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Recent Technology of Coke Oven Refractories

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Abstract

The oldest of Nippon Steel's operational coke oven batteries is 43 years old. Its structure is growing decrepit, and this is more or less true of all the other batteries. Faced with this situation, the company has developed and applied a variety of coke oven repair technologies, from such simple repair methods as gunning and hot spraying to partial brick relaying near oven doors and large-scale relaying of entire chamber walls. This paper describes the latest investigation of used silica bricks in shutdown coke ovens, the causes for their damage, a recently developed diagnosis and repair machine for coke ovens, and problems afflicting refractory technology—especially regarding construction of new batteries—that became clear through the large-scale relaying work at Nagoya and Muroran Works.

1. Introduction

Nippon Steel Corporation began to use domestic silica bricks for coke ovens about 100 years ago. **Table 1** summarizes the development history in Japan of silica brick and other refractories for coke ovens.[1] Thanks to the strenuous efforts of our predecessors, the service lives of the company's coke ovens have increased remarkably, and as a result, the oldest of them has operated for no less than 43 years, and most of the others for 30 years or more (see **Table 2**). But the coke ovens continue to age, and in this situation, various measures have been taken such as partial brick relaying near oven doors and large-scale relaying of an entire chamber wall, not to mention simple repair methods such as gunning and hot spraying.

Of the latest topics on refractories for coke ovens, this paper reports the damage to silica bricks found through investigation of coke ovens shut down after different periods of operation, the causes for their damage, the functions and use of a recently developed diagnosis and repair machine for coking chambers, as well as problems afflicting refractory technology that would arise in relation to large-scale repair by brick relaying and construction of new batteries.

2. Damage to Coke Oven Batteries

(1) Progress of refractory damage

Table 3 shows the types of refractories used for different parts of a coke oven battery. Silica bricks—noted for their excellent volume stability—are used for coking and combustion chambers, where the temperature is high and they come into direct contact with the coal, and the main structural members supporting the whole battery such as regenerator walls and cooling canals.

Since silica bricks in a coking chamber wall up to 2 to 3 m from the oven doors are frequently exposed to cool outside air, causing heat spalling from an early stage of operation, and as a consequence, flame gunning or similar brick repair methods are often applied to these portions. Bricks in the central part of the coking chamber walls begin to suffer damage at later stages of operation. **Fig. 1** schematically illustrates typical damage to bricks used to create the coking chambers and flues, and **Fig. 2** presents an example of the photographic scanning of a coking chamber wall at the Oita No. 2 Battery obtained using a diagnosis and repair machine,[2] which will be explained in more detail in Section 3. One can see in the photograph the occurrence of vertical through cracks at a constant pitch in the chamber length direction and depressions below the charging holes.

As coke ovens age further, through cracks expand and bricks sometimes fall out, forming holes through the wall, leading to leakage of coal into flues and regenerators. This results in a local fall in oven temperature, and causes the damaged portion to expand.

(2) Degrading of silica bricks and its mechanism

There have been many papers on damage to coke oven refracto-

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Table 1 Technology of silica bricks for coke oven

