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High Performance Construction Products Using Highly Pulverized Blast Furnace Slag in Nippon Steel & Sumikin Cement Co., Ltd.

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Abstract

Portland blast-furnace slag cement has superior characteristics such as a long-term strength increase, the restraint of heat of hydration, the durable improvement, and occupies 25% of domestic cement consumption. Specific surface area of a ground granulated blast furnace slag used for slag cement is approximately 4 000 cm²/g, but the fine pulverizing is one of the means to draw a further superior characteristic of the blast furnace slag. Nippon Steel & Sumikin Cement Co., Ltd. have been developing high performance ground improvement materials, ultrafine cements for grout and durable concrete repair materials by using highly pulverized slag and material design technology.

1. Introduction

Founded in Muroran City, Hokkaido in 1954, Nippon Steel & Sumikin Cement Co., Ltd. manufactures blast furnace slag cement, ordinary Portland cement, and so on, using blast furnace slag—a byproduct of steelmaking at Muroran Works of Nippon Steel & Sumitomo Metal Corporation—as the principal raw material. It sells its products mainly in Hokkaido and Tohoku. In recent years, the company's annual volume sales have been around one million tons. Blast furnace slag cement has also been exported to Sakhalin, Russia.

On the other hand, the company has come up with various high-performance, cement-based products for construction utilizing the advantageous features of blast furnace slag. The markets for them are expanding in not only Japan but also North America. This study shows the representative examples of such company products.

2. Utilization of Ground Granulated Blast Furnace Slag

Blast furnace slag cement has many advantageous properties such as the long-term strength development, the restraining of the alkali–silica reaction, good resistance to seawater, and the low hydration heat. It accounts for about 25% of the total consumption of cement in Japan. The blast furnace slag cement available on the market is mostly the Type B slag cement, whose raw material—ground granulated blast furnace slag—has Blaine specific surface area of about 4 000 cm^2/g, and the slag content is 40%–45%.

Finely grinding granulated slag is one means of improving the properties of ordinary blast furnace slag cement and effectively using the best properties of blast furnace slag. For example, by increasing the specific surface area and substitution ratio of slag, as shown in **Table 1** [1], it is possible to improve the properties of fresh concrete and increase the strength and durability of placed concrete.

Employing finely ground granulated blast furnace slag and advanced materials design technology, Nippon Steel & Sumikin Cement has developed a wide variety of construction materials, including high-performance, cement-based materials for ground improvement, ultrafine-grain cement for injection into the ground, and materials for repair of concrete structures.

3. Cement-Based Materials for Ground Improvement

Cement-based materials for ground improvement [2] are a special type of cement whose composition and particle size have been adjusted for soil consolidation. These materials are used to consolidate the building foundation ground, stabilize the subgrade/sub-base course, improve the excavated soil, and so on. The domestic de-

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Table 1 Influence of ground granulated blast-furnace slag fineness and substitution ratio on concrete properties [1)]

	Type	Ground granulated blast-furnace slag 4000			Ground granulated blast-furnace slag 6000			Ground granulated blast-furnace slag 8000		
	Blaine specific surface area (cm^2/g)	3000 ≦ < 5000			5000 ≦ < 7000			7000 ≦ < 10000		
	Substitution ratio (%)	30	50	70	30	50	70	30	50	70
Property of fresh concrete	Fluidity	○	○	○	◎	◎	◎	◎	◎	○
	Bleeding	○	○	△	◎	◎	◎	◎	◎	◎
	Setting delay effect	◎	◎	◎	◎	◎	◎	○	◎	◎
	Adiabatic temperature rise	–	–	◎	–	–	◎	–	–	◎
	Heat generation rate restraint	○	◎	◎	○	○	◎	○	○	◎
Property of strength	Initial strength	○	△	△	○	○	△	○	○	○
	28 days strength	○	○	△	○	◎	◎	◎	◎	◎
	Long-term strength	○	◎	◎	○	◎	◎	◎	◎	◎
	High strength	○	△	△	○	◎	◎	◎	◎	◎
Property of durability	Drying shrinkage	○	○	○	○	○	○	○	○	○
	Carbonation	–	–	△	–	–	△	–	–	△
	Freeze thaw	○	○	○	○	○	○	○	○	○
	Water-tightness	○	◎	◎	○	◎	◎	○	◎	◎
	Salt shield	○	◎	◎	○	◎	◎	○	◎	◎
	Seawater resistant	○	◎	◎	○	◎	◎	○	◎	◎
	Acid resistant, sulfates resistant	○	◎	◎	○	◎	◎	○	◎	◎
	Heat resistant	○	○	○	○	○	○	○	○	○
	Alkali-silica reaction restraint	○	◎	◎	○	◎	◎	○	◎	◎
	Abrasion resistance	○	○	○	○	○	◎	○	◎	◎

Symbol
◎ : Good property is provided in comparison with no mixture concrete.
○ : At the same level or a little good property is provided.
△ : Attention is necessary for use.
– : Property varies according to a condition.

mand for this type of cement in 2012 was seven million tons.

