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Historical Overview of Refractory Technology in the Steel Industry

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Abstract

The historical transitions and progress since the ancient times in refractory technology for iron and steelmaking is briefly reviewed. In addition to describing the core historical facts for each era and their features, some discussions on the history from specified viewpoints such as raw material resources, energy, ecological aspects, refractory-manufacturing, and R&D methodology are attempted. Modern refractory technology is not simply based on materials technology any more. It has grown into an integrated system technology including heat engineering, monitoring techniques, furnace design, lining installation, and furnace operation. The history proves that the most contributory factor to the development of refractory technology is the technlogical innovations of iron and steelmaking processes.

1. Introduction

One of the oldest technical texts in the history of mining and metallurgy, De Re Metallica (by Agricola, G., 1556), lists ore, fuel and refractory materials including heat insulators, as the three substances essential for metal refining. All through the Iron Age from ancient times up to now, refractory has been closely engaged in iron and steelmaking, contributing to human civilization.

The study of refractory technology along its historical development is not only useful for better understanding of its background and essence, but also for taking lessons from the past for the further advancement of technology. In this sense, the author would like to overview herein the history of refractory technology for iron and steel production from several viewpoints.

For further details of individual historical events in refractory technology, more specific data and details of technical literature, the readers are requested to refer to the publications listed as 1) to 12).

2. Characteristics of Different Historical Periods

2.1 Ancient times, middle ages and era of renaissance

Mankind probably first became aware of refractory as a material "resistant to fire" at the time that the temperature of primitive pit kilns dug into the ground for firing earthenware reached the upper limit of the decomposition temperature for clay minerals (ca. 800℃); that was some time in the early Bronze Age (BC 4000 - 3000). It is reasonable to presume that the pits for firing earthenware were dug into some kind of soil resistant to fire. The desired function of the soil was to retain the heat (thermal insulation) and not to deform under the heat (fire resistance, or refractoriness).

Upon the advent of the Iron Age (ca. BC 2000 and thereafter), iron was produced by reducing iron ore using charcoal in a furnace. Higher temperatures were required inside iron-producing furnaces, and the inner lining of such furnaces had to withstand not only the heat but also the mechanical and chemical corrosion inflicted by the materials charged into them (wear resistance). Therefore, it would be appropriate to presume that refractory in its present definition, characterized by thermal insulation, refractoriness, wear resistance and adequacy for furnace inner linings, was born in tandem with iron producing technology.

The refractories for the ironmaking furnaces in ancient times can be described as follows:

(1) Mostly devoid of definite shapes, while blocks cut from natural stones and fireclay bricks were only partially used.
(2) The main component materials were silica rock (SiO_2 system) or fireclay (Al_2O_3-SiO_2 system) containing numerous impurities.
(3) Refractory materials of carbon-metal oxide systems (mixture of

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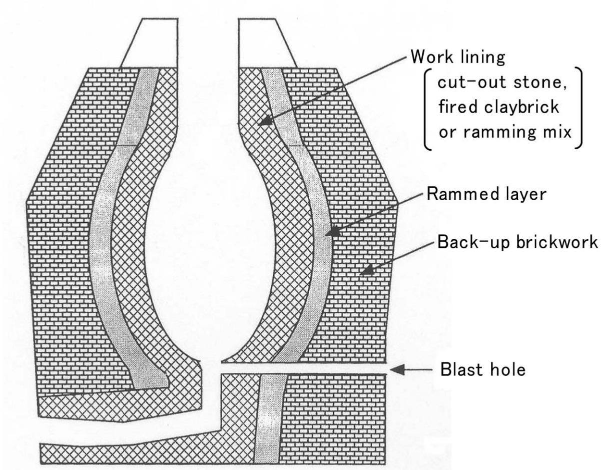

Fig. 1 Typical lining design of charcoal-fired blast furnace (16th-17th century)

fine charcoal and clay) were developed and widely used not only in Europe but also in Japan (the *tatara* furnaces blown by foot-activated bellows) and in China.

It is interesting to know that the history of refractories for iron and steel production began with mixtures without definite shape (unshaped refractories) and carbon-added composite materials, which account for most of the refractories presently used for the steel industry.

The first ironmaking furnaces capable of producing molten iron (charcoal blast furnaces) in Europe appeared sometime around the 14th century (see **Fig. 1**), but the advance of refractory technology was slow. In China, where charcoal blast furnaces had been built far earlier than in Europe, more advanced refractories were used, but their component systems were very similar to the European qualities.

2.2 Era of the industrial revolution

Modern refractory technology is considered to have begun during the era of the Industrial Revolution (the 18th to 19th centuries). After originating in the UK on three main pillars, namely, steam engines, coal and steel, the Industrial Revolution expanded to other European countries. As a result, many new industries using furnaces as their principal production facilities, popularly called "the smokestack industries", appeared, and a wide variety of industrial furnaces were invented and applied, spurring the advance of refractory technology.

The main drive in this advance was, no doubt, the steel industry; the basic concepts of the furnaces that form the production system structure of integrated steelworks (illustrated in **Fig. 2**) were established in the second half of this period. New types of iron and steelmaking furnaces from coke-fed blast furnaces to electric arc furnaces were built and new types of refractory were developed for different applications (see **Table 1**).

Typical iron and steelmaking furnaces developed during this period and their main characteristics are listed below.

