NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 109 JULY 2015

Technical Report

UDC 666 . 943 . 2

History and Utilization of Portland Blast Furnace Slag Cement

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Abstract

In Japan, production of Portland blast furnace slag cement (PBFSC) was started and 100 years passed. During this period, utilization of PBFSC was promoted as measures saving resource and energy, in late years as CO_2 reduction and has been used mainly in civil structure until now. There is the structure using PBFSC which passed more than 80 years and is used even now. And it is an important problem to apply to future spread promotion to evaluate long-term stability of PBFSC quantitatively. This study reports on the property of concrete used several types of PBFSC and cured for 45 years in water. As a result, the compressive strength improved and pore size distribution shifted to small pores diameter by slag replacement ratio increasing.

1. Introduction

The history of cement production in Japan dates back to 1873 when the cement plant of public works bureau of the Ministry of Finance was founded. There, the production of Portland cement was started. Until then, the country had been completely dependent on imports for the supply of cement; therefore, concrete was very expensive. Under that condition, the movement to domestically manufacture cement accelerated gradually. In 1901, the government-managed Yawata Steelworks—Asia's first integrated iron and steel works—was put into operation. In 1910, with the aim of effectively utilizing slag, which is a by-product of steel industry, test production of Portland blast furnace slag cement (PBFSC) employing the advanced technology introduced from Germany was performed for the first time in Japan. In the past 100 years, a cumulative total of 500 million tons of PBFSC has been used in many different structures, mainly in the field of civil engineering. In recent years, increasing attention is being paid to the application of PBFSC to save resources and energy or curb global warming. At present, PBFSC accounts for nearly one-fourth of the domestic sales of all types of cement. In this report, the author shall review the history of PBFSC and describe the effective utilization and properties thereof.

2. Portland Blast Furnace Slag Cement—Its Specifications and Effect to Reduce CO_2 Emissions

PBFSC is a kind of blended cement. It is a mixture of Portland cement and ground granulated slag obtained during the production of pig iron using a blast furnace. **Table 1** shows the JIS specifications of blended cements. Granulated blast furnace slag is similar to the chemical composition of Portland cement. The slag has a latent hydraulic property; it begins to hydrate and harden when it is stimulated by alkali from cement. Therefore, compared with other kinds of blended cements, PBFSC allows for a larger proportion of admixture to be added, making its use advantageous.

Table 1 JIS specification of blended cement

	Class	Amont of admixture (%)	Quality of admixture
Portland blast furnace slag cement (JIS R 5211)	A	Over 5, less than 30	$(CaO+Al_2O_3+MgO)/SiO_2$ is more than 1.6.
	B	Over 30, less than 60	
	C	Over 60, less than 70	
Portland silica cement (JIS R 5212)	A	Over 5, less than 10	$SiO_2 \geqq 60\%$
	B	Over 10, less than 20	
	C	Over 20, less than 30	
Portland fly ash cement (JIS R 5213)	A	Over 5, less than 10	Fly ash type I or type II according to JIS A 6201
	B	Over 10, less than 20	
	C	Over 20, less than 30	

In the Portland cement manufacturing process, limestone—the principal raw material—is burned at 1450°C. Therefore, as shown in **Table 2**,[1)] the process emits about 800 kg of CO_2 per ton of cement from the decarboxylation of limestone and the burning of fuel. Today, the PBFSC sold in Japan is mostly of type B and the proportion of blast furnace slag is 40%–45%. Thus, PBFSC is an eco-friendly type of cement that emits about 40% less CO_2 than Portland

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Table 2 CO_2 emissions (kg) per ton of cement

CO_2 emissions	Portland cement CO_2 emissions ①	PBFSC Class B CO_2 emissions ②	CO_2 emissions ① - ②	CO_2 reduction (%)
Limestone	468	268	200	43
energy	296	176	120	41
total	764	444	320	42

cement in the manufacturing process. Since 2001, it has been among the procurement items specified by the Green Purchasing Law.