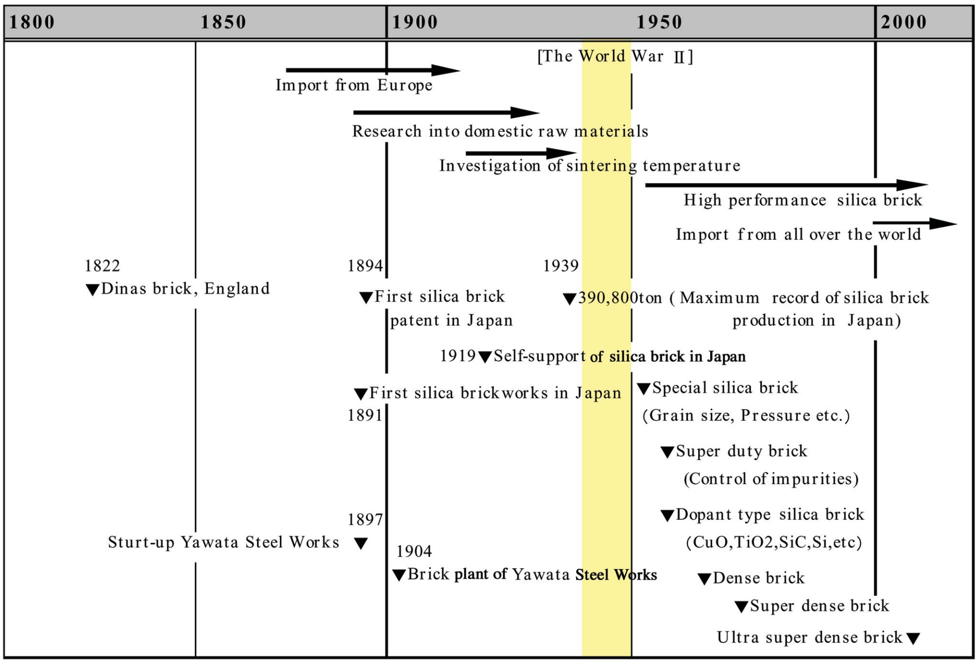

Table 2 Ages of Nippon Steel's coke oven in batteries

Works	Batteries	Hot run	Chamber	Age
Yawata	4	Jan. 1965	90	42
	5	Mar. 1970	110	37
Muroran	5	Jul. 1969	91	38
	6 (I)	Jan. 1965	42	26
	6 (II)	May 2007	42	0
Nagoya	1	Aug. 1964	75	43
	1A	Aug. 2005	25	2
	2	May 1967	110	40
	3	Sep. 1968	90	39
	4	Oct. 1969	100	38
Kimitsu	1	Oct. 1968	90	39
	2	May 1969	95	38
	3	Dec. 1969	100	38
	4	May 1971	92	36
	5	May 1973	57	34
Oita	1	May 1972	78	31
	2	Jan. 1972	78	35
	3	Oct. 1976	82	35
	4	Sep. 1976	82	31

ries, especially to silica bricks, but few of them relate to the change in properties of different types of refractory after roughly 30 years of use.[3] In view of this, the authors took silica brick samples from the Yawata No. 2, Muroran No. 3 and Nagoya No. 1A Batteries, which had been shut down after operation for 28, 17 and 7 years, respectively, and examined their properties.

Some of the samples were taken from positions about 1.5 m above the coking chamber floor and below a charging hole near the center of the chamber. **Fig. 3** shows the appearance of a sample brick taken from Yawata No. 2 Battery. There were two through cracks across the brick from the coking chamber side to the flue side, with brick surface layers flaking off from the cracks and brick joints, and as a result, the brick corners were rounded. **Fig. 4** shows a horizontal section of the sample brick in Fig. 3; there was a crack parallel to the wall surface starting from the two through cracks and a dovetail for brick mating, and in addition, there were many fine cracks on the surface of the coking chamber side. On the coking chamber side, there was an embrittled layer 20 to 30 mm thick where the aggregate was partially missing. Sintering of brick was so advanced from the flue-side surface to the center that the grain was unidentifiable, and the original brick microstructure did not remain.

To observe the samples in more detail, the authors examined their microstructures using a reflecting microscope. **Fig. 5** shows some of the photomicrographs thus obtained. To a depth of about 5 mm from the coking chamber side surface, there was a layer rich in CaO and Al_2O_3, presumably originating from coal, and having many fine cracks as mentioned earlier. Under the microscope, some cristobalite grains were found to have survived years of use, but cracks parallel to the brick surface were also seen, indicating that chipping occurred. At the center of a brick, the aggregate and matrix were found to have melted to form an indistinct mixture with evenly dispersed pores, which seems to indicate that rearrangement of the brick structure occurred.

A structure was observed on the flue side composed of a low-melting-point phase wherein CaO and Al_2O_3 are concentrated (probably a high-viscosity liquid at high temperature) and vitrified SiO_2 making up the balance, with coarse pores formed by coalescence of fine ones. This indicates that, in the flue-side half of a brick heated to 1,200 to 1,300℃ for prolonged periods, sintering advanced to the extreme under the existence of a liquid phase, transforming the original structure into an entirely different one.

Test pieces were taken from three positions of brick specimens, the coking chamber side, center and flue side, and their apparent hot moduli of rupture at 1,200℃ were measured. At the same time, their moduli of static elasticity were measured based on the deflection of

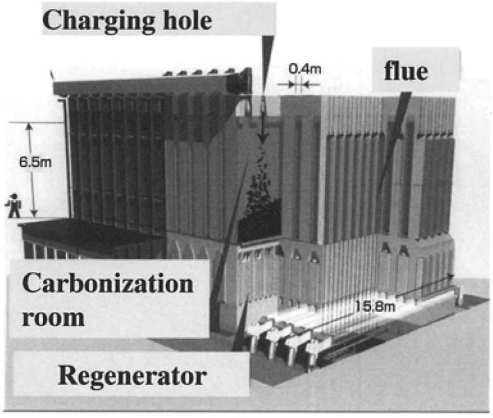

Table 3 Refractories for coke ovens

Part		Refractories
Roof		Fireclay brick
		Insulating brick
Flue	Wall	Silica brick
	Jumb (wall near oven door)	Insulating brick, Fireclay brick
Curved part		Silica brick
Regenerator	Wall	Silica brick, Fireclay brick
	Checker	Fireclay brick
Sole flue		Silica brick, Fireclay brick
Door		Cordierite precast brick
Ascension pipe		Cordierite precast brick
Chimney flue		Fireclay brick, Common brick

