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Technical Review

History of Silica Refractories for Coke Ovens

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Abstract

Coke ovens are made of numerous refractories for various component materials. The main materials used are silica bricks constituting the coke oven wall. In this report we first describe the problems and characteristics of the silica bricks of coke ovens and their installation at the facility. Next, we describe the imported fireclay bricks for coke ovens which were introduced to Japan in the late 1800s and the domestic production of high silicate fireclay brick called semi-silicate bricks used until the early 1900s. The history of the improvement of dense silica bricks over a period of more than 100 years is summarized and problems of recent coke oven silica bricks are introduced.

1. Introduction

1.1 Material characteristics of refractories used for coke ovens

Coke production began in the 18th century; the production method at that time was simply firing a pile of coal coated clay, mud or the like to shut off the air. In the early 19th century, when coke began to be used for iron production by blast furnaces, beehive coke ovens were devised, whereby coal was heated by burning the volatile matter distilled from the coal; this oven type was widely used. After that, the Holdy-type and Coppee-type coke ovens were developed, wherein the coal chambers and heating furnaces were separated from each other and the coal was heated indirectly. These types were the originals of the current chamber ovens, but since tar and other volatile matter were discharged into the atmosphere, they were environmentally harmful, and thermal efficiency was poor.

These deficiencies were improved in the Semet-Solvay coke ovens, and then, as a further improvement, the Koppers-type ovens were developed in Germany as the first of the modern ovens. The first coke ovens built in Japan were beehive ovens, and for over 100 years coke ovens of the Otto type, the Carl Still type, the Wilputte type, etc. were introduced. On the other hand, after the establishment of the Imperial Steel Works, Japan, the forerunner of the present Yawata Works, then as a government operation, coke ovens began to be designed in Japan instead of being imported or imitating European designs. Ovens of the Kuroda type, the Nittetsu type and the Miike type were constructed, and as a result, various types of coke ovens as listed in **Table 1** were built and operated in the 1870s to the 1920s.[1, 2)]

Before examining the historical changes of the material characteristics of the refractories used for Nippon Steel Corporation's coke ovens, let us study the structure of coke ovens presently in operation. **Figure 1** shows a typical coke oven battery. Coking chambers ①, into which raw material coal is charged, and combustion chambers ②, in which the fuel gas is burnt, are arranged alternately side by side so that the coal in the coking chambers is carbonized by the

Table 1 Coke oven in the early day of Japan[1, 2)]

Year	Company/Plant	Coke oven type
1871	Osaka Mint	Beehive
1890	Furukawa Co., Ltd., Fukagawa	Beehive
1892	Mitsui Mining Limited Partnership, Miike-yokosuhama Coke Plant	Beehive
1894	Kamaishi Iron Mining, Tanaka Ironwork Company	Beehive Coppee
1896	Mitsui Coal Mines Co., Ltd, Miike Plant	Coppee
1897	Osaka Seimikogyo, Iwasakicyo Plant	Beehive
1897	Tikuho Cokes Mfg.	Beehive
1898	Osaka Seimikogyo, Iwasakicyo Plant	Somet-Solvay
1905	Fukagawa Coke Mfg.	Emori
1907	The Imperial Steel Works, YAWATA	Somet-Solvay
1912	Mitsui Coal Mines Co., Ltd, Miike Plant	Koppers
1912	Tokyo Gas Co., Ltd, Omori Gas Plant	Koppers
1912	Mitsubishi Limited Partnership, Makiyama Coke Plant	Somet-Solvay
1918	Saibu Godo Gas Co., Ltd., Kokura Plant	Kuroda
1919	The Imperial Steel Works, YAWATA	Kuroda

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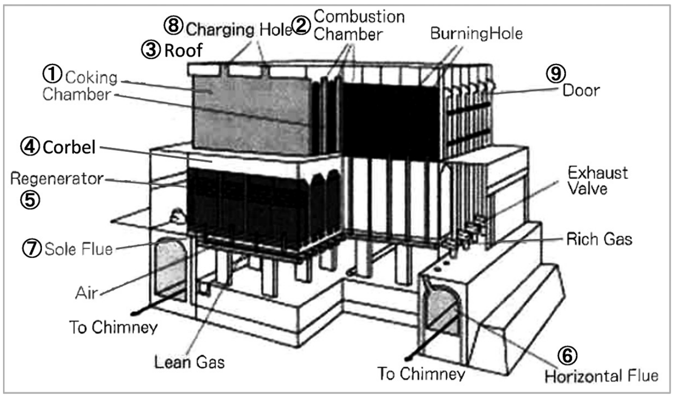

Part		Refractories
Roof		Fireclay brick
		Insulating brick
Flue	Wall	Silica brick
	Jumb	Insulating brick, fireclay brick
Corbel		Silica brick
Regenerator	Wall	Silica brick, fireclay brick
	Checker	Fireclay brick
Sole flue		Silica brick, fireclay brick
Door		Cordierite precast brick
Ascension pipe		Cordierite precast brick
Chimney flue		Fireclay brick, common brick

