New Applications for Iron and Steelmaking Slag

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Iron and steelmaking slag is a by-product of the iron and steelmaking process. Slag has traditionally been used as a component of cement and construction aggregate. NKK has led the industry in promoting the effective use of slag. In this paper, fine concrete aggregate, known as Sandy-S, and slag sand-capping material are introduced as new applications of granulated blast furnace slag. Other innovative uses of steelmaking slag are introduced: large carbonated slag blocks, called Marine Blocks, produced by injecting carbon dioxide into slag compact, and potassium silicate fertilizer produced by adding a potassium source to steelmaking slag.

1. Introduction

Iron and steelmaking slag is classified as BF (Blast Furnace) slag or steelmaking slag. BF slag is generated during the process of reducing iron ore by coke in a blast furnace. Its sources are the gangue content of iron ore, that is, constituents of iron ore other than iron, and lime content added to adjust the composition of molten slag. Most BF slag has traditionally been used as a component of cement. Steelmaking slag is generated in the process of refining hot metal produced by a blast furnace into steel, and has been mostly used as road material.

NKK has been actively promoting R&D aimed at creating new slag-based products that meet the needs of society by utilizing the useful constituents of BF and steelmaking slags. The world-leading new steelmaking technology developed by NKK, ZSP (Zero Slag Process)[1], is particularly significant in this regard. This technology lowers the amount of slag generated from the steelmaking process to a very low level, and also stabilizes the composition of slag generated through hot metal pre-treatment, thereby expanding the range of slag applications. The slow-release potassium silicate fertilizer, to be introduced later in this paper, is a typical example.

2. Granulated BF slag sand: Sandy-S

2.1 Fine concrete aggregate

Availability of natural sand, once believed to be inexhaustible, is decreasing year by year. Excavating beach sand has already been prohibited in parts of the Inland Sea area of Japan. In addition, the durability of concrete structures has become a serious social problem illustrated by the railroad tunnel collapse on the New Sanyo Line. Hence, the social demand for high-quality fine concrete aggregate has strengthened.

NKK and its group companies have developed a new technology for producing fine concrete aggregate from granulated BF slag. Molten BF slag is tapped from a blast furnace at a temperature of around 1500℃. It is then quickly cooled by applying pressurized water. The granulated BF slag produced is then lightly crushed to produce particles of a uniform size and shape. A consolidation inhibitor is added resulting in fine concrete aggregate. This product is marketed as granulated BF slag sand or Sandy-S.

2.2 Features of Sandy-S

In contrast to natural sand, Sandy-S is an industrial product produced under strict quality control, and has the following features:

(1) It is compatible with the JIS standard (JIS A 5011-1, Slag-based concrete aggregate).
(2) It does not contain substances that have harmful effects on the strength and durability of concrete such as chlorides, organic impurities, clay, and seashell. It also does not cause an alkaline aggregate reaction.
(3) Sandy-S, 7 to 28 days after concrete mortar is applied, has a compressive strength equivalent to natural sand. This strength continues to increase over time.
(4) Consolidation is effectively prevented due to the addition of a unique consolidation inhibitor[2)-4)].

The chemical composition and typical mechanical properties of Sandy-S are shown in **Table 1**.

Table 1 Quality of fine concrete aggregate

	Chemical compositions (mass%)			
	CaO	S	SO_3	FeO
Sandy-S	43.1	1.03	0.04	0.27
JIS A 5011-1	45.0≧	2.0≧	0.5≧	3.0≧

	Specific gravity	Coefficient of water absorption (%)	Mass of unit volume (kg/l)
Sandy-S	2.76	0.45	1.57
JIS A 5011-11	2.5≦	1.28≧	1.45≦

3. BF slag sand-capping material

3.1 Outline of sand-capping

Sand-capping is a marine environment improvement technology that covers organic sea-bottom sediments such as sludge layers with sand in order to suppress the elution of nutrient salts that cause eutrophication of seawater, and hydrogen sulfide that cause blue tides (**Fig.1**). Sand-capping suppresses the lowering of the amount of oxygen dissolved in seawater, which is caused by the decomposition of organic matter contained in the bottom sediments. It also improves the grain size of seabed sand. These aspects help create an environment that is conducive to organisms living on the seabed. In the past, mostly natural sand was used for sand-capping. However, excavation of natural sand causes environmental destruction. Hence, a new material for sand-capping has been sought.