The ground of Hokkaido where Nippon Steel & Sumikin Cement is located is characterized by peat. The peat was formed by dead hygrophytes that had been incompletely decomposed under low temperatures and high humidity. In Hokkaido, there are peat bogs about 2 000 km^2 in area.[3)] Peat is composed mainly of organic matter. Since peat contains large proportions of water and organic matter, it could not be consolidated with blast furnace slag cement or an ordinary material for poor subsoil.

Therefore, "Nittetsu EarthTight ET-201," a cement-based material, was developed to consolidate peat. **Figure 1** [3)] shows the unconfined compressive strength of peat samples added with ET-201 and various other consolidating materials. As shown, even for peat, which can hardly be consolidated with blast furnace slag cement, ET-201 develops high strength even with a low mixing ratio. The superior strength development capability of ET-201 is due to the formation of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), an acicular crystal containing a large proportion of water (**Photo 1**), via optimum mixing of cement minerals, finely-ground blast furnace slag, and gypsum.

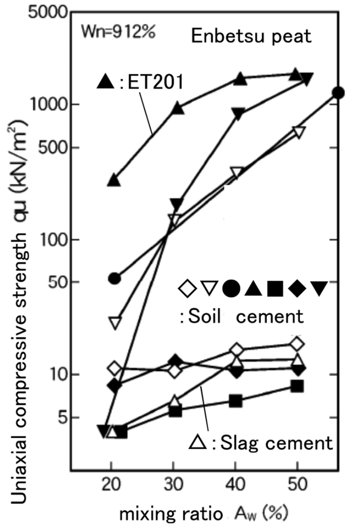

Fig. 1 Uniaxial compressive strength and mixing ratio of soil cement [3)]

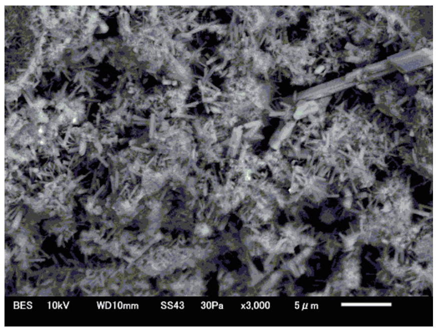

Photo 1 SEM photograph of ET201 paste

The EarthTight (ET) series comprises ET-104/ET-101 for ordinary poor soil, ET-104C for extraordinary soil, ET-201 for peat, and ET-104-Plus for restraining dust emission.

4. Ultrafine-Grain Cement for Grouting into Ground

In civil engineering works (e.g., dam foundation waterproofing, tunnel excavation, soil ground cutoff/stabilization), there are cases where the so-called grouting method, in which a consolidating material is injected into cracks in bedrock or pores in soil particles, is employed. The materials used in the grouting method are largely divided into chemical grouts and nonchemical grouts (cement-based grouts). The latter is further divided into general-purpose cement and ultrafine-grain cement developed specially for grouting.

4.1 Background of development of ultrafine-grain cement

The development of the ultrafine-grain cement originated in microfine blast furnace slag cement "Nittetsu Colloid",[4)] 230 000 tons of which were used in the Seikan Tunnel. In 1971, the "Committee for R&D on Grouting Materials for the Seikan Tunnel" consisting of the Japan Railway Construction Public Corporation, Nippon Chemical Industrial Co., and Nippon Steel & Sumikin Cement set the following quality targets for grouting cement.

(1) Micro-fine grain cement that can be injected into fine cracks.
(2) Cement that hardly weathers even within a tunnel subjected to high temperatures and high humidity.
(3) Labiles Wasserglas grout that has a gelation time of 3 min or

more.

(4) Cement whose strength is 40 kgf/cm^2 or more at the age of three days and is free from erosion by seawater when hardened.

With the technology available at that time, it was difficult to grind blast furnace slag cement to Blaine specific surface area exceeding 4500 cm^2/g and any cement of that grain size could not be injected into extremely fine cracks.

In the face of such problems, efforts were made to study the mechanism of cement agglomeration during grinding and find suitable grinding aid. Consequently, it was found that the addition of diethylene glycol to the cement facilitates in the grinding of the cement to a specific surface area of a maximum of 7000 cm^2/g and significantly improves the cement's resistance to weathering. Eventually, it led to successful mass production of the microfine-grain blast furnace slag colloidal cement "Nittetsu Colloid" (6000 cm^2/g).