Fig. 1 Schematic diagram of coke oven and refractories used for oven parts

Table 2 Coke oven types and kinds of bricks used[3)]

Type of coke oven		Wilputte		Otto		Koppers		Carl Still		Nittetsu	
Height of coke oven		5100 mm		6500 mm		7125 mm		755 mm		6500 mm	
Brick material	Weight/Chamber	ton	%	ton	%	ton	%	ton	%	ton	%
	Silica brick	134	58.6	150.2	49.2	211.1	63.4	232.8	58.3	214.8	63.6
	Fireclay brick	87.6	38.3	147.4	48.3	94.9	28.5	181	41.4	103.6	30.7
	Insulation brick	1.7	0.7	2.6	0.9	16.1	4.8	12.5	2.9	5.8	1.7
	Common brick	5.4	2.4	5	1.6	10.9	3.3	10.5	2.4	13.6	4
	Total	228.7	100	305.2	100	333	100	436.8	105	337.8	100

heat from both sides. The roof ③ covers the tops of the coking and combustion chambers, and below the corbel ④ forming the floors of the coking and combustion chambers, there are regenerators ⑤ for heat exchange between the combustion exhaust gas and air. There are sole flues ⑦ at the bottom of the regenerators, leading to the horizontal flues ⑥ followed by a chimney.

The structural parts of the coking and combustion chambers, the most important oven parts, are made of silica bricks in appreciation of their high strength and small volume expansion at high temperature, and the parts that undergo violent temperature change such as both the ends of coking chambers near the doors ⑨ and charging holes ⑧ are made of fireclay bricks excellent in spalling resistance. Concrete, which is not resistant to high temperature, is used for the oven base and the retaining walls at the battery ends, and they are insulated from the hot oven proper by heat insulating bricks or common bricks. Precast blocks of cordierite with low thermal expansion and good spalling resistance are widely used for oven doors ⑨ and ascension pipes.

The inner surfaces of horizontal flues, which contact the exhaust gas, are mostly made of acid-resistant bricks with low water absorption and joints of water-resistant and self-hardening clay mortar. The complicated parts around the waste gas outlets from the regenerators are formed of low-porosity, acid-resistant unshaped refractory widely used for smoke stacks, etc.

Auxiliary materials for coke ovens include blankets for heat insulation, fiber ropes for the seals between the oven frame and the bricks, and glazed tile bricks for the coke wharf.

Different types of air-setting mortar are used for the joints of the different brick types: silica mortar for silica bricks and clay mortar for fireclay bricks, and self-hardening and water-resistant mortar containing binder of alumina cement is used for the roof tiles and wall surfaces exposed to the atmosphere.

Table 2 shows examples of the weights of different types of refractories used for typical oven types and their percentages in recent years.[3)] In any of the oven types, silica bricks account for more than half of the oven proper in terms of weight, and it is no exaggeration to say that the performance of coke ovens is defined by the quality and characteristics of silica bricks.[3, 4)] The present paper mainly examines silica bricks.

1.2 Required properties and characteristics of silica bricks for coke ovens

As stated earlier, the walls between the coking and the combustion chambers are mostly made of silica bricks in appreciation of the following advantages:

(1) High volume stability due to small thermal expansion at and above 800°C; and
(2) High strength and high refractoriness under load at high temperature.

However, they have many deficiencies. The main raw material is natural high-purity quartzite consisting primarily of α-quartz, SiO_2. As shown in **Table 3**,[5)] under temperature change, silica undergoes various types of phase transformations such as the slow ones between cristobalite, tridymite and quartz, and the rapid ones between those phases, and the volume changes as a result; that is to say, the crystal system and specific gravity change at any of the phase transformations, accompanied by volume expansion or shrinkage.

Because the crystal system of SiO_2 differs at different temperature conditions and processing time, its volume changes at different transformation temperatures as stated above, fine cracks develop in its structure or corner chipping occurs under violent temperature change.[5, 6)] It is possible to minimize the volume change of silica bricks by increasing the percentage of tridymite and decrease that of residual quartz. Therefore, to improve the durability of silica bricks, it is very important to measure and evaluate the composition ratio of

Table 3 Phase transformation and volume change of silica[5)]

Phase transformation			Temperature (°C)	Linear expansion (%)	Volume expansion (%)	Transformation speed
α-tridymite	↔	β-tridymite	117–163	+0.17	+0.50	Rapid
α-cristobalite	↔	β-cristobalite	200–210	+1.00	+2.00–2.80	Rapid
α-quartz	↔	β-quartz	573	+0.26–0.45	+0.86–1.30	Rapid
β-quartz	→	β-tridymite	870	+5.55	+14.4	Very slow
β-quartz	→	β-cristobalite	1250	+6.60	≈+17.4	Very slow
β-tridymite	→	β-cristobalite	1470	+1.05	≈+0.1	Slow

cristobalite to tridymite and the amount of residual quartz. In addition, because the thermal conductivity of SiO_2 is lower than those of the other materials, it is also important for efficient carbonization of coal to improve the thermal conduction of the chamber wall by raising the density of silica bricks and reducing the wall thickness. Thus, the high-temperature strength and refractoriness under load have to be advanced.