3. History of Portland Blast Furnace Slag Cement [2, 3]

3.1 Birth of portland blast furnace slag cement

As mentioned earlier, PBFSC was developed in 1910—nine years after the government-managed Yawata Works was put into operation. It is Taizo Kuroda who gave the Japanese name "kouro semento" to PBFSC in English and Hochofen zement in German. Born in Sakai City in 1883, he joined Yawata Works after graduation from the Department of Applied Chemistry of the Imperial University of Tokyo (present University of Tokyo).

Kuroda's achievements in diverse fields were brilliant—PBFSC, coke, refractories, and coal chemistry. In Japan, he was among the originators and pioneers in those disciplines. Among others, the Kuroda-type coke oven developed by him was constructed at home and abroad in those days. For some time, he taught at the Imperial University of Kyushu (present Kyushu University) and the Imperial University of Tokyo. After that, he played an active role in various related business circles. (For example, he was once president of Yogyo-Kyokai (present Ceramic Society of Japan)). In 1910, Kuroda began studying PBFSC based on the knowledge of Kyutaro Miyoshi, his superior, who had learned the most advanced cement technology in Germany. His study record is still available as "Test Report on Slags: Vol. 1." It contains descriptions of his experiments on a trial-and-error basis, such as adding slaked lime or quicklime to granulated blast furnace slag and substituting it for cement. The Nippon Steel & Sumitomo Metal Group regards the year 1910 as the year wherein PBFSC was born in Japan.

In 1913, after many turns and twists, the first cement mill was installed in the Maeda district of Yawata Works and PBFSC production commenced on a full scale. At that time, the PBFSC was produced by intergrinding of Portland cement clinker purchased from Asano Cement Moji Plant, granulated blast furnace slag, and gypsum. At first, the production of PBFSC was about 20 barrels (3.4 t @170 kg) a day, which was steadily increased to 70–130 barrels (by installation of an additional mill) and then to 200 barrels. Reportedly, PBFSC produced in those days was sold partly to outside users. However, it was mostly used in works executed for Yawata Works.

In 1918, Yawata Works constructed a cement kiln and started production of clinker composed mainly of granulated blast furnace slag and limestone for itself. Using the clinker it produced, the Works began manufacturing PBFSC by applying the intergrinding method to a mixture of the clinker, granulated blast furnace slag, and gypsum. In those days, the slag replacement ratio of PBFSC was 60%–70%, which is equivalent to that of PBFSC type C of today. As a structure that was constructed in the 1920s and that still exists today, Yofukuji Dam can be cited (**Photo 1** shows the dam under construction). The results of our analysis of the dam are outlined below.

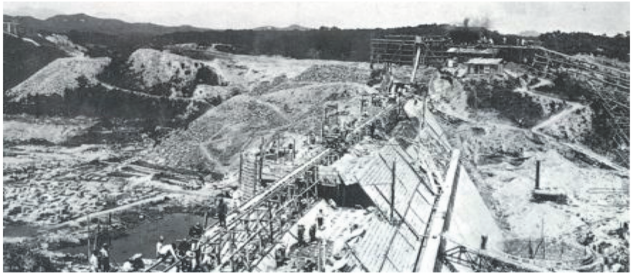


Photo 1 Yofuku-ji Dam under construction

Table 3 Estimating mix proportion of concrete

	W/C (%)	Unit weight (kg/m^3) W	C	S+G	Mass per unit volume (kg/m^3)
C-1	55.0	143	260	2075	2470
C-2	50.2	112	223	2138	2462
C-3	47.3	122	258	2077	2446
Average	50.8	126	247	2097	2459