(i) Coke-fed blast furnace, using coke as the reducing agent and heat source in place of charcoal.
(ii) Hot stove, employing regenerative heat exchangers of refractory to supply high-temperature air to a blast furnace.
(iii) Coke oven, to carbonize coal into coke.
(iv) Open hearth furnace, a reverberatory furnace for steel production employing regenerative heat exchangers to utilize its own

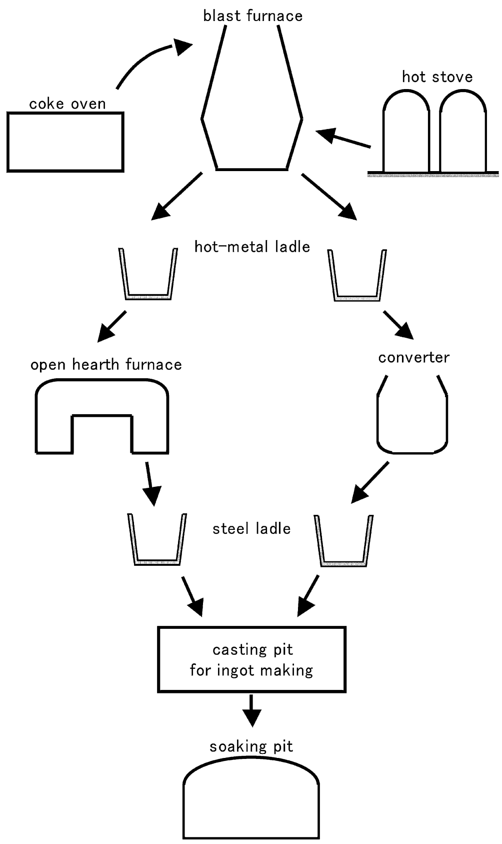

Fig. 2 Furnace make-up of typical integrated steelwoks in the latter Industrial Revolution Era

Table 1 Chronological table for steelworks refractories (I) (the Industrial Revolution Era)

14-15th century	Charcoal-fed blast furnace	
1709	Coke-fed blast furnace	
1735	Crucible steelmaking	
1784	Paddle furnace	
1806		Magnesia crucible
1810	Beehive coke oven	
1820		Silica brick (invented)
1834		Graphite crucible
1850	Saga paddle furnace	
1853	Water-cooled blast furnace	
1856	Bessemer converter	Silica brick (produced)
1857	Cowper hot stove	
	Kamaishi blast furnace	
1858	Siemens open hearth furnace	
1863		Carbon block
1864	Martin open hearth furnace	
1868		Silica brick for OH furnace
1879	Thomas converter	Tar dolomite brick
1880		Magnesia bottom (OHF)
1881		Magnesia brick
1885		Chrome brick
1899	Héroult electric arc furnace	

OH: open hearth, OHF: open hearth furnace waste heat (see **Fig. 3**).

(v) Converter, a steelmaking furnace to burn impurities in molten pig iron with air blown in from the bottom to use them as the heat source (see **Fig. 4**).

Whereas fireclay brick, or chamotte brick (Al_2O_3-SiO_2 system) which evolved presumably from ancient earthenware brick, accounted for most of the refractories before the Industrial Revolution, various new materials were developed during this period. However, the development of new refractory materials could not fully meet the increasingly demanding requirements of diverse functions of the new types of furnaces developed one after another.

The state of refractory technology at that time can be summarized as follows.

(1) The quality of fireclay brick was improved, and in addition, silica, tar-dolomite, and magnesia bricks appeared as new and high-performance types of bricks.

(2) Besides the traditional application of refractories to the inner lining of kilns and vessels, new applications were introduced to exert new functions: these included regenerators, gas-blowing tuyeres, and stoppers and nozzles to control the flow of molten metal.

(3) The development of the tar-dolomite brick made the Thomas (basic) converter viable, and silica brick made the Bessemer (acidic) converter and open-hearth furnace commercially operable.

(4) Various new techniques were developed in the fields of furnace construction, cooling of refractory lining, and heat insulation, and they were incorporated as the core constituents of refractory technology.

(5) Diatomaceous brick was developed (UK patent in 1893) as the first lining material specially designed for heat insulation.

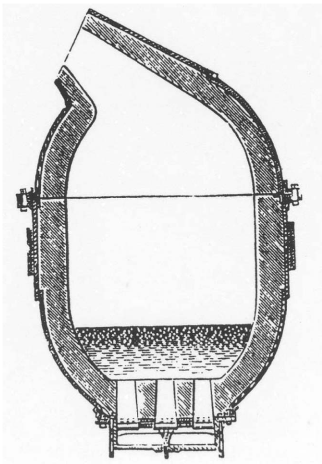

Fig. 4 Bottom-blown converter patented by Bessemer in 1860

2.3 Opening of Japan to international society

The Industrial Revolution in Japan, which began more than half a century later than in Europe when the country opened its doors to international society, showed rapid development during the decades from the end of the Shogunate Period to the beginning of the Meiji Era (1850s to 70s). The year 1851, when the first reverberatory furnace (a paddle furnace) in Japan was commissioned in the present Saga Prefecture, can be called Year One of Japan's modern refractory technology.

Thereafter, the country quickly absorbed various refractory technologies from abroad and incorporated them with traditional ones in a dramatically short period, to the amazement of Western society. Noteworthy events in this period are as follows:

(1) Traditional technologies unique to Japan such as furnace construction accumulated with the *tatara* furnaces and pottery manufacturing using climbing kilns (*noborigama* kilns), etc. were utilized effectively.

(2) Highly siliceous fireclay brick (*roseki* brick or pyrophyllite brick) developed independently in Japan remained as the principal material for ladle linings for a long period.