2. Historical Change of Silica Bricks for Coke Ovens

Idiomatically, various types of silica bricks including small amounts of additives and impurities, are referred to collectively as "silica bricks," but hereinafter, only high-purity silica bricks containing lime milk are called "silica bricks," and high-silica fireclay bricks with clay addition "semi-silica bricks."

Silica bricks have greatly contributed to the modernization of Japan, for they have been developed not only as the main construction material for coke ovens, but also as that for open hearth furnaces for steelmaking and glass melting furnaces. They are very important also for Nippon Steel, because the company has developed various new types of silica bricks since the establishment of the Imperial Steel Works. As seen in **Fig. 2**, the history of silica bricks in Japan can be traced back for more than 100 years to the middle of the 19th century. The history of the silica bricks for coke oven use is outlined below in the following four periods:

(1) The period of brick import in the early days of coke oven operation in Japan;
(2) The period of domestic production of semi-silica bricks;
(3) The period of densification and property improvement of silica bricks; and
(4) Higher functionalization and the second international silica bricks procurement period.

2.1 Refractories of Japan's early coke ovens

The world's first silica bricks were reportedly those made from the sand of Dinas, Wales, UK in 1822.[6)] The first coke ovens of Japan, however, seem to have been built using mainly fireclay bricks imported from Europe. Beehive ovens were introduced to Japan around 1871, and coke production on an industrial scale began at Kamaishi (Iwate Prefecture) in 1894 using a beehive oven with 48

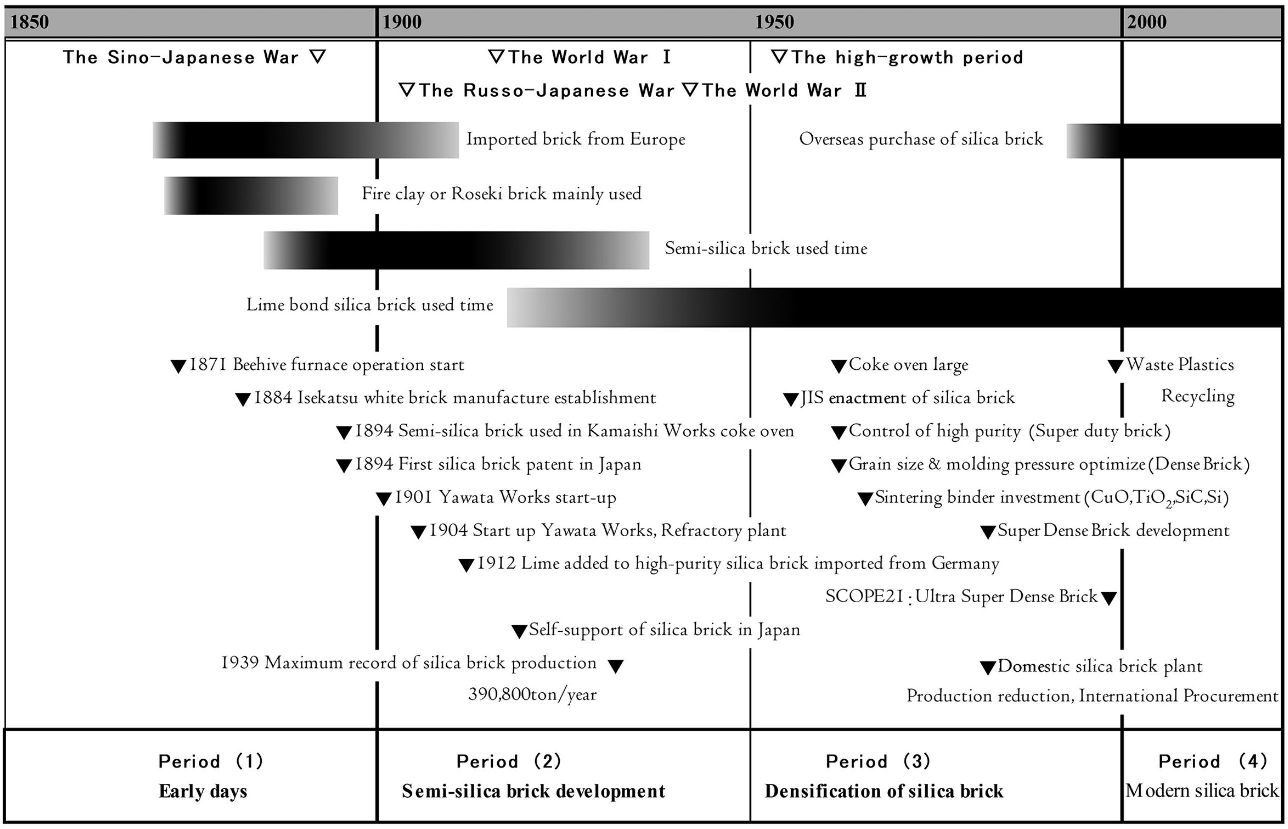

Fig. 2 History of silica bricks for coke oven

chambers, but it is said that the blast furnaces did not use coke but mainly charcoal as the reducing agent soon after the blow-in. However, the iron production of Kamaishi's blast furnaces increased rapidly when coke production began there in the same year with a Coppee-type coke oven battery with 43 chambers using the coal from the Yubari mine in Hokkaido.