The slag content of the Nittetsu Colloid was estimated as 55%, the value was set high in view of the expected seawater resistance and gelation time. The examination results of a hardened grout 30 years after the execution of the grouting work [5] showed that the hardened material in the core was very hard and had prescribed strength, demonstrating that the blast furnace slag-based grout had a good long-term durability even under a severe seawater environment.

In 1979, in order to meet the growing need for foundation grouting in the construction of dams throughout Japan, Nippon Steel & Sumikin Cement developed the ultrafine grain cement "Nittetsu Superfine" (SF). After that, the company put on the market SF-L for use in seawater/hot water (1990) and early-hardening cement SF-X3 (2006). Since 2007, extreme ultrafine-grain grout "HNP-1500" has been manufactured, especially for works executed to prevent liquefaction, reinforce earthquake resistance, and so on.

4.2 Permeability of cement-based grout

Figure 2 shows the particle size distribution of cement-based grouts of Nippon Steel & Sumikin Cement. The average particle size is 20 μm for the blast furnace slag cement (BB), 8 μm for the Nittetsu Colloid (NC), and 3 μm for the Superfine (SF). HNP-1500, the extreme ultrafine-grain grout, has an average particle size of 1.5 μm. As shown in **Fig. 3**, the smaller the average particle size of the cement, the wider the scope for the application of the cement.[6] For example, HNP-1500 is applicable even to silt-containing fine sand to which only a chemical-based grout could be typically applied.

To improve the permeability of cement-based grouts, it is indispensable to reduce their particle size. However, merely refining the grains will not improve the permeability because it results in formation of coarse grains as the result of particle cohesion and hydrate generation. The grouts of Nippon Steel & Sumikin Cement have excellent permeability, which is made possible by extremely fine grinding with a high-performance grinder/classifier and the materials design,[6] that is, by the controlling of the amount of blast furnace slag with grain size, controlling of the initial hydration by adjusting the cement mineral composition, and retention of dispersibility using an exclusive polycarboxylic acid disperser and a special high-speed agitation technology.

4.3 Examples of the execution of works using ultrafine cements

Since 1979, the ultrafine cements of Nippon Steel & Sumikin Cement have been applied to more than 200 dams and tunnels throughout Japan. Recent examples of the execution of works using the ultrafine cements are outlined below.

4.3.1 Kurashiki national LPG stockpiling base (SF-X3)

The Kurashiki national LPG stockpiling base is a water-sealed underground bedrock storage having a capacity for 400000 tons of LPG. It consists of four tunnels, 14 m in width, 24 m in height, and 640 m in maximum length, constructed at EL.−160 to 180 m.

In constructing the storage, a low-permeability improved zone was built with grout at a distance of 8 m around the storage space to control the amount of spring water and secure the required groundwater pressure.[7] Since the target value for bedrock improvement was as high as 0.35 Lu (Lu: Lugeon unit ≈ 1.0×10^{-5} cm/s) on average, the ultrafine cement having an excellent permeability was adopted. However, the ultrafine cement requires considerable time to harden, and SF-X3 was developed to solve this problem.[8] While SF-X3 is comparable in permeability with SF (**Fig. 4**), the setting time of SF-X3 after pressure filtration is only 4 h or one-fourth that