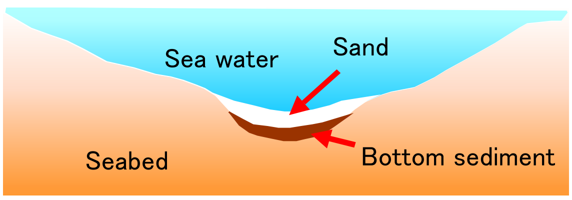

Fig.1 Scheme of sand-capping on the seabed

3.2 Sand-capping properties of BF slag sand

(1) Hydrogen sulfide generation suppression properties

In an experiment, BF slag sand and beach sand were laid over bottom sediment. Hydrogen sulfide concentrations in interstitial water within each type of sand layer were compared with that in an untreated bottom sediment layer[5]. The results are shown in **Fig.2**. The hydrogen sulfide concentration in the interstitial water in the slag sand layer remained at levels markedly lower than that in the untreated bottom sediment or beach sand layers over a two-year period. The pH value of the interstitial water in the slag sand layer remained at levels of 8.2 to 8.6[5]. This result is supposed to be attributable to the effect of BF slag in suppressing the activity of a certain type of bacteria whose function is to redox sulfuric acid ions in seawater[6]. Thus, BF slag sand has a greater ability than natural sand in suppressing the generation of hydrogen sulfide that causes blue tides.

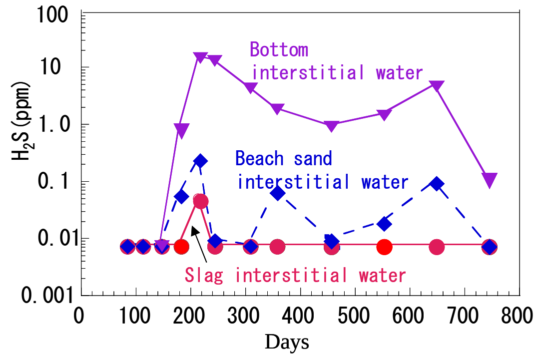

Fig.2 Changes of H_2S in seawater

(2) Effect of feeding silicate

Black acrylic containers were placed, opening down, on BF slag sand laid over the bottom sediment. Silicate concentrations of the seawater in the container were measured. The seawater in the area where BF slag sand was laid had higher silicate concentrations than that in the area where bare bottom sediment was exposed. It was confirmed that the BF slag sand had the effect of feeding silicate to seawater[7]. Silicate concentrations of more than 0.28 ppm are required for the growth of diatoms, the primary food source for various organisms living in the sea[8]. Diatoms are said to compete with dinoflagellates that cause red tides, hence diatoms are effective in the prevention of red tides[9]. BF slag sand has the potential of increasing the productivity of the sea and preventing red tides.

(3) Effect of cultivating marine organisms

It was observed that various marine organisms were living in the sea area where BF slag sand was experimentally laid over the bottom sediment. Species identified included: shrimp, fish such as goby, marine plants such as diatoms, and marine worms such as clamworm. The total number of benthonic species living in the sea-bottom sampling areas, each covered by BF slag, beach sand, and untreated bottom sediment, was counted as well as the total number of individual organisms. The total wet weight was also measured. The results are shown in **Fig.3**. It was confirmed that far more organisms lived in the slag-covered sea bottom area than in the sediment-covered area. Their number and weight were more than equal to those of organisms living in the area covered by beach sand. Both the number of species and number of individual organisms are affected by sand grain size. It is reported that more benthonic organisms live in the sea bottom composed of sand of a larger grain size[10]. BF slag sand has intermediate grain sizes of 1.0 to 1.5 mm, which are larger than those of typical natural sand (0.3 to 1.0 mm). Hence, BF slag sand presents the possibility of creating a sea-bottom environment in which a more diverse range of marine organisms can live.