Figure 3 shows the structure of a Coppee-type oven.[1] It was the first indirect-heating chamber oven in Japan having vertical flues and coking and combustion chambers separate from each other. This design was carried over to the ovens built at the Imperial Steel Works in Yawata and the Miike Mine (in Kyushu) of Mitsui Coal Mines Co., Ltd. Later, another Coppee-type oven was built at Kamaishi, but no records remain regarding the refractories used for it. However, Kawaguchi wrote in a report of his business trip to Kamaishi in 1870 that 2 500 pieces of British refractories were landed at the port of Kamaishi,[7] and it is likely that many of them were for the Coppee-type oven.

In this period, Isekatsu White Brick Manufacturing, the forerunner of the present Shinagawa Refractories Co., Ltd., started up at Fukagawa, Tokyo, in 1884. A deposit of roseki, a mineral consisting mainly of pyrophyllite, was found in Okayama Prefecture in the late 1870s and Mitsuishi Fire Bricks Co., Ltd. was established in 1892 to produce bricks from roseki. Many other brick manufacturing companies were established in this period, including Iwaki Fire Bricks Co., Ltd. in coastal Fukushima Prefecture and Owari Refractory Manufacturing Co., Ltd. in Aichi Prefecture. A test report of refractories[8] published in 1893 discloses a vast amount of data collected by domestic refractory manufacturers; most of the data were on fireclay and roseki (pyrophyllite) bricks, but semi-silica bricks were also included.

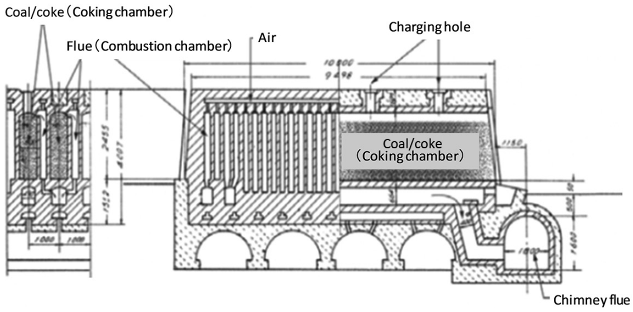

Fig. 3 Schematic diagram of Coppee coke oven[1]

In the Refractory Yearbook of 1941, Kuroda wrote, "Most of Japan's coke ovens in the Meiji Period (up to 1912) were of the beehive and Holdy types, made of roseki bricks. It is said that a chamber oven of the Coppee type, a little more complicated than the above, was constructed using roseki bricks unsuccessfully. Reportedly, semi-silica bricks were manufactured in Belgium or elsewhere at that time, and were widely used. The bricks of Yawata's Coppee and Somet-Solvey ovens were also semi-silica bricks from Belgium …"[9] It is presumed from the above descriptions that, in the early days of the Somet-Solvey and other types of chamber ovens in Japan, fireclay bricks and semi-silica bricks imported from Belgium, Germany, UK, etc., were mainly used for the high-temperature portions, and domestic fireclay bricks were used for the low-temperature and low thermal shock portions.

2.2 Period of domestic production of semi-silica bricks

The semi-silica bricks mentioned in Kuroda's report above were developed in order to combine the advantages of silica bricks with those of fireclay bricks; they are sometimes called high-silicate fireclay bricks or fireclay silicate bricks. They were used for as long as 40 years or more in the first half of the 20th century, and are still used in East Europe for oven portions of milder operation conditions such as the sole flues in the lower oven and the roofs. They are included in the DIN standard as the refractories for coke oven applications,[10] but there are very few reports specific to their service life and damage. In terms of chemical composition, there is no clear distinction between semi-silica bricks, fireclay bricks and roseki bricks, but the bricks made of quartzite with the addition of 10 to 30% fireclay to improve plasticity were once called semi-silica bricks.

Table 4 shows examples of the composition of semi-silica bricks used in this period.[11, 12] Although strength and refractoriness under load were not very high, they were satisfactory for practical purposes. In addition, because they had a low thermal expansion and were excellent in thermal spalling resistance, they were presumably very effective for coke oven parts that are subject to large temperature change during coal charging and coke pushing. Furthermore, the raw materials were easily available in Japan, and the firing temperature was similar to that for fireclay bricks. For these reasons, after initial import from Europe, semi-silica bricks were manufactured in Japan for wide application to low-temperature parts of coke ovens, while high-grade semi-silica bricks had to be imported up to around 1900.