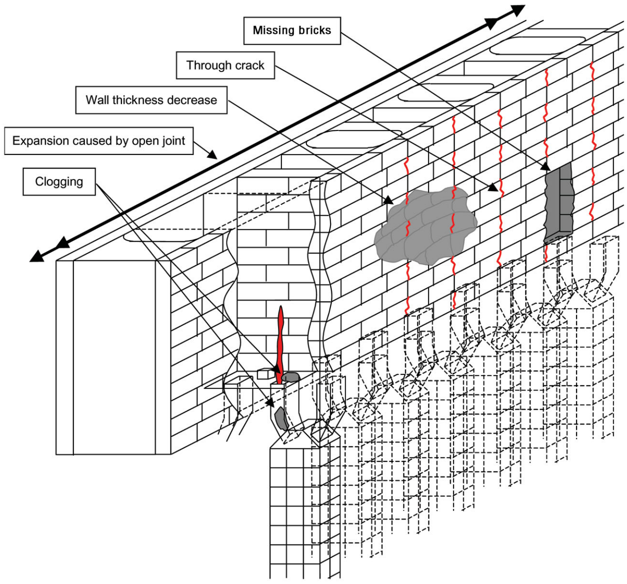

Fig. 1 Typical kinds of damage to chamber wall bricks

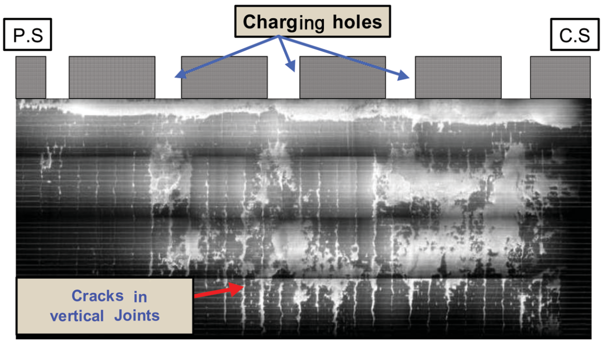

Fig. 2 Example of wall surface survey at Oita No.2 Battery

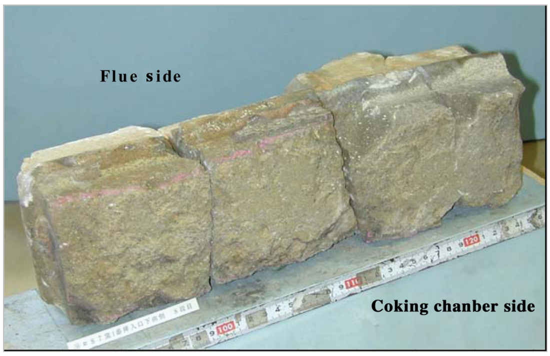

Fig. 3 Appearance of silica brick of Yawata No.2 Battery after 28 years of operation

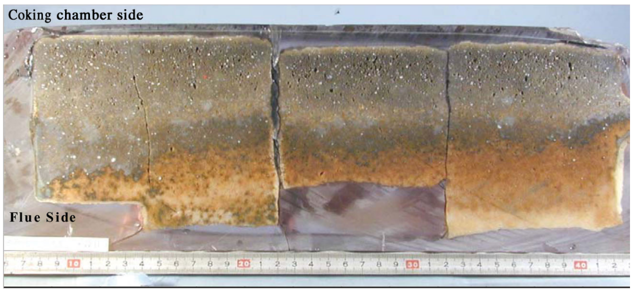

Fig. 4 Cross section of silica brick of Yawata No.2 Battery

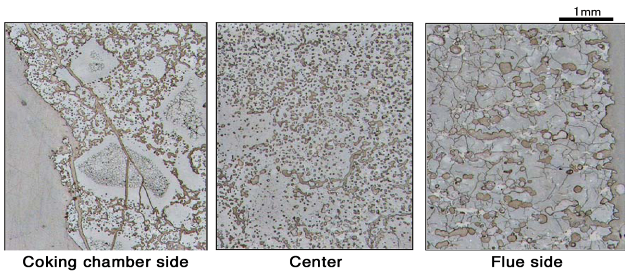

Fig. 5 Microstructures of silica bricks in oven walls of Yawata No.2 Battery

the test pieces at the hot bending test. As stated earlier, there were many fine cracks in the surface layer on the coking chamber side, and in consideration of this, to express the brick strength in actual use accurately, the authors defined an indicator of apparent hot bending strength, Sap, such that the strength of a specimen was 0 MPa if it was impossible to cut out a test piece 25mm × 25mm × 120 mm in size. **Fig. 6** plots the measurement results against the oven age. Because of the fine cracks on the coking chamber side, the apparent