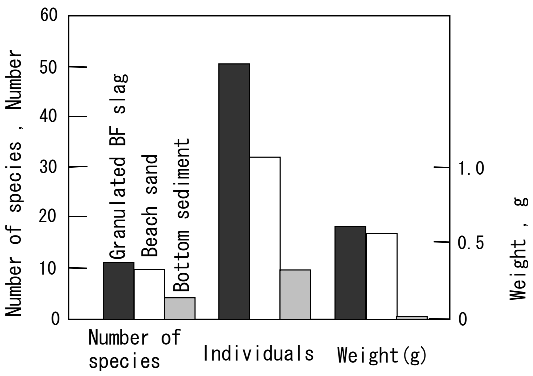

Fig.3 Observational results of benthonic organisms in granulated BF slag, beach sand, and bottom sediment

3.3 Field application example

NKK's BF slag sand-capping technology was recently adopted in the Naka-umi Sea Purification and Sand-capping Project carried out by the Ministry of Land, Infrastructure and Transportation in Shimane Prefecture, West Japan. Naka-umi is an enclosed area of sea connected to the Sea of Japan by a narrow channel. **Photo 1** shows the construction scene.

Photo 1 Construction of sand-capping with BF slag sand in Naka-umi, Shimane Prefecture

4. Marine Blocks used in the construction of artificial reefs

4.1 Production technology

By forming steelmaking slag into cubes and solidifying them by injecting CO_2, solid 1-cubic-meter blocks of slag were successfully produced. NKK started marketing these blocks under the registered trade name - Marine Blocks. Its production technology, properties, and field experiments using it for the construction of artificial reefs are introduced below.

After adding an appropriate amount of water, steelmaking slag was packed into an airtight mold. In order to solidify the slag, CO_2 was injected through the bottom of the mold at a designated pressure. A large carbonated solid block of slag was obtained. The carbonating reaction started from the bottom, gradually moved up, and finished when it reached the top of the mold. Various exhaust gases are usable as CO_2 sources. In order to prevent the slag from being dried by exhaust gas injection, the gas was kept saturated by steam. Large blocks of slag solidified by carbonation are shown in **Photo 2**. Each of these blocks was 1 m×1 m×1 m. They were the largest slag blocks reported produced by carbonation.

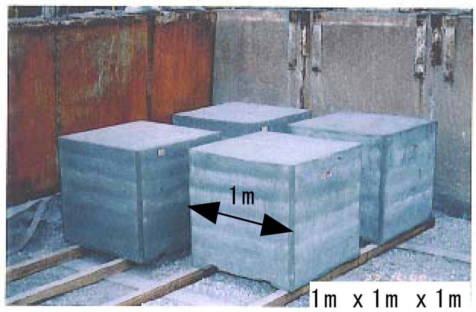

Photo 2 One cubic meter blocks of steelmaking slag produced by carbonation

The microstructure of this carbonated slag block is shown in **Photo 3**. CO_2 was introduced into open pores and carbonated the slag particles around its flow paths. Thus, the slag particles were coated by $CaCO_3$ and firmly joined to each other. Open pores were distributed uniformly throughout the solidified block. Contrary to concrete blocks, the slag blocks did not show strong alkalinity when immersed in seawater, thanks to this microstructure. The rate of carbonation was nearly uniform throughout the slag block. Its porosity was 25%, compressive strength was 19 MPa, and density was 2.4 g/m^2. This density was similar to that of a concrete block. One shortcoming of a conventional carbonated block has been expansion cracking. The carbonated slag blocks shown in **Photo 2** did not experience any expansion cracking even five years after they were produced. This demonstrates their long-term stability.