(3) Many outstanding technical leaders appeared and took the lead in catching-up and superceding the West, such as Tarozaemon Egawa (the reverberatory furnace at Nirayama), Takatoh Ohshima (the blast furnaces at Kamaishi based on western concepts),

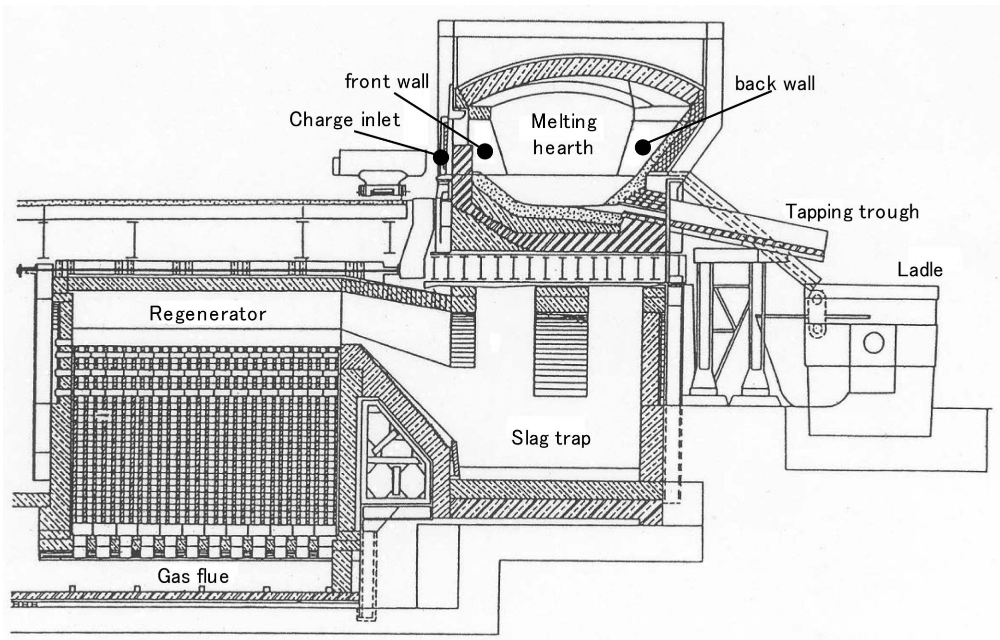

Fig. 3 Structural illustration of the stationary-type open hearth furnace in the 1960's

Saburo Utsunomiya (brick manufacturing), and Jintaro Takayama (refractory testing methods).

(4) The state-owned Yawata Steelworks inaugurated in 1901 became a virtual national center for the research, manufacture, and use of refractories for iron and steel production.

2.4 The 20th century up to the end of WWII

U.S. Steel was founded in 1901 as the world largest steelmaker, and Harbison Walker Refractories in 1902 as the world largest refractory manufacturer. These events clearly showed that the center of steel and refractory production was shifting across the Atlantic, and the U.S.A. was becoming the new world center in the new century. During that period, some Japanese technologies, typically the first development of chrome magnesia brick, etc., began to attract attention for their originality. While the two world wars forced the steel industries of developed countries to expand rapidly, the advance in steelmaking technology was rather slow in this period besides a few exceptions such as wider use of electric arc furnaces and vertical integration of rolling processes.

In the field of refractory, on the other hand, various technical advances such as the following were achieved during this period.

(1) Many types of new refractories including unshaped mixtures and non-oxide materials were developed (see **Table 2**).

(2) Refractories of various new materials were developed for use in other industries such as electro-fused cast brick for glass furnaces, silicon carbide brick for pottery-firing furnaces, and many of them were then transferred to the steel industry.

(3) Exploration and utilization of natural resources advanced in many countries. Typical examples in Japan that attracted attention include silica rock deposits at Tsukumi and Tamba, etc., and the magnesite deposit at Dashiqiao in Manchuria (now the northeastern region of China).

(4) Commercial use of synthetic raw materials such as seawater magnesia, fused alumina, and silicon carbide started.

(5) Testing methods for refractory materials were standardized, technical journals specialized in refractories appeared, industrial and academic associations related to refractories were organized in many countries, and thus, a field of technology centered on refractory engineering and covering other related fields gained public recognition.

Table 2 Chronological table for steelworks refractories (II) (the first half of the 20th century)

1901	Yawata Steelworks	
1910		SiC brick (US)
1913		Alumina cement (Frn)
		Unfired magnesia brick (US)
1914		Plastic refractories (US)
1917	Induction-heating furnace	
1920	Silica-bricked coke oven	
1924		Forsterite brick (Ger)
1925		Chrome-magnesia brick (Jpn)
1926		Fused-cast mullite brick (US)
1930	Basic-roofed OH furnace	
1931		“Sinter Korund” brick (Ger)
1932		Castable refractories (US)
1933	Renn-ironmaking process	Zircon brick (US)
1934	Basset-ironmaking process	Cr-Mag brick (UK, US, Ast)
1935		Stabilized dolomite brick (UK)
1936		Fused-cast alumina brick (US)
1938		Unfired Cr-Mag brick (Jpn)
1939	Steel-continuous casting pilot plant	
1940		Unfired Cr-Mag brick (US)
		Calcia crucible (US)

OH: open hearth

2.5 Period of technical innovations and rapid expansion after WWII

The most significant technical advance in most industries since the Industrial Revolution took place after WWII in the developed countries including the defeated ones, Japan and Germany. In the case of Japan, while most of the new technologies were introduced from the western countries, they were quickly and smoothly digested and improved as seen in the Meiji Period nearly a century before, and this was one of the main driving forces of Japan’s high-rate economic growth that lasted into the early 1970s.

The innovative technologies for principal steel production processes that became widely used during this period include high-pressure, high-blast-temperature blast furnaces, oxygen blowing into open-hearth and electric arc furnaces, oxygen top-blown converters, vacuum degassing, and continuous casting. All these were closely related to refractories, and their successful development and commercial operation depended largely on the development of new purpose-made refractory materials.

In the meantime, as the relationship between the material properties and performance of refractory in different service conditions gradually became clearer, methodologies for material design in consideration of service conditions and development of new materials were established. On the other hand, requirements related to refractories diversified as a consequence of the increase in the size of furnaces, need for laborsaving in furnace relining and repair, and longer furnace lining life for higher productivity.

