine the high corrosion resistance of calcined anthracite and the good thermal conductivity of artificial graphite. Currently used carbon blocks, however, are free from embrittlement, as can be seen in Part (b) of Fig. 2, thanks to measures such as: addition of alumina that is resistant to acidic slag for improving the resistance to wear by molten iron; the addition of metallic Si to form Si-O-N to generate finer whiskers in the pores; and the change of the forming method from extrusion to press forming to densify the material (see **Fig. 3**). In appreciation of the development of carbon blocks, the Japan Institute of Invention and Innovation, on behalf of the Director-General of the Science and Technology Agency, awarded the company the National Commen-

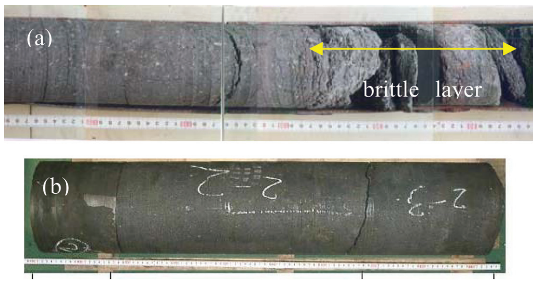


**Fig. 2 Conventional (a) and developed (b) carbon bricks after use**

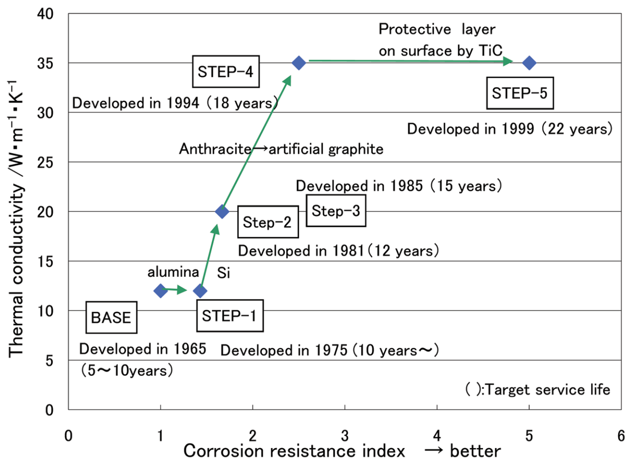


**Fig. 3 History of carbon brick development**

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dation for Invention in 1987. Carbon blocks have been instrumental in extending the campaign life of Nippon Steel's large blast furnaces; they sustained the operation of the Kimitsu No. 4 BF, Oita No. 1 BF, etc. for more than 15 years. In addition, the latest version of carbon blocks contain TiC and supply Ti to the molten iron that contacts them in order to increase its viscosity, and thus to improve the service life of the blocks. This type of carbon block has actually been applied to blast furnaces, contributing to the extension of their campaign life[1].

### 2.2 Microwave drying of refractory materials

Conventionally, the refractory materials for the inner lining of iron- and steelmaking facilities were mostly bricks of different kinds, but the use of monolithic refractories has increased due to advantages, such as energy and labor saving through the use of machines. While the share of monolithic refractories was roughly 30% in the 1960s, its use expanded to the cast house runners of blast furnaces, ladles, and degassers, and as a result is 70 to 80% at present. Monolithic refractories are easy to install, but it is necessary to dry them thereafter. During drying, the vapor pressure inside the casted monolithic layer sometimes exceeds the material strength, leading to explosion and spalling of the lining. As a countermeasure against this problem, Nippon Steel has developed an efficient method for drying moldable refractories using microwave dryers that is free from the fear of explosion, and has applied this process to the drying of the lining of ladles, RH degassers and pre-cast blocks for other furnaces.

As seen in **Fig. 4**[2], electromagnetic waves of 300 MHz to 300 GHz are considered to be microwaves. The developed microwave dryer uses the 915 MHz and 2.45 GHz frequency bands.

**Fig. 5**[2] shows the principles of microwave heating. When a refractory layer is irradiated with microwaves, dipoles form in the mixture of the refractories and water. The water molecules thus vibrate and rotate, causing internal friction, which generates heat and causes an increase in the temperature of the irradiated material. After all of the water in the irradiated layer has evaporated, the refractory material absorbs the energy of the microwaves, and its temperature rises further.