After 1900, beehive ovens and other small coke ovens were replaced with large ones such as the Koppers type, the Refractory

Table 4 Characteristics of semi-silica bricks used in 1890 to 1920[11, 12]

User			Yawata Works					Osaka Gas					
Type			Coppee	Coppee	Koppers	Koppers	Koppers	Somet-Solvay					
Country of origin			Belgium	Belgium	Germany	Germany	Germany	Belgium	Otto	UK	UK	UK	Japan
Chemical composition	SiO_2	mass%	77.70	76.82	64.40	85.70	79.50	82.50	74.64	88.70	92.30	88.00	84.12
	Al_2O_3		20.15	21.18	31.28	11.23	16.78	15.57	20.61	9.10	5.80	7.90	
	Fe_2O_3		1.87	1.47	3.30	1.86	2.31	2.00	0.91	1.00	0.50	1.20	
	CaO		0.54	0.54	0.52	0.44	0.44	-	0.35	0.20	tr	0.40	
Refractoriness		°C								1 600	1 600	1 600	
Bulk density									1.90	1.93	1.90	1.85	1.98
Apparent porosity		%							24.2	23.6	23.3	27.7	23.4
Thermal expansion		%							0.533			0.533	0.544
Crushing strength		MPa								10.2	55.4	8.6	

Plant was established at the Imperial Steel Works in Yawata in 1904, and Yawata Works Laboratory in 1916,[13] and as a consequence, the dependence on imported semi-silica bricks fundamentally changed. In response to rapidly growing coke production and operating conditions becoming increasingly harsh, the Laboratory investigated the deposits of quartzite and fireclay all over Japan, studied how to combine those mineral resources to produce refractories of high durability, and developed adequate forming and firing processes. The mineral deposits found at that time include those of composite quartzite "AKASHIRO-KEISEKI," the red-white silica rock of Tamba (Kyoto Prefecture), Ichijima (Hyogo Prefecture), Wakayama, Mie, Usuki (Oita Prefecture), and even Lueshun and Dalian in Northeastern China. As a result, the share of domestic semi-silica bricks began to increase gradually from 1910, but since the Usuki deposit of the above mentioned red-white silica rock began to run dry, the material supply source was shifted to the deposits of red, white and blue quartz rock of Tamba and Wakasa (Fukui Prefecture).[14]

In the meantime, high-purity silica bricks containing lime milk were introduced from Germany as "pure Dinas bricks" around 1912,[15] and the Engineering Laboratory in Yawata gradually shifted focus to this new type of brick. At the beginning, however, high quality was not obtained: many of the research papers reported the difficulties encountered in those days. It seems that in reality the Laboratory, while developing semi-silica bricks, looked for minerals and sintering aids that could make the "pure Dinas bricks."

In this situation, it was found that a combination of red and white quartz rock containing small amounts of iron oxide peculiar to Japan and high-purity white quartz rock, with the addition of finely crushable soft quartz rock, would make bricks with excellent properties. When Japan's steel production increased during the period from World War I (1914–1918) to the Chino-Japanese War (1937–1945), this finding was commercially applied, the bricks exhibited very good durability, and high-purity silica bricks gradually replaced semi-silica bricks for coke oven use. The transition from semi-silica bricks to silica bricks is considered to have occurred around 1935, probably triggered by the increased demands for coke due to those wars.

In that period, in response to the quickly increasing demand for silica bricks, Japan Iron & Steel Co., Ltd., which operated Yawata and other steelworks until 1950, faced a short supply of silica bricks from its own refractory plants, and while maintaining a close relationship with the then Kurosaki Firebrick Manufacturing Co., Ltd., established Japan Refractories Manufacturing Co., Ltd. jointly with Kurosaki in 1938. The silica brick supply formation of three companies was established and covered from Muroran in Hokkaido to Yawata in Kyushu.[16, 17]

2.3 Period of durability improvement of silica bricks

There were more than 30 coke oven batteries in Japan just before World War II, but the number was reduced to only 7 in 1946, the year after the end of the war. To improve the situation and meet the rapidly increasing demands for steel products, the oven temperature was raised to increase productivity in the late 1940s. This was an excessively demanding condition for the refractories, and it became necessary to enhance the thermal conductivity and raise the refractoriness under load of the bricks. To increase coke production, the coke oven size was expanded rapidly, and in the high-growth period of the 1960s and 70s, many large coke ovens were built, some of them having coking chambers 7 m or more in height.[18] Such large ovens, however, required silica bricks of improved thermal conductivity, smaller higher thermal strength and better refractoriness under the harsher operating conditions. In this situation, it was necessary to improve not only brick quality, but also the manufacturing process.