What happened in Japan during this period can be summarized as follows.

(1) The overall unit consumption of refractories for steel production continued to decrease as shown below.

1950	127.0 kg/t-steel
1960	77.0
1970	29.1
1980	15.3

This dramatic decrease resulted mainly from the process changes such as the shift from open-hearth furnaces to basic oxygen converters and conversion from ingot making to continuous casting.

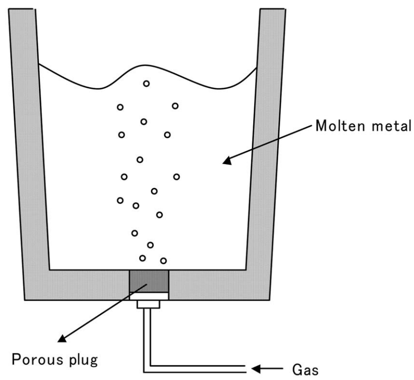

Fig. 5 Gas-bubbling into molten metal by a porous-plug

Table 3 Chronological table for steelworks refractories (III) (1945-1970, Japan)

1945	Only 3 BFs in operation out of 37	
1949	Oxygen applied to OHF (trials)	Seawater MgO (Ube Chem. Ind.)
1950		"Ritex" introduced (Shinagawa Ref.)
1951	Oxygen applied to EAF (Yawata)	Carbon block for BF bottom
1952	Test LD converter (NKK)	Zebra-type OHF roof US-made fireclay brick for BF Tar-bonded taphole mix for BF Stabilized dolomite brick (Kyuushu Ref.)
1955	Steel continuous-casting (Sumitomo Metal Ind.)	
1957	LD converter (Yawata)	Baked tar dolomite brick (Kurosaki Ref.) All basic roof- OHF
1960		Basic ladle lining (trials)
1961	Torpedo car (Wakayama) DH vacuum degassing (Yawata)	Hot gunning repair for OHF
1962	High pressure BF	Zircon brick for ladle-lining
1963	RH vacuum degassing (Hirohata) External combustion chamber for hot stove (NKK)	
1964	Large-sized coke oven	
1965		Direct-bonded Cr-Mag brick
1966		Slide-gate valve
1967	Stave-cooled BF (Wakayama)	Porous plug (hot metal de-sulfurizing)
1968	Russian-type stave (Nagoya)	Immersion nozzle (fused silica)
1969	UHP-EAF (Kobe Steel)	
1970		MgO-carbon brick (EAF) Immersion nozzle (CIP'ed alumina-graphite)

BF: blast furnace, OHF: open hearth furnace, EAF: electric arc furnace,
UHP-EAF: ultra high power electric arc furnace, CIP'ed: formed by cold isostatic pressing

(2) Use of purpose-made, highly functional refractory products became common practice. Typical examples of such products are porous plugs for secondary refining (see **Fig. 5**), slide-gate valves for steel ladles, and immersion pouring nozzles for continuous casting.
(3) The performance of refractories improved significantly. The most notable trends were those towards more basic qualities, higher purity and expanded use of carbon-added composite materials. The firing temperature in refractory manufacture rose. The development of new products such as dolomite bricks for converters and zircon bricks for molten steel ladles attracted attention internationally (see **Table 3**).
(4) Introduction of USSR-type staves for blast furnace cooling led to fundamental changes in the technology of refractories for blast furnaces.

2.6 After the oil crisis

The two-staged oil crisis in the 1970s had extremely serious effects on refractory technology, both directly and indirectly. In parallel, environmental problems in relation to substances such as hexavalent chromium and coal tar became serious issues. Accordingly, since the 1970s, resource-saving, energy conservation and environmental protection have been newly included in the evaluation criteria for refractory technology as well as in the field of steel technology.

Besides the above, refractory technology quickly responded to the new requirements from the steel production side for steel quality enhancement and higher added value in addition to those for cost reduction and higher productivity in consideration of the new energy-conscious business situation.

At the same time, refractory technology expanded: while it had been concerned mainly with refractory materials, attention shifted to different related aspects, and it became a comprehensive system of knowledge encompassing the fields of reline-repair methods (flame-gunning repairs, etc.), furnace lining design (heat insulation, cooling, etc.), monitoring and measurement (lining monitoring system, etc.), and furnace operation for lining protection (slag control, etc.).

In order to convey refractory-related technical information to the world, the Technical Association of Refractories, Japan, began to publish a technical periodical in English "The Taikabutsu (refractory) Overseas" in 1981, and hosted the First International Conference on Refractories in 1983 in Tokyo. Thus, it was considered that Japanese refractory technology had at last gained a position among the top tiers of the world, a long-cherished dream since the country opened itself to the outside world in the 1860s.

Noteworthy topics among the developments during this period, which are shown in **Fig. 6** and **Table 4**, are as follows.

(1) The lives of iron and steelmaking furnaces were extended, and their unit refractory consumption decreased. In fact, the campaign life of blast furnaces has been extended to 15 years or more, the lining life of most converters increased to between 2,000 and 7,000 heats, and the unit refractory consumption of electric arc furnaces decreased drastically thanks to the intensive water cool-

ing of roofs and walls. These achievements are regarded as historic.