W: Water, C: Cement, S: Sand, G: Gravel

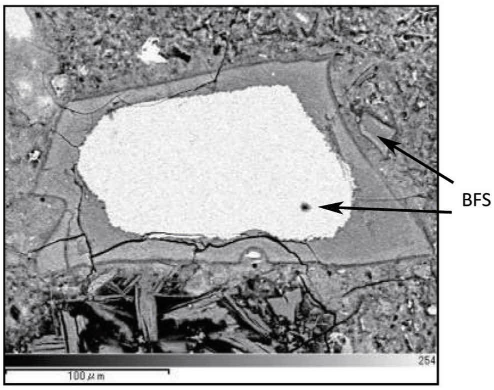
Construction of the Yofukuji Reservoir Dam was started in 1918 and completed in October 1927. It is a concrete structure which has been in service for over 80 years. According to a report at that time, it was in 1918 that the production of clinker was started at the Maeda cement plant. Then, it is considered that a cement equivalent to PBFSC type C made from that clinker was used for the dam. Reportedly, a "concrete containing stone" was used. However, as data about the mix proportion of the concrete was absent, we examined samples of the concrete in accordance with the "F-18 Method of Estimating the mix proportion of Hardened Concrete" (Japan Cement Association). Consequently, it was confirmed that the water cement ratio of the concrete was around 50% as shown in **Table 3**. It is close to that of the exterior concrete of present-day dams. In addition, the mass per unit volume of the concrete is relatively large (2400 kg/m^3). Thus, it is presumed that even today the dam body is sufficiently stable.

Figure 1 shows the results of an observation of the cement particles on backscattered electron image (BEI) of thin pieces of ground core. On BEI, the unhydrated slag and clinker appear whitish on the dark background because they are relatively heavy. From the figure, slag particles were found to be about 20 μm or 200 μm or more in size. The particles about 20 μm in size had been hydrated almost completely, whereas the particles exceeding 200 μm in size were partly unhydrated. Furthermore, clinker particles had an unhydrated phase about tens of μm in size, and belite (spherical crystals) and interstitial phases were observed. The average particle size of cement used today is approximately 15 μm and particles as large as that are seldom observed. In recent years, in particular, there is a tendency that PBFSC with a larger specific surface area is used to secure higher early strength. It is presumed that PBFSC from 80 years ago contained larger particles and had lower early strength than the present-day counterpart. However, considering that the Yofukuji Reservoir Dam is still used as a stable concrete structure, it is thought to be a valuable industrial heritage that suggests the way the future PBFSC should be.

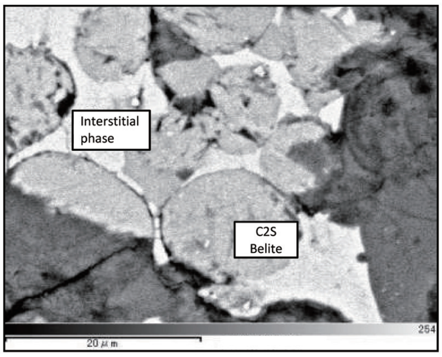
3.2 Promoting spread of portland blast furnace slag cement

When Japan plunged into the Pacific War, cement makers were specified as among the munitions companies. As the shortage of commodities continued during the war, the production of cement decreased both in quality and in quantity. As PBFSC is added with blast furnace slag, manufacturing it requires a smaller proportion of clinker than that the ordinary cement does. During the war, therefore, the ratio of PBFSC produced sharply increased. In addition, in order to compensate for the shortage of cement, "Portland pozzuolanic cement" and "lime slag cement," which are made mainly of blast furnace slag and which contain very little clinker, were included in the JIS. It was in 1960 that the three types of PBFSC—A, B, and C—were standardized. At that time, Type B PBFSC was generally referred to as PBFSC. PBFSC became widespread in the 1980s. The boom originated in the so-called oil crisis that broke out twice in the 1970s. In those days, many cement plants were burning their clinker using heavy oil as the fuel. The oil crises, however, made them pay attention to using PBFSC, which significantly helps save energy. As a result, many cement plants, mainly those in West Japan, started manufacturing PBFSC.