The principal improvement measures were as follows:

(1) Search for natural raw materials containing as little iron, alumina and other impurities as possible and easily transformable into tridymite, and their effective utilization;
(2) Brick density increase by optimizing the grain size of the raw materials;[19–21] and
(3) Density increase by adequate addition of lime milk and other sintering aids such as CuO, TiO_2, SiC, Si_3N_4 and metallic Si.[22–25]

The changes in porosity and other physical properties as a result of such improvement measures are given in **Table 5**.[21] Brick density was remarkably improved: apparent porosity was lowered from 25–27% before World War II to 22% by 1970. **Table 6** lists some examples of the attempts of (1) to (3) above to add sintering aids.[19–25] The quality immediately after manufacturing was improved and made better, but it seems that the results after many years of oven operation were not as good as expected because of the increase in furnace problems. **Table 7** shows the properties of typical silica bricks developed in this period and presently in service.[19, 25, 26] Currently, dif-

Table 5 Characteristics of silica brick from 1935 to 1969[21]

▽ The World War II

Year			1935	1940	1945	1950	1955	1959	1965	1967	1969
Chemical composition	SiO_2	mass%	92.30	93.60	93.91	94.05	93.67	94.80	94.64	94.92	94.82
	Al_2O_3		1.45	1.23	0.87	0.88	0.91	0.41	0.74	0.82	0.91
	Fe_2O_3		1.50	2.47	1.50	1.33	1.44	0.95	1.14	1.08	0.89
	MnO		-	-	0.12	0.18	0.13	0.06	0.06	-	-
	CaO		4.40	3.00	3.12	2.78	3.00	3.40	3.66	2.53	2.67
	MgO		0.40	0.47	0.15	0.18	0.15	-	-	0.23	0.22
Refractoriness		SK	31	31	32	32	32	32	32+	32+	32+
Apparent density			2.34	2.35	2.33	2.33	2.32	2.32	2.33	2.32	2.32
Bulk density			1.76	1.70	1.75	1.77	1.79	1.79	1.80	1.81	1.82
Apparent porosity		%	24.9	27.6	24.8	24.0	23.0	22.9	22.8	22.2	21.6
Refractoriness under load	T_2	°C	-	-	1603	1628	1623	-	1617	1624	1630
Crushing strength		MPa	-	-	33	34	43	40	48	51	64
Thermal expansion	1000°C	%	-	-	1.12	1.14	1.18	1.11	1.19	1.15	1.15

Table 6 Examples of addition of sintering aids [19–25]

Additive material			Cu_2O: 5%	TiO_2: 3%	Si_3N_4: 5% NH_4NO_3: 3%	M-Si: 10%
Chemical composition	SiO_2	mass%	91.5	93		
	Al_2O_3			0.5		
	$Ca(OH)_2$		3.5	3.2		
	Fe_2O_3			0.3		
Bulk density			1.92	1.96	1.94	1.96
Apparent porosity		%	20	18	15.4	15.5
Modulus of rupture		MPa	8.5	9.9		
Cold crushing strength		MPa		50		78
Thermal conductivity		W/(m·K)	1.64 at 1 070°C	1.86 at 1 093°C		1.76 at 400°C

Table 7 Characteristics of typical silica bricks currently used [19, 25, 26]

Silica brick type			Normal brick	Dense brick	Super-dense brick	Hyper-dense brick*
Additive material			CaO	CaO	CaO, Si_3N_4	CaO, M-Si
Chemical composition	SiO_2	mass%	95	95	96	
	Al_2O_3		1.0	1.0	1.0	
	Fe_2O_3		0.8	0.8	0.7	
Apparent specific gravity			2.31	2.32	2.27	
Bulk density			1.79	1.83	1.94	
Apparent porosity		%	22	19	15	9.7
Cold crushing strength		MPa	60	70	95	
Refractoriness under load	T_1	°C	1 640	1 660	1 650	
Thermal expansion	1 000°C	%	1.20	1.20	1.20	
Thermal conductivity	800°C	W/(m·K)	1.81	1.93	2.28	2.44

* denser than super-dense brick

ferent types of refractories are used for different oven parts: high-density silica bricks (dense, super-dense and hyper-dense bricks in the table) are used for the walls of coking and combustion chambers, and general-purpose silica bricks (normal bricks) for the other parts.

2.4 Refractories for present and future coke ovens

The world steel demands ceased to grow around 1975 and adjustment of steel production began. As a result of the import of inexpensive coke from China and other sources and a change in procurement policy, steelmakers' self-sufficiency in coke decreased. Nevertheless, the service life of coke ovens continued to increase because of the advance in the repair methods such as the introduction of spraying, hot gunning, welding, casting, etc. of unshaped refractories, intensive oven condition management and brick relaying of coking chambers near the oven doors and regenerators.[27] As a consequence, no new coke ovens were constructed and no large oven rebuilding by brick relaying was conducted for more than 30 years after the construction of Muroran No. 6 Coke Oven in 1979. Incidentally, this type of coke oven rebuilding is also called pad-up repair or revamping in Japan.