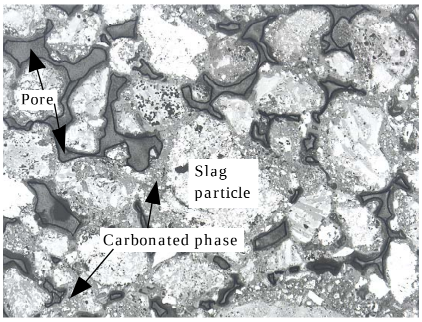

Photo 3 Microstructure of carbonated steelmaking slag block

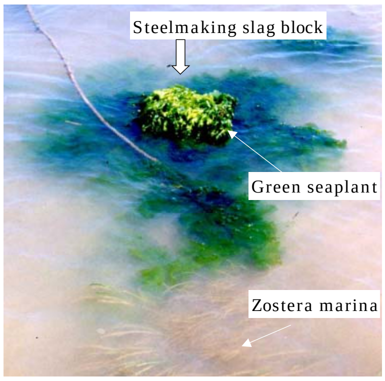

Photo 4 View of the carbonated slag block on the sea bottom

4.2 Effect of absorbing CO_2

Theoretically speaking, 1 mol of CO_2 (44 g) is absorbed by 1 mol of CaO (56 g) when solidifying steelmaking slag by carbonation. The main sources of CaO in the slag are calcium silicate compounds such as $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$. They form calcium carbonate and silica gel as a result of the carbonating reaction[11]. Steelmaking slag can have a wide variety of compositions dictated by the steelmaking process applied. When the slag has a CaO content of 50 mass% and the reaction rate is 50%, 1 ton of slag can absorb 200 kg of CO_2. If 4 million tons out of all the slag produced each year in Japan were used for absorbing CO_2, 800 thousand tons of CO_2 would be fixed. This amount corresponds to 220 thousand tons in carbon-equivalent terms and is one-tenth of the CO_2 emissions reduction target (base year: 1995) established by the Japan Iron and Steel Federation in response to the COP3 Kyoto Conference of 1997.

4.3 Cultivating marine plants experiment

The surface of the pores in the slag block is covered by $CaCO_3$, the same substance that comprises coral reefs and seashells. An experiment was performed to investigate the effect of slag blocks in cultivating marine resources (mainly marine plants).

In November 1997, 25-cm-cube slag blocks were placed on the bottom of the Inland Sea off the coast of Setoda Town in Hiroshima Prefecture, and their surfaces were monitored. It was confirmed as early as by the end of January 1998 that marine plants were growing on the surface of the slag blocks and shellfish adhered on the slag blocks surface. In the summer of 1998, green marine plants were proliferating on the slag blocks, as shown in **Photo 4**. The same types of marine plants were also growing on natural stones scattered around the slag blocks, indicating the beneficial effects slag blocks gave to the surrounding sea bottom.

Marine plant growth on slag blocks was compared with that on granite blocks and concrete blocks in the same area of sea[12]. All the blocks were the same size (10 cm × 10 cm × 1 cm), set on the sea bottom, and monitored for a 9-month period from April 1998 to January 1999. The number of sargassum plants growing on each type of block is shown in **Fig.4**. The slag blocks had the largest mean number of marine plants growing on their surface.

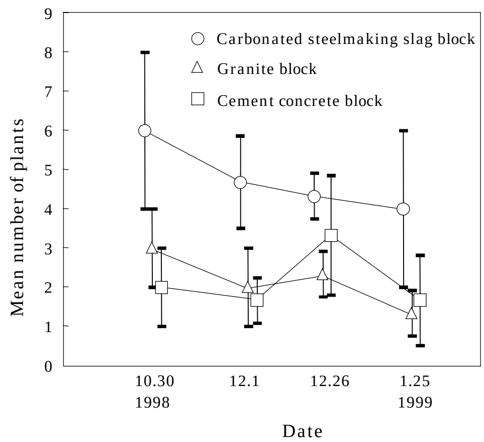

Fig.4 Mean number of sargassum plants on slag, granite, and concrete blocks

A probable reason for this finding is as follows. The slag block was porous, and its surface had a roughness of 328 μm, rougher than concrete blocks (273 μm) and granite blocks (67 μm). In contrast, the sargassum plant embryos were in the range 100 to 300 μm. Thus, the slag block had many more surface cavities, the sizes of which were larger than those of marine plant embryos, making their stay and growth on its surface easier. In addition, slag blocks did not exhibit strong alkalinity in seawater, this had a beneficial effect on the growth of these embryos.