(2) Use of unshaped refractories for the lining of ladles and other applications has become common practice as a result of the development of new materials, devices, and installation methods. The percentage of unshaped refractories in the total refractory

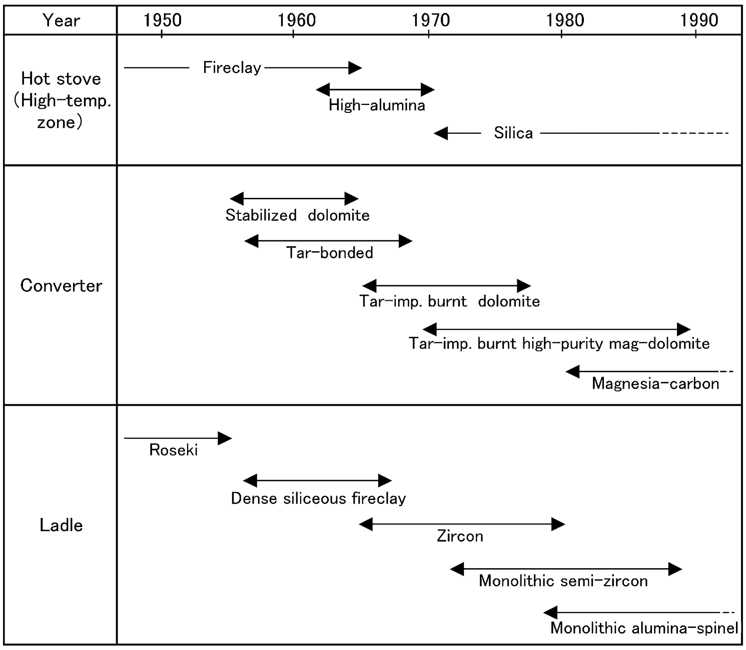

Fig. 6 Typical life-cycles of refractory qualities in the 20th century latter half

Table 4 Chronological table for steelworks refractories (IV) (1971-1994, Japan)

1971	De-sulfurizing inside torpedo (Sakai) LF process (Daido Steel)	Slinger process for relining ladles
1972	Entirely CC steelworks (Oita)	Slag control for converter lining
1974		Trial use of SiC brick (Muroran BF)
1975		Hexavalent Cr pollution (Cr-Mag brick waste) Strengthened regulations on coal tar application Converter lining life world record (10, 110 heats, Kimitsu)
1976	Coke dry quench process (Hirohata, Keihin)	
1977	Q-BOP (Kawasaki Steel) Japan’s last OHF gone (Tokyo Steel)	MgO-C converter brick (Oita) Cementless castable
1978		Nippon Steel flame-spray repair (coke oven) Nippon Steel cast-relining process (ladle)
1980	Top-bottom-blown converter Wider application of water-cooling to EAF	
1981	Big progress in BF lining-repair	Al_2O_3-SiC-C brick (torpedo)
1983		Alumina-spinel castable (ladle)
1985	EBT-type EAF (Topy Ind.)	Fourth-generation stave developed All ceramic-fiber lined RF (Kimitsu) Refractories imported from China
1988	DC-EAF (Topy Ind.)	
1989		Automatic bricklaying machine (converter)
1990		Lining-monitoring senser (ladle)
1992		Selfflowing-type castable
1993	DIOS pilot plant	Gigantic flame spray-gun (6t/h, Oita)

LF: ladle furnace, CC: continuous casting, BF: blast furnace, OHF: open hearth furnace, EAF: electric arc furnace, EBT: eccentric bottom tapping, RF: reheat furnace, DC-EAF: direct current-electric arc furnace, DIOS: direct iron ore smelting consumption of the Japanese steel industry rapidly increased as shown below.

1970 18.9%
1980 37.7%
1990 51.9%

(3) As a consequence of improvements in stave cooling systems and their wider application to the upper portions of blast furnaces, the hearth became the most critical portion as the furnace life-determining lining. High-durability carbon blocks were developed, and these became the standard lining quality for blast furnace hearths.
(4) Magnesia carbon brick for converters and other carbon-added composite materials were developed, and through expanded use in appreciation of their excellent performance, became one of the mainstay refractory materials.
(5) Japan became an exporter of refractories, mainly of highly functional products such as slide-gate valves. On the other hand, import of refractory products from China began in the mid-1980s.
(6) Recycling of waste refractories was studied and put into widespread practice. This expanded in terms of the kinds of material and quantity in response to increased demand to reduce the environmental load.

3. Principal Factors Affecting Historical Development of Refractory Technology

3.1 Changes and development of iron and steel production technology

Development of new materials is spurred overwhelmingly by the requirements of the user side (market), and this is true also with refractory for iron and steel production. When we consider the fact that the performance of refractory is especially sensitive to its service conditions, it is easy to understand that the change and development of iron and steel production technology has had the most significant influence on the advancement of refractory technology.

Here, “change and development” means not only the advent of a new production process but also other related factors such as a raise in furnace temperature, switching to a new heat source, shape modification or increased capacity of a furnace, and requirements for cost reduction.

There have been uncountable cases evidencing this, ranging from the development of clay-charcoal mixes for the lining of ancient iron-making furnaces to the wide variety of refractory materials that appeared since the Industrial Revolution, as well as the improvements currently being made and put into practice one after another.

In order for market requirements to spur technical development in an adequate and prompt manner, there must be a methodology established to some extent. Up to the middle of the 20th century, however, most technical development of refractory depended on repeated trial and error, and a methodology worthy of the name only came to be used as late as in the 1960s, when refractory application technology reached a certain maturity, as explained herein later, with the mechanisms of refractory wear and the effects of furnace operation conditions on refractory performance being clearer.

3.2 Problems of natural resources and energy

Shortage of raw material resources is fatal for highly consumable products such as refractories for steel production. Once when the unit consumption of refractory exceeded 50 kg/t-steel, refractory was regarded rather as an auxiliary raw material than a component of production equipment, and steel industries in many countries expended great effort to secure adequate supply of raw materials.