Another event that helped promote the spread of PBFSC was the TV program "Concrete Crisis" broadcast by NHK in 1983. It dealt with the early deterioration of concrete caused by the alkali-silica reaction and salt damage. Triggered by that program, the research institute under the Ministry of Construction began to study the matter. Consequently, it was confirmed that blast furnace slag, fly ash, and certain other admixtures were effective to restrain the alkali-silica reaction. As the finding was reflected in the Ministry's notification, blast furnace slag became widespread in the Chugoku and Kansai areas. The spread of PBFSC is also attributable to global environmental problems. Under the so-called Green Purchasing Law mentioned earlier, PBFSC was designated as one of specific procurement items. Hence, PBFSC began to be positively used across various parts of the country. Thus, the share of PBFSC expanded in East Japan including not only the Chubu and Kanto areas but also the Hokuriku and Tohoku areas where PBFSC had seldom been used.



(a) Blast furnace slag (BFS)



(b) Cement clinker

Fig. 1 Microstructure of concrete by BEI

4. Longterm Development of Strength of Portland Blast Furnace Slag Cement [4)]

About 100 years have passed since the test production of PBFSC was started in Japan. To promote the utilization of PBFSC in the future, it is an important point to understand its durability and physical properties from a longterm standpoint. Described below are the results of a longterm study of the physical properties of various types of PBFSC concrete that have been cured underwater ever since 1964.

4.1 Materials used

The cements used are these five types manufactured in 1963–1964: normal Portland cement (N); PBFSC type A (BA: blast furnace slag ratio 20%); PBFSC type B (BB: slag ratio 50%); low-heat PBFSC (LBB: slag ratio 50%); and PBFSC type C (BC: slag ratio 65%). According to a record, the cement clinker was manufactured using a wet kiln and the PBFSC was manufactured using the separate grinding method used by ball mills. **Table 4** shows the chemical compositions and physical properties of the cements used. The cement physical tests were performed in accordance with JIS R 5201-1964 and the strength tests were performed using Toyoura standard sand.

4.2 Concrete mixing and test method

Table 5 shows the mix proportion of concrete. Sea sand was used for fine aggregates (density in saturated surface-dry condition: 2.56 g/cm^3, fineness modulus (F.M): 2.76), and gravel was used for coarse aggregates (density in saturated surface-dry condition: 2.64 g/cm, F.M: 6.68). In the past, chemical admixtures were not as popular as they are today. Therefore, plain concrete without admixtures

Table 4 Chemical compositons and pysical properties of cement

Sample code	Chemical compositions (%)						Density	Blaine	Compressive strength (N/mm^2)		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	(g/cm^3)	(cm^2/g)	3d	7d	28d
N	22.52	4.92	3.26	64.74	1.50	1.85	3.18	3080	11.4	19.6	41.1
BA	22.60	7.90	2.50	59.40	2.60	1.90	3.11	3930	9.9	21.0	42.8
BB	27.26	11.29	2.09	52.53	2.76	1.63	3.01	3940	8.3	14.7	37.4
LBB	26.24	10.83	2.51	52.94	3.42	2.18	3.02	3480	6.3	12.7	31.7
BC	27.32	15.00	1.46	48.00	4.60	2.16	2.98	3940	8.2	17.3	38.7

d: days

Table 5 Mix proportion of concrete

Sample code	Room temp. (˚C)	Concrete temp. (˚C)	Gmax (mm)	Slump (cm)	W/C (%)	s/a (%)	Unit weight (kg/m³) W	C	S	G	AE agent (C×%)
N	13.0	12.0	20	19±0.5	63.0	42	189	300	753	1074	–
N-A		12.0			58.3		175	300	737	1048	0.04
BA	10.5	10.5			63.0		189	300	753	1074	–
BB	18.0	17.0			65.0		194	300	750	1067	–
LBB	11.0	10.0			64.0		192	300	750	1069	
LBB-A		10.0			59.3		178	300	732	1045	0.04
BC	11.0	9.0			63.0		189	300	753	1074	–
BC-A		9.0			58.3		175	300	737	1048	0.04