In April 1999, 15 slag blocks, each with a 1-m-square bottom and 50 cm in height, were piled up on the 5-m-deep sea bottom in a pyramid-like shape to investigate the growth of large-sized marine plants and other organisms (**Photo 5**). It was observed that a large number of fish gathered in the space created by the slag blocks on which marine plants were growing (**Photo 6**).

Photo 5 A pile of carbonated slag blocks

Photo 6 View of the space created by carbonated slag blocks

4.4 Marine environment improvement by combined use of slag products

Shoals have disappeared in many coastal areas of Japan due to dredging for land reclamation and beach sand excavation. Recreating shoals in these areas are expected to bring about improvements in the marine environment through:

(1) Promoting the growth of marine plants, fish, and other marine organisms,

(2) Oxygen production by marine plants,

(3) Effects of sand-capping including suppressing the elusion of nutrient salts, and

(4) Creating a sandy sea bottom where versatile benthonic organisms can live.

NKK is developing a technology for recreating shoals by combining iron and steelmaking slag products. **Fig.5** schematically illustrates this technology, which is characterized by the fact that no natural materials are used, combining the unique properties of sand-capping material made from BF slag and Marine Blocks made from steelmaking slag.

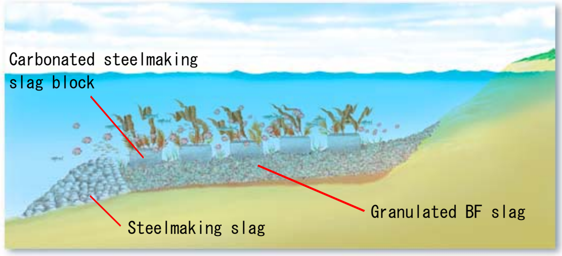

Fig.5 Schematic drawing of demonstration test using iron and steelmaking slag products

Currently, demonstration tests for marine environment improvement are being carried out at Inno-shima Island in Hiroshima Prefecture with the financial support of the prefectural government. **Photo 7** shows a construction scene for these tests.

Photo 7 Construction scene for marine environment improvement tests in Hiroshima Prefecture

In this project, about 1000 tons (800 m^3) of BF slag sand-capping material and 20 Marine Blocks, both produced at NKK's Fukuyama Works, were used to improve a 600 m^2 area of seabed. Currently, follow-up monitoring is being carried out to confirm the creation of the maintenance-free artificial reef.

5. Slow-release potassium silicate fertilizer

5.1 Production technology

The effect of silica (SiO_2) as a fertilizer is generating interest since it increases the resistance of rice to various diseases and vermin. Slag generated in the hot metal desiliconization process is mainly composed of silica. Using this desiliconization slag as the main material, a potassium silicate fertilizer has been developed. The newly developed fertilizer is difficult to dissolve in water, and slowly dissolves in the weak citric acid released by plant roots.

This slow-release potassium silicate fertilizer is produced by adding a potassium material to desiliconization slag. This fertilizer contains potassium in slow-releasing from, which was effectively absorbed by plant. At the desiliconization station in the hot metal pre-treatment process, hot metal is first subjected to desiliconization treatment and then, potassium carbonate (K_2CO_3) is continuously added into the hot metal ladle from the hopper above the ladle while agitating the hot metal using nitrogen gas (**Fig.6**). Uniformly melted slag is recovered from the hot metal ladle, solidified by cooling, and crushed into a granular form.