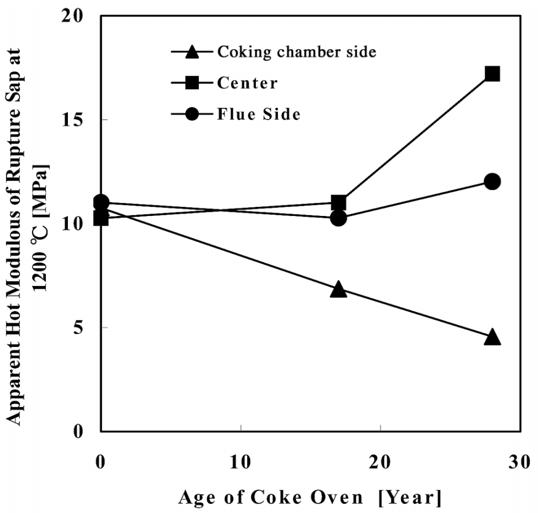

Fig. 6 Apparent hot modulous of ruputure against oven age

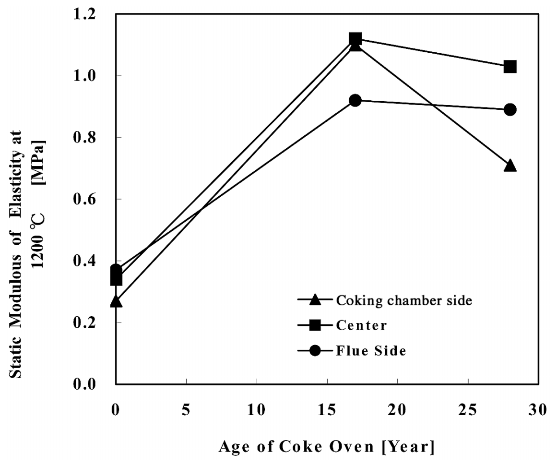

Fig. 7 Static modulus of elasticity against oven age

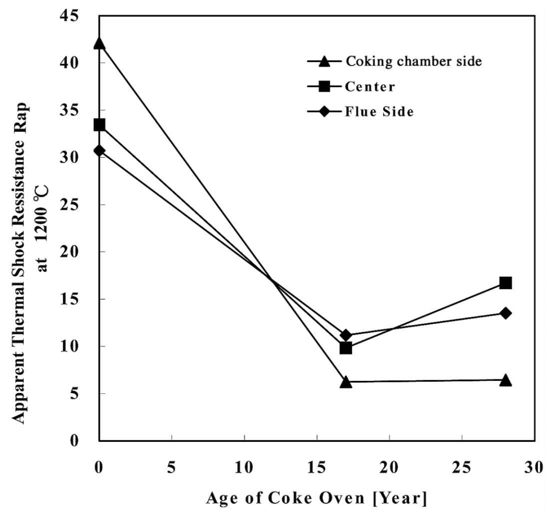

Fig. 8 Relation between oven age and apparent thermal shock resistance

hot moduli of rupture of the test pieces taken from this side decreased as the oven age increased. In contrast, the same for the test pieces taken from the flue side increased with increasing oven age, presumably because of the advanced sintering of the brick material.

The above means that, while the brick material degrades with age on the coking chamber side, the strength increases on the flue side, and consequently, the strength of a brick as a whole does not decrease significantly. As seen in **Fig. 7**, however, the hot static modulus of elasticity calculated from the stress-strain curves increased to about three times that of a new brick. **Fig. 8** shows the relationship between oven age and apparent thermal shock resistance Rap.[*1] Here, Rap is a value defined based on the apparent hot bending strength Sap and static modulus of elasticity E, and is similar to the commonly used thermal shock resistance R′. The graph is interpreted to indicate that the thermal shock resistance of bricks forming a coke oven battery gradually decreases with age.

This means that once a coke oven battery is 15 years or older, because of the progress of sintering, the degree of which depends on the operating temperature, the silica bricks forming the coking chambers and flues transform such that their properties change gradually and continuously from the coking chamber side to the flue side. In addition, although the average strength of each brick does not change significantly, its static modulus of elasticity changes remarkably, and the material becomes less resistant to thermal shock. This can be related to the fact that numerous large and small cracks were found at the visual and microscopic observations on the coking chamber side, where the temperature fluctuates considerably.