Gmax: Maximum size of gravel s/a: sand/aggregate AE : Air entraining

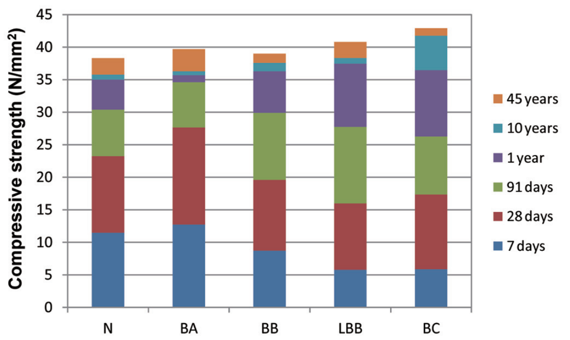


Fig. 2 Compressive strength of plain concrete

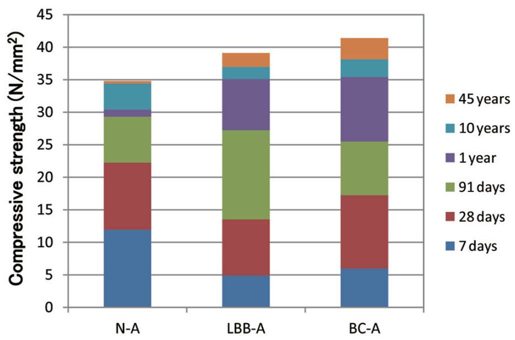


Fig. 3 Compressive strength of AE concrete

was the mainstream. However, AE concrete—a concrete that is added only with an air entraining (AE) agent and which reduces the unit weight of water—was also studied. In Table 5, the sample code suffixed with -A indicates AE concrete. The unit weight of cement and the sand aggregate ratio (s/a) were made the same for all the samples. The unit weight of water was varied to obtain the target slump value. First, the specimen was molded in the cylinders of 15 × 30 cm² and was demolded one day later. Then, it was cured to the prescribed age in an outdoor water curing tank installed in Kita-Kyushu City. The cured samples were subjected to a concrete compressive strength test in accordance with JIS A 1108 and a measurement of dynamic elasticity modulus in accordance with JIS A 1127.

4.3 Test results

Figure 2 shows the results of the compressive strength test of plain concrete. After the demolding, each concrete specimen was subjected to water curing outdoors. Therefore, the 7 days strength of BB, LBB, and BC, which began to be cured in winter, did not reach 10 N/mm², and the early strength of concrete decreased as the proportion of slag was increased. From a comparison among the type of cement, it was confirmed that with the increase in slag ratio, the increase in longterm strength of concrete, 91 days or more, became conspicuous.

Figure 3 shows the development of strength of concrete added with an AE agent. With the 91 days concrete strength as 100%, the 45-year concrete strength is about 120% for N, about 140% for LBB, and about 160% for BC. Thus, the results obtained were similar to those obtained with the plain concretes. Thus, it was confirmed that the increase in longterm strength of PBFSC concrete is according to the blast furnace slag ratio, regardless of the presence or absence of AE agent.

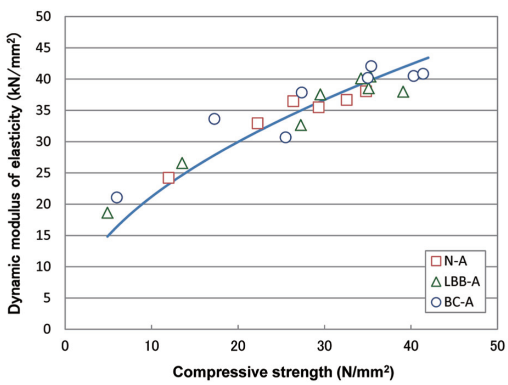


Fig. 4 Relationship between dynamic modulus of elasticity and compressive strength

Figure 4 shows the relation between compressive strength and dynamic elasticity modulus of AE concrete up to 45 years. With the increase in compressive strength, the dynamic elasticity modulus increased at the same time. Thus, their relation could be approximated by a single recurrence formula. It is considered that the dynamic elasticity modulus is not influenced by the presence or absence of slag and can obtain a stable concrete structure over a long period of time.