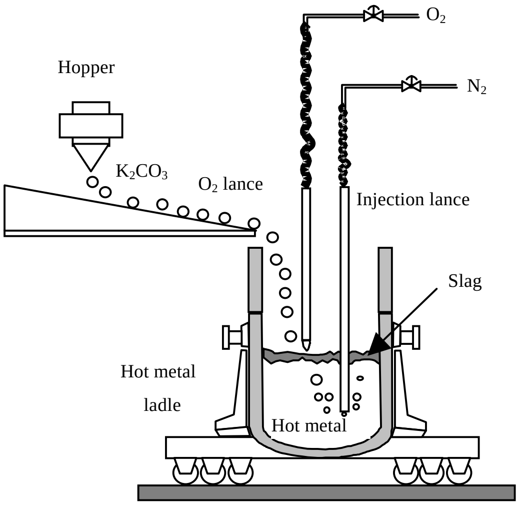

Fig.6 Production of potassium silicate fertilizer from steelmaking slag

5.2 Fertilizing properties

The chemical composition of the slow-release potassium silicate fertilizer developed by NKK is shown in **Table 2**. Potassium (K_2O) originating from potassium carbonate and silica (SiO_2) originating from slag are the main constituents. 93% of the total potassium content and 75% of the total silica content have a slow-release property. It also contains other slow-release constituents originating from slag such as CaO, MgO, MnO, and FeO[13].

Table 2 Chemical composition of NKK potassium silicate fertilizer (g/kg^{-1})

K_2O	SiO_2	CaO	MnO	MgO	FeO	Al_2O_3
221	377	213	37	9	31	35

This fertilizer is composed of the vitric portion, and crystalline portion such as $K_2Ca_2Si_2O_7$[15]. Both portions are slow-release compounds. Due to these properties, this fertilizer is difficult to dissolve in water, and thus is slowly released into the soil.

Its effectiveness as a fertilizer was investigated by the Japan Fertilizer and Feed Inspection Association. Various fertilizers including NKK's were applied to rice, cabbage, spinach, and other vegetables. In every growth test, NKK's fertilizer showed its effectiveness being more than equal to other types of potassium silicate fertilizers. The results of the rice growth test are shown in **Table 3**. NKK's fertilizer demonstrated an effectiveness equal to other commercial potassium silicate fertilizers and combined potassium chloride-calcium silicate fertilizers[14].

Table 3 Results of the rice growth test with potassium fertilizers

Fertilizer	Yield (g)	Absorbed	
		K_2O (mg)	SiO_2 (mg)
NKK potassium silicate fertilizer	63.3	1134	1423
Commercial potassium silicate fertilizer	61.5	983	1326
Potassium chloride + Calcium silicate	68.0	1114	1222
Control (K-free, Si-free)	41.0	319	795

In January 2000, as a result of these tests verifying the effectiveness of a potassium silicate fertilizer made from steelmaking slag, the Ministry of Agriculture, Forestry and Fisheries of Japan issued a new official fertilizer standard "Fused potassium silicate fertilizer" in its Notice No.91 based on the Fertilizer Control Law. NKK registered its fertilizer as "Mn-containing 20.0 fused potassium silicate fertilizer" with the Ministry in April 2000 and started marketing it in December 2001.

5.3 Prospects for new fertilizers

Iron and steelmaking slag has a long history in agricultural use: BF slag as a calcium silicate fertilizer, and steelmaking slag as a soil conditioner. The Zero Slag Process developed by NKK simplified the composition of slag generated from hot metal pre-treatment. It is believed this technology will further increase the effective use of slag as fertilizers in future.

6. Conclusion

Iron and steelmaking slag is being generated at a rate of 40 million tons per year in Japan. It is becoming increasingly important to use iron and steelmaking slag effectively in order to promote resource recycling. NKK will continue to be a pioneer in developing new applications of slag and contribute to the establishment of a recycling-oriented society.

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