The examination results for used silica bricks indicate that, because of the progress of sintering over a long period, the material of the silica bricks change into another quite different from the original one and becomes highly susceptible to cracking, and as a result, the following two types of damage are inflicted on them:

(i) Thinning of wall bricks due to repeated surface unevenness resulting from chipping in small areas of surface layers. This results from thermal shock cracking owing to the temperature fluctuation of coking chamber walls due to coke pushing (discharging), combustion of carbon deposits, etc.

(ii) Large cracks for reasons of oven structure and brick shape such as through cracks running at right angles to the wall surface of a coking chamber and cracks parallel to the wall surface and originating from brick dovetails for mating.

3. Development of Technology for Diagnosis and Repair of Coke Ovens

(1) Methods for repairing coking chamber walls

As stated above, the properties of bricks change with oven age, and the number of cracks and through openings increases in chamber walls. Faced with this problem, Nippon Steel has developed methods for diagnosing oven insides and repairing the damage while hot. One such technology is flame gunning of refractory powder onto coking chamber walls together with combusting gas to repair local depressions while hot. By combining the flame spraying with a CCD camera, the company has recently developed a diagnosis and repair machine for coking chamber walls.[2)] A second approach is the boring method,[4)] along with other varieties of partial relaying of chamber wall bricks; this was developed as an extension of conventional

Note [*1] Apparent thermal shock resistance
$R' = Sap\,\lambda(1-\nu)/(E\alpha) \propto Sap/E \Rightarrow Rap$,
where Sap is the apparent hot bending strength, ν the Poisson ratio, α the coefficient of thermal expansion, λ the thermal conductivity, and E the modulus of elasticity. Since all the test pieces were of the same material, their values of λ, ν and α were regarded as nearly equal.

brick relaying work, which used to be applied only to the portions near oven doors. A third approach is large-scale brick relaying of an entire battery composed of tens of coke ovens, similar to construction of a new coke oven battery.

(2) Local repair method

Conventionally, local damage to coking chamber walls was identified visually by oven operators from the end of the chamber with the door open, and repaired by flame gunning likewise involving rigorous manual labor. For this reason, it was not easy to find brick damage in portions further from the end, and the accuracy of damage evaluation relied on personal experience. Consequently, the shape and durability of refractory deposits after repairs were often far from satisfactory. To resolve this problem, Nippon Steel has developed a diagnosis and repair machine aimed at the following:

(i) Quantitative measurement of loss of smoothness along coking chamber walls;
(ii) Accurate location of damaged parts;
(iii) Swift diagnosis of the two walls of a coking chamber;
(iv) Smooth and flat surface of the deposited layer; and
(v) Significant labor saving through automated operations.

Fig. 9 shows an outline of the developed machine. It is mounted on a traversing car running on the same rails as the coke pusher, and has two sets of extendable beams, each consisting of a water-cooled beam prop similar to a pushing ram and a beam drive and cooling systems. One of them carries a wall diagnosis device comprising a CCD camera, laser range finder, and their control systems, and the other a manipulator with a laser profile meter, with a flame gunning head mounted at the moving end. The machine works as illustrated in **Fig. 10**; that is, the diagnosis device first locates the damaged bricks, and then the second extendable beam enters the chamber to accurately survey the damaged area requiring repair, automatically calculates the gunning head trajectory and the required amount of spray material, and the repair work starts with the press of a button.

The flame gunning system developed by Nippon Steel has a capacity of about 20 kg/h, and the newly introduced burner head is capable of concentrating the gunned material at the center of the flame to fill a depression about 45 mm deep to a flatness of ±10 mm or less. A high-purity silica system is used as the spraying material; its SiO_2 content is substantially the same as that of silica bricks to make its thermal expansion behavior equal to that of the wall bricks and prevent its dripping due to over-melting.[5)]

The developed machine has made it possible for only two operators to carry out the entire repair work sequence, which used to require 10 or more workers in a hot and harsh environment to prepare and supply the utilities, namely oxygen, LPG and cooling water, handling of the long burner lance, and scaffolding, depending on the repair position.

Another type of flame gunning apparatus was developed for wall repairs from the flue side. It is mounted on a traveling car driven by a standby coal-charging car, and consists of a flame gunning head and CCD camera provided at the end of a lance that can enter the flue through the inspection hole at the oven roof. This has also improved working conditions significantly.[6)]

(3) Partial brick relaying method

Fig. 11 shows different types of partial brick relaying work. One of these methods is selected in consideration of the area and extent of brick damage and the temperature conditions:[7)] using the “total wall relaying method”, all the bricks in an entire coking chamber wall are replaced with new ones; using the “boring method”, which was first conducted at Hirohata Works in 1992, bricks in only the central portion of a chamber wall are re-laid; and using the “door repair extension method”, bricks around the end flue or those near the door are replaced.