Figure 5 shows the pore size distribution of a piece of mortar collected from the center of a 45-year-old concrete. It was confirmed that with the increase in blast furnace slag ratio, the proportion of 6–20 nm pores increased, whereas that of 20–1 000 nm decreased. Although PBFSC shows row early strength compared with normal

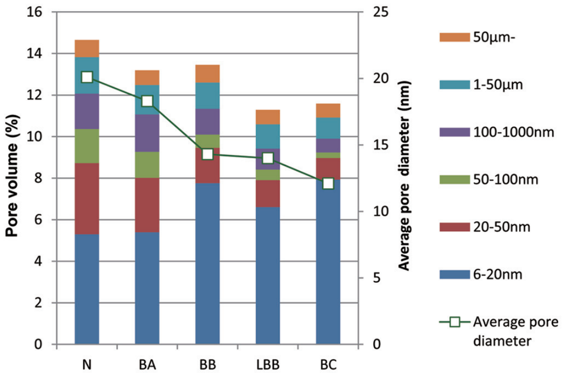


Fig. 5 Pore size distribution

Portland cement (N), it became a dense, stable concrete in the long run when it is subjected to sufficient moisture curing. The effectiveness of adding blast furnace slag to concrete could be verified by the above test.

5. PBFSC—Future Assignments

According to the Cement Technology Roadmap[5] of the International Energy Agency (IEA), it is estimated that world production of cement will continue to increase, mainly in the developing countries, from about 2500 million tons in 2006 to about 3700 to 4400 million tons in 2050. Based on the above estimate, the CO_2 emission from cement production that was estimated to be 1880 million tons in 2006 will increase to a maximum of some 2300 million tons by 2050. Under that condition, it is of urgent necessity to develop and spread new technology for reducing CO_2 emissions. The new technologies that are currently being developed include: recovering CO_2 and storing it under the ground (CCS: Carbon dioxide capture and storage) and lowering the cement burning temperature by adding a mineralizer in the clinker manufacturing process. Putting these technologies into practical use requires additional investment in plant and equipment.

Conversely, PBFSC allows for the reduction of CO_2 to nearly equal in volume to the blast furnace slag and can be produced by using the existing equipment. In addition, as mentioned earlier, JIS permits adding many admixtures to the PBFSC as compared with other types of blended cement. Therefore, the unit volume of CO_2 reduction by PBFSC is large. The use of blended cement has become popular around the world. According to Holcim, Ltd.,[6] one of the major cement producers, its production of blended cement in the world accounted for 39% in 1995 and 75% in 2009, thereby cutting CO_2 emissions by 20% as compared with the 1990 figure. Conversely, the company's production of Portland cement remained at 20% in 2009. Accordingly, there is much room for a rapid spread of PBFSC in Japan. In this context, it will become necessary in the future to establish technical standards for PBFSC and give publicity to it, especially in the field of architecture wherein PBFSC has been seldom used.

6. Conclusion

Today, the terms "recycling" and "creating a recycling-based society" are commonly used in various fields. In this connection, it is interesting to note that the PBFSC was developed some 100 years ago with attention paid to effective utilization of a by-product (i.e., slag) of steel industry. Although PBFSC has a modest early strength, its longterm strength improves significantly if it is sufficiently cured. In fact, there are PBFSC concrete structures that are 80 years old or older and are still in service. Now that careful consideration for the environment is strongly called for, it is very meaningful to promote the utilization of PBFSC, which helps reduce the emissions of CO_2 and prolong the life of concrete structures. By changing the blast furnace slag ratio and/or fineness appropriately, it is possible to manufacture cements suitable for specific uses or purposes. It is hoped that the use of PBFSC will be further promoted in the future.

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