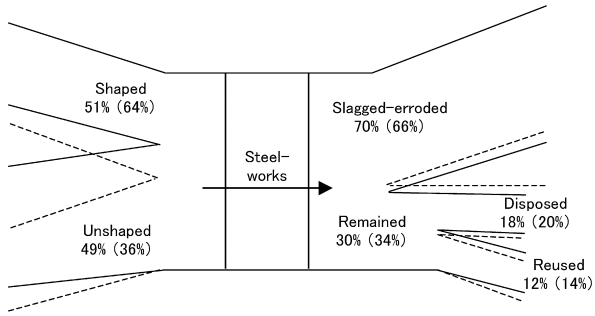

Fig. 7 Material balance of refractories at an integrated steelworks in 1981 (1974)

In its industrial development, Japan experienced much difficulty because of the scarcity in domestic natural resources, and for this reason, past technologies that allowed effective use or supply of resources such as the following were highly appreciated:

(i) Domestic natural materials such as *roseki* (pyrophyllite-based clay), quartzite, and dolomite;
(ii) Synthetic materials such as magnesia, alumina, mullite, spinel, and alumina cement;
(iii) Utilization of grog (chamotte) made from the clay-tailings of coal mines; and
(iv) Import of fireclays (from China and USA.), magnesia (from Dashiqiao, China), chrome ore (from the Philippines), zircon (from Australia), and graphite (from China).

Of the above, the use of *roseki* from domestic mines and the utilization of grog from coalmine waste constitute technologies unique to Japan for effective use of available resources.

Wear due to erosion or corrosion, etc. was once responsible for about 70% of the refractory consumption of the steel industry (see **Fig. 7**). While the ratio of the slag-eroded portion is gradually increasing, more efforts must be exerted to utilize the refractory remaining after use more effectively through reuse and recycling.

Since the beginning of iron production, the refractories for iron and steel production have consisted mainly of O, Si, Al, Ca, and Mg, etc., the so-called ubiquitous elements based on the Clarke Numbers (indices of element abundance in the earth’s surface). The abundance of raw material resources will become increasingly critical in the future.

From the viewpoint of energy, there are two different aspects to refractory: while it contributes to energy conservation, its manufacture requires a very large amount of energy. The energy-saving effects are due to its functions to extend the life of furnaces, make its operation stable and efficient, and insulate, preserve, regenerate, and exchange heat. On the other hand, the unit consumption of energy in refractory production, including that in raw material production, is often larger than that in steel production (about 5 million kcal/t-steel).

Nevertheless, it is understood that the total of the energy-saving effects of refractory in the whole iron and steel production system is far larger than the energy consumed in manufacturing the refractory. However, the fact that refractory is a “condensed mass of energy” makes recycling and reuse of waste refractory all the more important.

3.3 Principal environmental problems

Environmental problems related to refractories are divided into those of the environment inside work areas and environmental loads outside plants.

As has been pointed out in many countries since the early 20th century, a typical environmental problem in work areas is dust arising from refractory manufacturing, work for relining or repair, and dismantling after use. Dust that contains SiO_2 causes silicosis, and for this reason, has attracted special attention. Various protective measures against it were taken in Japan in the 1950s, and since then, there have been no serious problems in this relation. Later, in the 1970s, coal tar used mainly as binders and impregnating materials for bricks was included in the specified chemical substances under the Industrial Safety and Health Law, and various protective measures were taken.

Air pollution due to exhaust gasses from industrial furnaces became a major public nuisance, and refractory firing furnaces were listed as emission sources together with power plant boilers and other industrial furnaces. In the 1960s to 80s, emission regulations on soot were enacted, followed by those on SO_X and then NO_X, and respective countermeasures were taken. The problem related to NO_X was especially serious in the 1960s to 70s when the use of bricks fired at high temperatures (direct-bonded magnesia-chrome and high-purity magnesia-dolomite bricks, etc.) was at the peak, but it was eventually solved largely owing to a change in brick qualities.

A rare example of pollutants related to refractory production is fluorides in the exhaust gas from furnaces for firing clay-based refractories. In Japan, a case of grape leaf blight caused by the substance was reported in Okayama around 1970. A near-by brick plant firing chamotte and fireclay bricks was determined to be the origin. The fluorine was confirmed to come from mica-minerals in the raw material clay, and the introduction of several defluoridation processes solved the problem.

Problems caused by hexavalent chromium have not been eradicated yet despite intensive studies. The first case of this problem related to refractory that caught public attention occurred in central Japan some time around 1975: many trees died around a landfill site for used chrome-magnesia bricks from cement kilns. Countermeasures now being studied include use of Cr-free bricks such as magnesia-spinel brick and treatment to render the used bricks harmless.

3.4 Refractory production structure

It is understood that, during the period of charcoal ironmaking before the Industrial Revolution in Europe, the production, laying and dismantling of refractory linings were all done by the furnace operators inside the same plant as part of the iron production business. This was the same with the *tatara* furnaces of Japan and the ancient iron production in China.

Special machines for the ceramics industry such as crushers, mixers and forming presses were developed in the early 19th century, and were used for manufacture of clay building materials and chinaware. Production of refractories began to shift from furnace operators to ceramics-manufacturing specialists presumably at that time.

In contrast to fireclay bricks that had gradually evolved from ancient earthenware bricks, the silica brick was a new high-performance refractory product at its advent, and it was manufactured in specialist pottery plants. Judging from the above historical background, the argument of Western schools that the modern refractory industry started in 1856 when W. W. Young, the inventor of silica brick, began its production at Neath Pottery Factory is quite understandable.

The first specialist refractory manufacturer in Japan was Isekatsu White Brick Manufacturing (now Shinagawa Refractories), founded as a private company by Katsuzo Nishimura in 1884, which was then followed by the respective predecessors of the present Yotai Refractories and Nippon Crucible. Since then for about a century, there were two refractory supply routes for the Japanese steel industry: specialist private producers and the in-house manufacturing plants described earlier. The situation was similar also in Europe and North America up to the middle of the 20th century.