However, many quartzite mines in Japan were closed during this period, the forming facilities and firing kilns for silica bricks shut down, skilled refractory labor decreased in the meantime, and at the beginning of the current century, there were no longer any Japanese refractory manufacturers capable of supplying silica bricks for coke ovens in large quantities.

The import price of Chinese coke began to rise rapidly around 2000, and for stable steel production, it became necessary again to self-produce coke. Nippon Steel built Oita No. 5 Coke Oven after 30 years of no new oven construction. It is characterized by being the first commercial oven to apply the technology of the "Super Coke Oven for Productivity and Environmental enhancement toward the 21st century (SCOPE21)," whereby coal is quickly heated through pretreatment processes before being charged into the coking chambers so as to enhance the coke quality and significantly shorten the coking time. A pilot plant of SCOPE21 was constructed beforehand and various tests were conducted for process verification.

One of the achievements obtained through the SCOPE21 development in the field of refractory is commercially usable highly heat-conductive hyper-dense bricks (denser than super-dense bricks); metallic Si was added so that internal pores are closed by the expansion due to its oxidation during firing, the porosity of the developed bricks was 10% or less, and the heat conductivity at 1 000°C was 2.44 W/m·K. The thickness of the coking chamber walls of the pilot plant was 70 mm using the developed bricks, and satisfactory results were obtained, but because the test period was only one year and long-term stability was unknown, and the cost was high,[26] their use for Oita No. 5 Coke Oven became surplus to requirements.

On the other hand, regarding the normal silica bricks for the low-temperature parts, the possibility of domestic procurement was studied, and found to be feasible as long as the quantity was to the order of 1 000 tons for the pilot plant. However, as far as full-size coke ovens of Nippon Steel were concerned, it was extremely difficult to procure 10 000 to 30 000 tons of large and high-precision silica bricks economically from domestic sources for reasons of precarious raw materials supply and environmental regulations. It was thus necessary to look for overseas manufacturers of large capacity and improve the arrangements for long-distance transport. **Table 8** lists Nippon Steel's coke ovens that have been newly constructed or rebuilt by large-scale brick relaying since 2000. The silica bricks for the recently built coke ovens such as Muroran No. 6 and Nagoya No. 5 were imported 100% from China, India, Europe and other overseas sources.

This situation is very much similar to that in the age of imported refractories in the Meiji period more than 100 years ago, but in order to use overseas silica bricks for raw materials and manufacturing processes different from domestic products, there are many items to consider. It is necessary to adequately confirm and evaluate their quality, appearance and dimensional accuracy.[28] The standards for refractories were instituted in the Japanese Engineering Standards (JES) first in 1924. After that, after some temporary standards, the specifications for refractories were included in the Japanese Industrial Standards (JIS) in 1949 based on the discussions of the special committee for standardization of the Technical Association of Refractories, Japan (TARJ) at the time of its foundation. The JIS specifications were revised in 1949, and the revised version in 1955 is the basis of the present standards.[29] With increasing international exchange, it became necessary to secure consistency with foreign standards such as the DIN, the ASTM and those of the ISO, and lively discussions have been maintained in the special committee for standardization of the TARJ and relevant entities.

Table 8 Recently constructed or rebuilding coke ovens of Nippon Steel

Works/Battery		Startup	Remark	
Oita	#5	Feb. 2007	New construction	SCOPE21
Muroran	#6	Jun. 2007	Pud-up rebuilding (Revamping)	
Muroran	#5 East	Dec. 2011	Pud-up rebuilding (Revamping)	
Nagoya	#5	Mar. 2013	New construction	SCOPE21
Kashima	#1 F	Aug. 2016	Extension	
Kimitsu	#4	Jan. 2017	Pud-up rebuilding (Revamping)	
Kashima	#2 E	May 2018	Extension	
Kimitsu	#5	Feb. 2019	Pud-up rebuilding (Revamping)	
Muroran	#5 West	Oct. 2019	Pud-up rebuilding (Revamping)	

Silica bricks were specified as JIS R 2303 in 1955. As the proportion of the silica bricks for coke ovens to the total refractory production increased remarkably thereafter, and large bricks of complicated shapes began to be manufactured, they were separately specified as JIS R 2401 "Silica Brick for Coke Oven" in 1970, and JIS R 2303 was revised to cover silica bricks for general use. Then in 1976, compression strength was newly included, the figure of apparent porosity was tightened, and in 1995, all the units were converted to the ISO units and the random sampling regulation for irregular-shaped bricks was relaxed. However, silica brick production in Japan dwindled to virtually zero at that time, and JIS R 2401 was abolished in 2000.

Because JIS R 2303 was also abolished in 2002, now there are no JIS standards for silica bricks. **Table 9** compares the main specifications of silica bricks of JIS R 2401 with those of the DIN, both in the 1995 versions.[30] Both the standard systems stipulate the methods of inspection by random sampling, determination of property figures, etc. as related standards, but obligatory measurement items and standard values are different between the two.[30, 31] To evaluate the increasing amount of imported silica bricks, Nippon Steel has established its own standards for refractories based on JIS R 2401 and incorporated its own test methods.