The heat energy P (W/m$^3$) inside a substance converted by irradiation with microwaves is expressed as follows:

$$P \propto f E^2 \varepsilon\gamma \tan \delta$$

Here, the frequency f (Hz) and the electric field intensity E (V/m) depend on the equipment, and the specific permittivity $\varepsilon\gamma$ and the loss angle $\delta$ on the material. The terms depending on the material depend also on the frequency and temperature. Microwave heating is characterized as an internal and selective heating with a controllable heating rate.

The commercial application of microwave drying began in 1979 at Hirohata Works for 100 t ladles, and then was expanded to the ladles of the Nagoya, Oita and Kimitsu Works. **Fig. 6** shows a diagram of a microwave dryer with hot air blowing for the ladles[3]. The

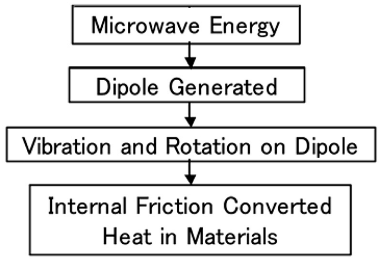


**Fig. 5 Mechanism of microwave heating[2]**

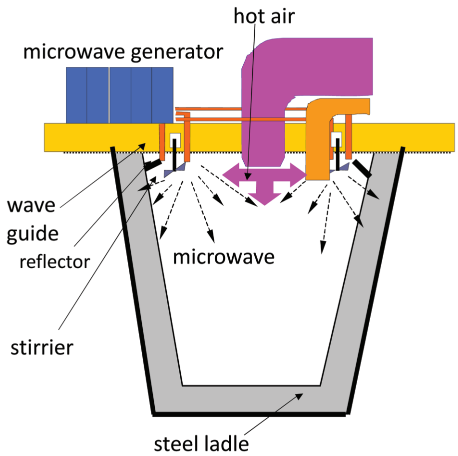


**Fig. 6 Schematic diagram of a microwave drier[3]**

hot air is blown through a duct, and microwaves are transmitted through waveguides to the inside of the ladle. Mode stirrers and reflectors are provided to homogenize the heating.

### 2.3 Refractory repair by flame gunning

Nippon Steel began developing the flame gunning refractory repair method in 1972. The capacity of the gunning burners, which was initially 50 kg/h, was increased to 6,000 kg/h over a period of 20 years. Burners of different capacities were developed for actual application to coke ovens[4], RH and other types of degassers[5], ladles[6] and converters[7, 8] based on the ease of field use and the type of refractory material to gun. They are being used effectively as part of integrated repair systems.

To deposit a refractory layer with specific properties using flame gunning, it is essential to heat the refractory powder in high-temperature and high-speed flames, and to keep it in a molten or semi-molten state until it hits the refractory surface that is being repaired. Nippon Steel selected propane gas as the fuel, designed propane-oxygen burners with increased capacity for this use, and created flame gunning systems for different applications that are capable of form-

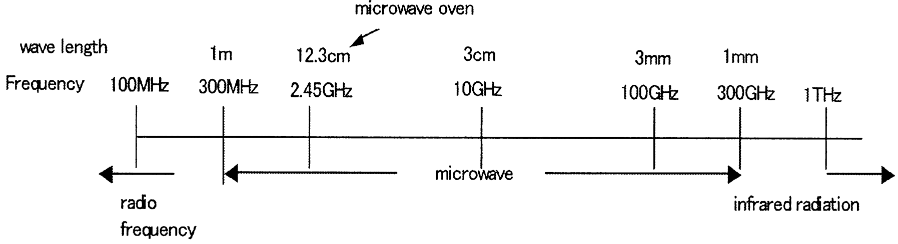


**Fig. 4 Frequency and wavelength of microwave[2]**

**Fig. 7 Flame gunning repairing machine for a BOF**

**Fig. 8 Recycling plant in Oita Works**

ing dense and durable refractory layers.