The bricks used for these types of relaying work must have the following properties:

(i) Thermal expansion as small as possible to withstand rapid heating immediately after laying, which is required especially in the case of hot relaying, and temperature fluctuation during oven

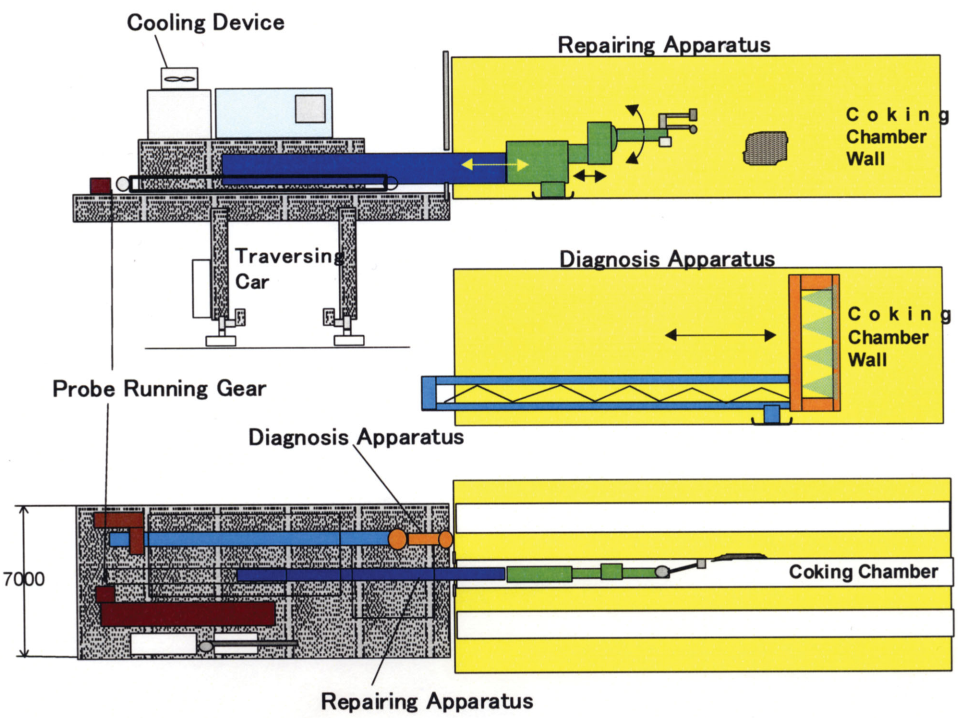

Fig. 9 Schematic illustration of the coking-chamber wall diagnosis and repair equipment