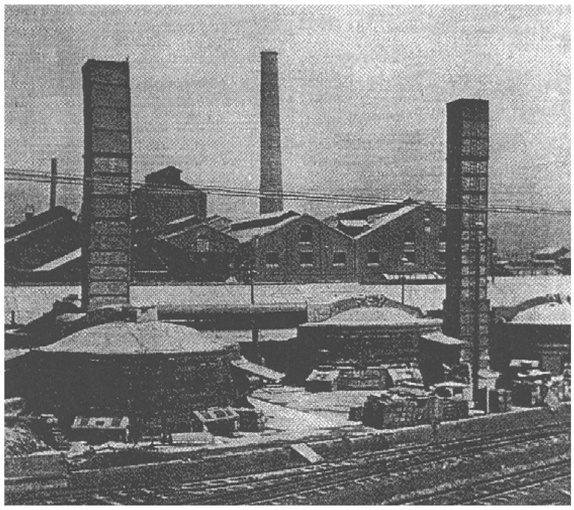

Fig. 8 Refractory plant of Yawata Steelworks in the 1930's

The refractory plant at Yawata Steelworks (shown in **Fig. 8**), which was responsible for about 30% of Japan's total refractory production in the 1930s, was transferred to Kurosaki Refractories (now Krosaki Harima Corporation) in 1956, and then, the refractory plant at Nippon Kokan (now JFE) to Shinagawa Refractories and Asahi Glass. In 1967, the last of the steelmaker's in-house refractory plants, that at the Muroran Works of Fuji Iron & Steel (now Nippon Steel) was transferred to Harima Refractories.

An evaluation of the pros and cons of the two refractory supply routes from the technical-historical point of view has not been completed. Whereas the in-house production allows easier intercommunication between the user and producer sides, the free-market mechanism works more effectively in the outside supply system, and more technical information from other industrial fields (glass, non-ferrous refining, cement, etc.) can be utilized. Now that refractory manufacturing and steel production belong to different fields of industry, how to maintain close intercommunication between the both sides is one of the most vital issues.

Needless to say, development of refractory manufacturing technology brought about immeasurable advantages to the steel industry. The development, especially, of equipment for crushing, mixing, firing and defect sensing since the middle of the last century, the details of which it is impossible to enter into herein, had a remarkably positive effect on improving refractory quality. For example, various types of high-performance, high-functionality refractory products, which are indispensable for the latest steelmaking and casting processes, such as slide-gate valves, could not have come into being without the development of the cold isostatic press (CIP) forming technology.

3.5 Clarification of refractory wear mechanisms and the influence of service conditions

Refractory technology has advanced through research and development employing widely varied methodologies from fundamental approaches based on phase diagrams through measurement and evaluation of material properties and structures to comparative trial tests in commercial furnaces.

Of those innumerable historical events, clarification of refractory wear mechanisms in real furnaces and investigation of the effects of service or operational conditions are of special importance in terms of the significance and contribution to refractory application technology.

The water model method and other simulative testing methods were employed to research refractory wear mechanisms, but the most effective and widely used of them was deterioration examination of refractories after use. The first report of this kind was by Le Chatelier in 1917 investigating used silica bricks from an open-hearth furnace roof.[13] After that, many researchers in various countries conducted similar studies, and from the 1950s to 70s, the range of examination objects expanded from the refractories of blast furnaces, coke ovens and various steelmaking furnaces to nozzles for casting (on clogging, etc.).

The findings obtained through these studies on wear mechanisms contributed remarkably to the improvement in refractory quality and development of new products, and some of them led to improved furnace operation practice at steelworks. The clarification of refractory wear mechanisms also led to the development of various refractory testing methods, which include the alkali resistance test for blast furnace bricks and the slagging-under-load test designed for basic bricks for steelmaking furnaces.

The examination of used refractories, which was once called "post-mortem examination (Chesters, J. H., 1957)" after the medical anatomy of cadavers, is a classic investigation method now, and will remain as an effective tool when combined with rapidly advancing analysis technologies.

The effects of operational conditions on the performance of refractories have been known empirically, if not systematically, through field experience in many steelworks since the 19th century. However, it was as late as in the 1950s that the data were statistically and methodologically sorted out and publicized. For example, the relationship between the life of fireclay brick lining for ladles and the conditions of molten steel (temperature, [Mn]/[Si] ratio, etc.), when numerically clarified, offered important guiding principles. The investigation result of the effects of operational conditions on the life of dolomite lining for converters in the 1960s (see **Table 5** for a summary)[14] clearly shows the advantages of slag control for enriching MgO, a novel technology in that period.

Bearing in mind possible future development of the monitoring technology for operational and lining conditions, information technology for data processing and formulation of new fundamental theories, the above investigation methods are expected to develop yet further.

Table 5 Effects of operatioal conditions on converter lining life in the 1960's

Operational factors	Effects on life	Degree of influence
Hot metal		
[Si]	−	B
[Mn]	+	C
[Ti]	−	C
Slag		
Total Fe content	−	A
Basicity (CaO/SiO_2)	+	B
CaF_2 addition	−	B
MgO content	+	A
Al_2O_3 content	−	C
Lime addition	+	B
Blowing		
End point temperature	−	A
Blowing duration	−	B
Production rate (heats/day)	+	B
Slag volume	−	C
Atmosphere (CO/CO_2)	+	B
Delay in charging lime	−	B
Converter design		
Vessel volume	+	C
Cone angle	+	C
Blow lance	Longer life with multi-holed lance than single-holed	

Notes: Mark "+" means longer life and "–" shorter with increased factor value. Mark "A" shows the highest, "B" medium and "C" lower degree of influence on lining life.

3.6 Notable special background factors contributing to development of new technologies

Formulation of an assumption based on a theory and its verification through experiments is a well-known standard method for the development of a new technology; this is true also with refractory technology.