The most important problem in procuring and using bricks from abroad is how each standard is considered in different countries. In Japan, the JIS is regarded as the strictly protected base or the absolute standard of supply contracts, and if a product supplied is found not to satisfy the relevant standard figure at a prescribed test, it must be returned to the supplier or replaced with a good one. In Germany and other European countries, in contrast, the DIN (or any other applicable standard system) is generally regarded as a guideline for price negotiation, and unless a random-sampling specimen is found not to meet a standard figure, sometimes no replacements will be supplied. In China, on the other hand, standards are regarded as target figures, and the price of a product lot is defined based on the number of approved samples at relevant tests or the number of inspection items satisfied, and it is often the case that, when some pieces of a lot are rejected at the test, the price is greatly reduced on the assumption that they are used for the oven construction after remedial measures or repair.

Since the attitude about standards differs from country to country as mentioned above, it is important for price negotiation and

Table 9 Comparison of JIS and DIN standards of silica brick[30]

Silica brick type			JIS R 2401 (1995)			DIN 1089-1 (1995)		
			SC1	SC2	SC3	KN	KD	KS
Additive material			(CaO)	(CaO)	(CaO)	(CaO)	(CaO)	(CaO)
Chemical composition	SiO_2	mass%	≥93	≥93	≥93	≥94.5	≥95	≥95
	Al_2O_3		1.5≥	1.5≥	-	2.0≥	1.5≥	1.5≥
	Fe_2O_3		2.0≥	2.0≥	3.0≥	1.0≥	1.0≥	1.0≥
	CaO		-	-	-	3.0≥	3.0≥	3.0≥
	R_2O		-	-	-	0.35≥	0.35≥	0.35≥
Apparent specific gravity			2.35≥	2.35≥	2.35≥	-	-	-
Apparent porosity		%	22≥	24≥	26≥	24.5≥	22.0≥	22.0≥
Cold crushing strength		MPa	≥34.323	≥29.420	≥19.613	≥28	≥35	≥45
Refractoriness under load	T_1 (0.2 MPa)	°C	≥1580	≥1580	≥1550			
Creep-in compression	Z5-25*		-	-	-	≥0.12	≥0.12	-
Thermal expansion	1000°C	%	1.25≥	1.25≥	1.25≥	-	-	-

* 1°C/min up to 1450°C, maximum load 0.5 MPa

purchase contracts in the international market to fully understand the difference in consideration of cultural and business environment conditions.

On the other hand, new additional functions are now required for coke ovens, and the requirements for silica bricks are changing accordingly. For instance, in relation to the mixing of waste plastics with the charging coal to solve environmental problems,[32] the bricks are required to be resistant to corrosive elements such as chlorine in plastics. On the other hand, the coke oven's function to generate hydrogen[33] is viewed as a promising new source of energy, and in relation to this, material degradation of silica bricks due to the reduction of impurities such as iron oxides is a concern, and higher purity will be required.

3. Summary and Closing

(1) The history of silica bricks used for the coke ovens in Japan, especially for those of Nippon Steel, has been reviewed hereinabove in four periods. The history began with the import of clay bricks, and after the years of domestic manufacture of roseki bricks and semi-silica bricks, the present day high-density, high-purity silica bricks containing lime milk and various sintering aids appeared. The period of clay and semi-silica bricks was very long, which seems to indicate that these types of bricks served effectively for the long service life of the ovens. Reevaluation of low cost refractories used in the past is significant in modern operating conditions.

(2) The history of silica bricks of Nippon Steel is closely linked with that of Japan. However, as Japan's raw material sources have run dry, tight environmental regulations have been enforced, and the domestic manufacture of the bricks is no longer viable, the company, as well as the country, is totally dependent on imported silica bricks. It is important in procuring the bricks from abroad to investigate and evaluate brick quality based on correct understanding of the stipulations of applicable standards, and how the standards are regarded in relation to supply contracts in different countries.

(3) Different types of refractories have been used for different parts of coke ovens in consideration of the widely varied structure and operation condition, and accordingly refractories of various types have been developed. On the other hand, new functions will be additionally required for coke ovens, and there will arise many problems that cannot be solved from the viewpoint of refractory technology alone. It will therefore be important to develop new technology to fully utilize refractories through discussions with engineers of various technical fields such as furnace design, plant operation, and mechanical engineering.

The present paper has delineated, within space constraints, only some fractions of the 100-year plus history of the refractories, especially silica bricks, used for the coke ovens of Nippon Steel and Japan. Many issues remain undisclosed herein regarding technical details such as specific standards on the appearance and dimensions of bricks, which are fundamental to brick procurement from abroad and oven construction work, the change in material properties during oven operation, damage mechanisms, internal oven monitoring devices, oven management measures,[27] repair methods and recycling technology.[34, 35] If you, the readers, would like more details, please make sure to refer to the relevant technical documents and papers.

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