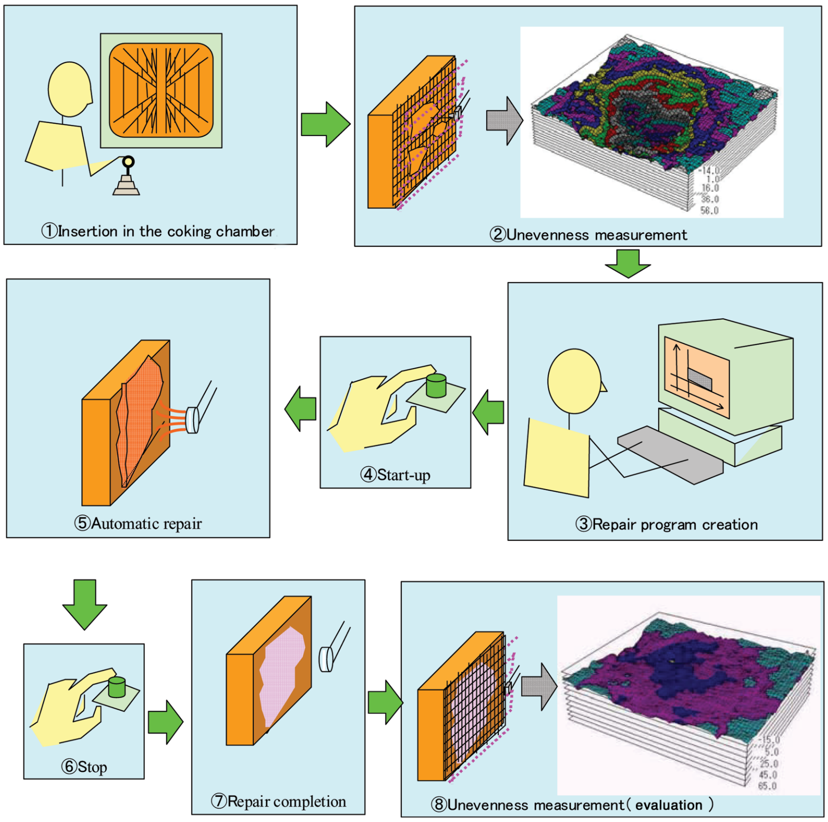

Fig. 10 Automatic repair process

	Total wall relaying method	Door repair extension method	Boring method
Brick relaying area	Relaying area; CS; PS; Curved part	Relaying area; Non repair; CS; PS; Curved part	Expansion allowance; Non repair; Relaying area; Non repair; CS; PS; Curved part
Expansion allowance between new brick and old brick	Unnecessary	Unnecessary	Necessary
Workinng term	1 month	3 months	1.5 month
Working condition	Reasonable	Not too harsh	Harsh
Brick cost	Expensive	Not expensive	Cheap

Fig. 11 Comparison of brick relaying methods for coke ovens

operation;

(ii) High strength at high temperatures to prevent abrasion by coal and coke; and

(iii) Minimal sintering shrinkage during prolonged use at high temperatures.

Three kinds of bricks are commonly used for the partial brick relaying methods: “silica repair bricks” with a higher volume porosity than that of common silica bricks; “fused silica bricks,” burned or unburned, virtually free of thermal expansion; and “advanced silica bricks for hot repairs” which combine crystalline and fused silica and are highly resistant to thermal shock.[8, 9] **Table 4** shows the typical characteristics of these materials for partial repairs.

Although the silica repair bricks are sufficiently strong, they are prone to cracking if the heating rate after laying is too high, and require careful thermal control. The fused silica bricks are widely used outside Japan because they are practically free of thermal ex-

Table 4 Characteristics of silica brick for oven chamber repair

Characteristic		Silica bricks for repair	Fused silica bricks	Advanced silica bricks for hot repair	
			Unburned	A	B
Bulk density		1.74	1.78	1.82	1.85
Apparent porosity	(%)	24.4	19.5	18.9	16.7
Apparent density		2.30	2.21	2.25	2.23
Crushing strength	(MPa)	36.1	21.2	38.0	36.9
Modulus of rupture at 1,200°C	(MPa)	6.4	6.6	2.1	0.4
Thermal expantion at 1,000°C	(%)	1.19	0.15	0.98	0.87

pansion and resistant to rapid heating, not requiring complicated expansion calculation, but are prone to cracking after devitrification (crystallization) and to wear during operation because of their lower strength at high temperatures. The advanced silica bricks for hot repairs, on the other hand, are in between the first two, and for this reason, it was feared at the beginning that many problems would arise as side effects of their advantages. Examination of samples of this type of bricks after six years of use, however, revealed that there were no cracks, and as seen in **Fig. 12**, the hot modulus of rupture was found to have increased to a level comparable to the apparent hot modulus of rupture on the coking chamber side of conventional silica bricks after 17 years of use, described in Item (2) of Section 2 hereof (see Fig. 6). For this reason, this type of brick has been widely used for hot repairs.

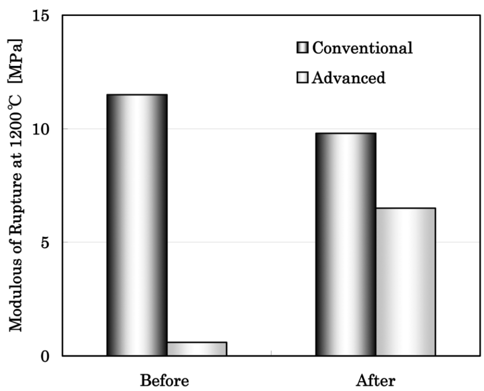

Fig. 12 Hot modulous of rupture for advanced silica bricks before and after operation

4. Repairs involving Large-scale Brick Relaying

The bricks for two coke oven batteries were totally renewed at Nagoya and Muroran Works in increasing work scales. **Table 5** shows the outlines of the two batteries, and **Fig. 13** the appearance of Muroran No. 6 Coke Oven Battery after the renewal.

The brick relaying work for the Nagoya No. 1A Battery covered the entire structure above the curved duct portions of the regenerators as well as all the checker bricks of the regenerators. The tonnage of bricks totaled some 4,000 t, with silica bricks accounting for about half, and the work took about five months.