To form refractory layers with the desired properties using flame gunning with easily-handled fusible materials, the selection of the gunning material based on the operating conditions of the furnace or vessel that is being repaired is very important. For example, the gunning material for high-temperature, atmospheric furnaces must naturally have a different composition from that used for smelting furnaces. The effectiveness of the flame gunning process depends on the selection of the material properties, such as thermal expansion and abrasion and corrosion resistance, based on the operating conditions of the furnaces.

The performance of the burner is also critical for achieving satisfactory results with flame gunning, and in the development of the process, attention was especially paid to the material fusing and spraying capacity, the burner size, and the safety. Generally, a burner must have many small-diameter flame holes, with the number increasing as the burner capacity increases. This rule applies also to the material ejection holes. Efficient spraying burners were therefore designed such that the arrangement of the flame and material ejection holes enables even distribution of the material in the flames.

Noteworthy advances were made also made regarding other components of the system components. Factors that had the potential to cause problems during field use were corrected or eliminated from the system, and the structure of the multi-fluid swivel joints and the gas and feed flow controllers were designed to ensure a secure, safe, even, and stable flow of oxygen, propane, refractory powder and cooling water. **Fig. 7** shows an operating flame gunning system for converters. This large-capacity flame gunning technology was awarded the Okochi Memorial Production Prize in 1988.

Adequate operation of the flame gunning facility is essential for making the most of the technology; important factors include the gunning distance, the material feeding rate, the burner shifting speed, and preheating and cleaning of the refractory surface that is to be repaired.

A typical example of the latest applications of flame gunning is the system for diagnosis and repair of coke oven chambers, which has been provided for all of Nippon Steel's coke ovens [9]. The system is capable of gunning refractory material precisely in the desired areas, and is significantly contributing to the extension of the service life of coke ovens.

### 2.4 Refractory recycling

A wide variety of refractories is used in a steel mill for the refining and heating furnaces and vessels for molten metal handling. When damage to the refractories is so severe that stable operation of the equipment is hindered, the material is removed and discharged as waste. Recently, however, it was necessary to reduce the amount of waste refractories, and consequently, effective utilization of used refractories became an important issue. Nippon Steel has actively expanded the reuse of used refractories over the last several years. **Fig. 8** shows an example of a refractory recycling facility[10].

Refractories of hundreds of different qualities and chemistries are used in a steel mill. After use, they contain slag, metal and other impurities, and therefore, if reused without treatment, the durability of the recycled products will be very poor. For this reason, the mixing ratio of used refractories for manufacturing new products has been 10 to 20% at best, and the rest of the material has been used mostly for applications such as roadbeds on the mill's premises.

To raise the recycling ratio of used refractories for new refractory products, Nippon Steel focused attention on the grade of the used refractories, and increased its mixing ratio for producing new products for comparatively mild applications, and at the same time developed a method of crushing used refractories, classifying them by size and blending the material in large quantities to manufacture new products. With respect to recycling, the company developed an efficient refractory material recovery system to collect a variety of used refractory materials, classify them by type, crush them, and separate out the impurities, and designed and constructed manufacturing plants for the production of refractory products from recycled materials. These developed facilities made it possible to eliminate slag and metal, which are the main causes of deterioration of refractory lining performance, from the recovered material, and as a result, crushed refractories of middle-sized grains to fine powders that used to contain significant impurities, became reusable.

Thanks to the development of the above methods and processes, the mixing ratio of used refractories for the manufacture of new refractory products increased to roughly 80%. The Clean Japan Center, on behalf of the Director-General of the Industrial Science and Technology Policy and Environment Bureau of the Ministry of Economy, Trade and Industry, selected the refractory recycling system for the Award for 3R (Reducing, Reusing and Recycling)-Oriented, Sustainable Technology for 2009.

## 3. Closing

Advanced refractory technology is essential for developing new manufacturing processes for steel products, reducing production costs and maintaining stable operation of high-temperature equipment. Furthermore, refractory technology is indispensable for not only the steel industry, but any industrial processes that work at high temperatures. As economic globalization occurs, the sources of supply for refractory materials will also expand further, and so will the application of refractory technology. There will be many opportunities for the refractory technology that Nippon Steel has developed and cultivated as a major user to prove its worth.

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