For instance, the chrome-magnesia brick that was developed by K. Kato of the Refractory Section at Yawata Steelworks in the 1930s originated from an idea to turn low-melting-temperature silicates in chrome ore into higher melting-point minerals by addition of magnesia; the idea was a theoretically conservative one. Many other new refractory products have been developed through such theoretical approaches. On the other hand, however, many revolutionary technologies emerged out of very special backgrounds or were triggered by unorthodox events.

Some interesting and special situations that triggered development of new technologies found through investigation of past events are introduced below.[15]

(1) Mere curiosity: Direct-bonded chrome-magnesia brick

In the 1950s, J. Laming et al. of Sheffield University were not specially interested in the traditional empirical rule to the effect that the firing temperature during manufacture of refractory brick should be higher than the temperature at which it is used in a furnace, but one day they tried to fire bricks at as high a temperature as possible without caring about the durability of their test furnace, and fired chrome-magnesia bricks at 1760℃ to discover the formation of direct-bonded microstructures. The direct-bonded chrome-magnesia brick was launched on the market in 1961.

(2) Urgent need in wartime: Plastic refractories and stabilized dolomite bricks

Many cargo ships were needed for transatlantic transport in WWI, but bricks for ship boilers were in short supply. W. A. L. Schaefer worked out a mixture of fine refractory powder for emergency application, plastic or moldable refractories that did not require forming and firing for manufacturing. Plibrico Co., which marketed plastic refractories, was established in 1914.

During WWII, the supply of chrome ore to the UK was halted by the naval blockade by German U-boats, and a substitute for chrome-magnesia brick, one of the essential refractory materials for steelmaking, was sought. The fundamental technology for producing stabilized dolomite bricks as the substitute quality had already been developed in 1935, but some difficulties hindered its commercial production. The UK Government's supreme command made it possible to meet the urgent demand for its production in quantities.

(3) Borrowing of alien technologies: Tar-dolomite bricks, and slide-gate valves

Manufacture of bricks from calcined dolomite powder requires a hydrophobic binder to avoid hydration. In the second half of the 19th century, coal tar was used to waterproof building materials, etc. In consideration of this, G. Thomas invented tar-dolomite bricks for converter use in 1879.

Slide-gate valves were commonly used for pipe organs in many churches and steam engines. In 1884, D. D. Lewis applied its structure to a valve made of refractory materials and was issued the first patent for a slide-gate valve for metal casting. It wasn't, however, until the 1960s that the patented valve was actually used industrially.

(4) Tough salesmanship to expand sales: Porous plugs, and slag splashing

E. Spire originated the idea of using a porous plug to stir molten metal by gas blowing, and the Steel Research Institute of France (IRSID) planned its development. The idea attracted the attention of L'Air Liquide, then making every effort to expand the sales of its gas products (especially Ar and N_2), and the company actively promoted the plan to successfully commercialize it in 1955 as the GAZAL Process for desulfurizing molten pig iron.

Slag splashing is widely practiced today as an effective measure to extend converter life. It was developed by a US gas supplier, Praxair Co., in cooperation with an American steelmaker (US patent granted in 1983). The technology resulted, to a considerable extent, from their active sales efforts.

(5) Serendipity (the aptitude for making desirable discoveries by accident, or not to overlook a hint possibly leading to an invention): Electro-fused cast mullite bricks

H. Hood, a researcher at Corning Glass Works, was studying stones (or sand grains, particulates of insoluble inclusions in glass), and focused attention on a kind of stubborn glass-insoluble inclusion that had been observed frequently, and identified it as mullite crystals. An idea occurred to him that this substance would make refractory materials highly resistant to molten glass. Together with G. S. Fulcher, a friend of his, Hood looked for a method to use it for the inner lining of glass-melting furnaces, and in the mid-1920s, invented electro-fused cast bricks and commercialized them under the trade name of "Corhart". Later, electro-fused cast bricks found a big market also in the steel industry.

4. What We Should Learn from History

One can draw boundless lessons from history. Some instructive suggestions of special importance for the future technical development of refractories for steel production are listed below. Note that the selection of issues and the comments are purely the author's personal ones.

(1) History repeats itself, if only sometimes. It is desirable that refractory scientists and engineers be so modest as to look back to past history every now and then. It is interesting to note that the latest trend is towards the increased use of unshaped and carbon-added composite materials, like the typical features of the refractories for ancient iron-making furnaces. Development often follows a spiral route.

(2) A big leap is accomplished only through tackling difficult problems. Dodging a difficult problem does not result in any progress. The problems in relation to natural resources, energy sources and the environment may induce many significant breakthroughs.

(3) Let us keep our antennae well tuned to catch information from other fields of science, technology and industry. Technology is advancing at increasing speed, and now, intercommunication with different fields of activity is more important than ever.

(4) In every field of technology there are always fundamental problems that need to be pursued, however inconspicuous they may be. In the field of refractory technology for steel production, the interaction between molten metal and refractory is one such issue.

(5) Refractories for steel production are especially sensitive to service conditions, and the correlation between them is particularly varied and complicated. Such being the case, close communication and cooperation between the technical fields of refractory application and manufacture are essential. In this relation, more importance should be attached to an "interpreter" function that links these two fields.

5. Closing

The technology of refractories for iron and steel production, which has developed since the beginning of ironmaking in the ancient days, saw remarkable progress during the periods of the Industrial Revolution and the decades after WWII. As a result, the types and shapes of refractory products diversified, and refractory technology itself, which once dealt only with material properties, grew into a comprehensive system covering technologies even for cooling, heat insulation and slag control.

History clearly shows that, of many factors that exert influence over refractory technology, the change in the iron and steel production processes has had the most significant influence. We look forward to seeing the development of refractory technology in response to changes in steel technology and triggering its innovations in the future.

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