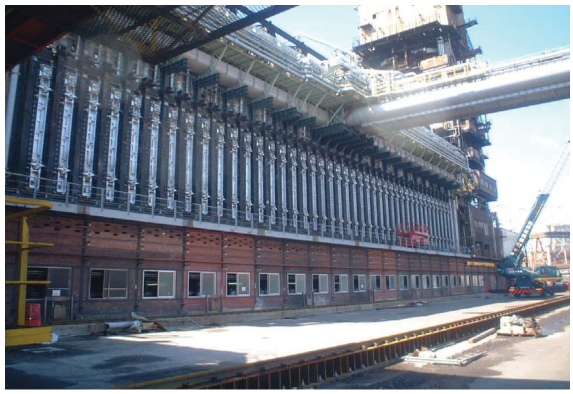

Fig. 13 Newly rebuilt Muroran No.6 coke oven

Table 5 Outlines of rebuilt coke oven batteries

			Muroran No.6	Nagoya No.1A
Batteries	Type		Modified NSC-M	DKH-R compound
	Number of ovens		42	25
	Height	(mm)	6,500	5,000
	Width	(mm)	430	450
	Taper	(mm)	76	60
	Length	(mm)	15,800	13,724
	Effective volume	(m^3)	35.1	27.3
	Number of flues		30	32
	Thickness of wall brick	(mm)	110/100	100
Rebuilding work	Demolition		Mar. 2006-	Sep. 2004-
	Bricklaying		Jun. 2006-	Jan. 2005-
	Drying	(day)	Feb. 2007 (71days)	May 2005 (59days)
	Start-up date		21 May 2007	27 Aug. 2005

In the case of the Muroran No. 6 Battery, all the refractory structures above the concrete foundation amounting to about 13,000 t were dismantled and replaced with new ones using the so-called pad-up rebuilding method. Silica bricks accounted for about two thirds of the total, with chamotte and heat-insulating bricks, and ceramic fiber, etc. making up the balance. The work took about seven months.

Although the above two projects were internally classified as repairs by relaying, they were virtually construction of new coke oven batteries after 26 years. For this reason, many problems arose in relation to the work method and materials supply, but they were solved and the work was completed on schedule.

5. Expected Problems in Construction of New Coke Ovens

In addition to the two large-scale brick relaying projects above, a new coke oven battery was constructed and commissioned at Oita Works on May 30, 2008. Many problems arose during this new construction and the above relaying projects, which made it clear that many improvement measures were required in relation to the refractory for coke ovens. The most important of these, which cannot be solved by Nippon Steel alone but through collaboration between all the steel-related industries in Japan, are as follows:

(i) An enormous volume of bricks, mostly silica bricks, of standardized shapes is used in the construction of a new coke oven battery. During the last 30 years, few coke ovens were constructed in Japan, however, so many domestic mines for brick materials and furnaces specially designed for firing such bricks were closed, and it is now impossible to procure them from Japanese sources. Therefore, these refractory materials have to be imported from abroad, principally from China. There are, however, big differences in commercial practice between Japan and these countries with respect principally to dimensional accuracy of products, quality stability in different production lots, and quality assurance up to the point of final delivery, etc. It is important to establish close communication at the pre-manufacturing stage between Japanese users and overseas suppliers through dispatch of buyers' specialists not only for refractory production but also for its field use at construction sites.

(ii) Specialist workers with different skills are required for construction of coke ovens: these include bricklayers to combine small bricks of different and complex shapes correctly and position them accurately, arrangers to prepare the right types of bricks on site based on drawings and in accordance with work progress, joint pointers to fill brick joints with mortar, and woodworkers to fabricate formworks and templates. There were not many specialists who acquired their expertise during the days when many coke ovens were built, and many of them have already retired. Preservation of these skills by measures such as personnel allocation and the transfer of expertise to young recruits is strongly and urgently required for steel-related industries.

(iii) Environmental consciousness has grown significantly, and therefore, operational methods for coke ovens have changed greatly in relation to environmental measures. Regulations on soot emissions have become increasingly demanding, and to use a coke oven battery for 50 years or more, it is necessary to develop and introduce oven structures totally different from conventional ones such as those to enable local cooling and repair while leaving the rest of the battery operational, and to prevent gas leakage even when brick joints develop cracks to some extent. To this end, engineering and technical development combining structural design, refractory properties and oven construction/repair methods is indispensable.

6. Closing

There have been numerous studies and investigations regarding silica bricks for coke oven use. Examination of used silica bricks taken from some coke ovens shut down after operation for different periods disclosed that the brick material changed into a quite different microstructure from the original, resulting in inferior resistance to heat shock, which aggravated the rate of heat spalling.

The newly developed diagnosis and repair machine has enabled periodic inspections and quick and accurate repair of coking chamber walls while still hot for the first time. Nippon Steel is expanding its use to all of its coke oven batteries. This is expected to extend the service life of coke ovens through preemptive repair of damaged bricks and to be instrumental in developing new repair methods, refractory materials and new designs of coke oven structures.

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