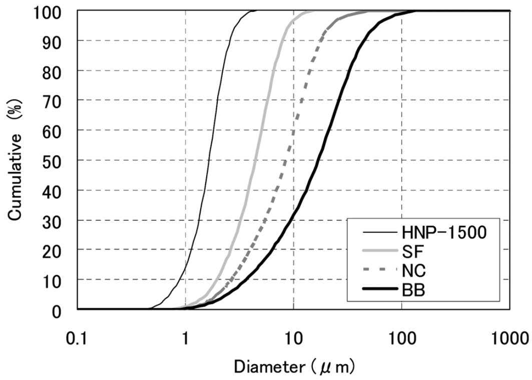

Fig. 2 Particle size distribution of injection cement

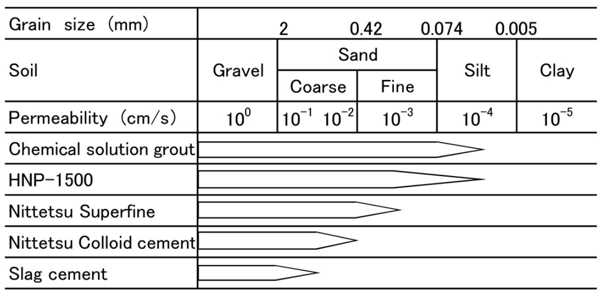

Fig. 3 Ground coverage of grout

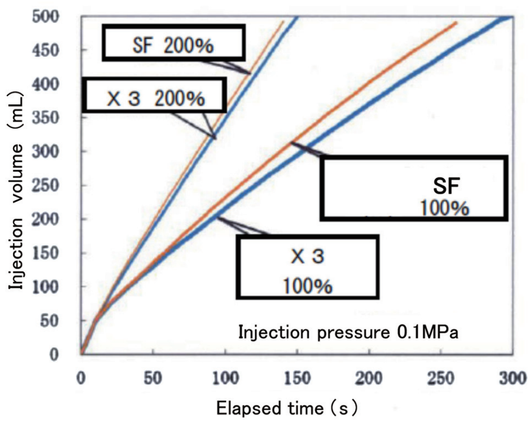

Fig. 4 Injection volume of SF and SF-X3 in slit test

of SF. Thus, SF-X3 dramatically helped to secure the water-sealing function of the storage and reduce the tunnel excavation process.

4.3.2 Kitanomine Tunnel (HNP-1500)

The Kitanomine Tunnel is a 3-km-long tunnel planned to be constructed on the Asahikawa–Tokachi Highway. Since the tunnel is to pass under a confined aquifer with a small overburden, a water-sealing grouting section was planned, and a permanent bulkhead required to possess high water sealability and strength was designed for certain parts of the section.

The ground was an alluvial fan composed of fine sand that the suspension can barely permeate. Therefore, an indoor test for comparative evaluation of various types of grout was performed.[9] Consequently, extremely ultrafine-grain grout HNP-1500, which was superior in permeability and strength development, was selected.

The results of test works confirmed sufficient permeation of the grout into the core and improvement in the permeability coefficient (10^{-5} cm/s order). In addition, the amount of spring water in the tunnel during excavation of the bulkhead (**Photo 2**) was lesser than expected, proving that the bulkhead constructed using the high-quality water-sealing grouting method [10] was effective.

4.3.3 Arrowhead Tunnels (SF)

The Arrowhead Tunnels (**Photo 3**) are the 15.6-km-long aqueduct tunnels (east and west tunnels 9.2 and 6.4 km, respectively) located near the San Bernardino mountain range in South California, U.S.A. The tunnels were constructed by employing a tunnel boring machine under extremely complicated geologic conditions. To conserve the water resources, the inflow of groundwater into the tunnels was limited. As pregrouting materials for sealing water, water glass, polyurethane, colloidal silica, and ultrafine cement (SF) were used.

Photo 2 Face of Kitanomine Tunnel

5. Cement-Based Repair Materials

In recent years, the deterioration of concrete structures due to aging has become a problem. Under such a condition, it has become increasingly important to prolong the life of concrete structures by means of proper repair and/or reinforcement. For repairing of concrete structures, methods such as grouting into cracks, restoration of damaged sections, covering of surfaces, and electroprotection are possible. For repair materials, organic (e.g., epoxy resin) and inorganic (e.g., polymer cement mortar) materials are available. In 1984, Nippon Steel & Sumikin Cement developed high-strength, high-durability mortar compound called "NEM," which is a mixture of ground granulated blast furnace slag 8000, cement, and fine slag aggregate.[11] Next, the company put on the market a series of inorganic repair materials based the NEM technology.

5.1 "NEM-R" series ultrafine-grain blast furnace slag based mortars for repair of concrete structures

NEM is a high-performance mortar that has excellent properties such as fluidity, strength, wear resistance, freeze–thaw durability, and resistance to salt invasion. It utilizes the following mechanisms of hydration of blast furnace slag.

(1) Dense structure by a mixture of three types of granules that differ in grain size distribution—ground granulated blast furnace slag, cement, and fine slag aggregate.
(2) Enhancement of initial strength by refinement of blast furnace slag and retention of good workability by slow initial hydration.
(3) Dense structure by formation of a slag hydrate that contains a large proportion of gel water.[12]
(4) Consumption of $Ca(OH)_2$ crystals derived from cement hydration by hydration of ground granulated blast furnace slag.
(5) Consolidation by the chemical bond between aggregate and paste owing to the latent hydraulic property of the surface of fine blast furnace slag aggregate.
(6) Restraining of the formation of a brittle leached layer on the surface of the fine slag aggregate by reduction of $Ca(OH)_2$.

NEM-R has a high strength of 60 N/mm^2 or more and excellent wear resistance. Since it permits reducing capillary voids, it also has high freeze–thaw durability made possible by decreasing the amount of frozen water. NEM-R has been used to repair trunk waterways in Hokkaido (**Photo 4**).[13]

Because of its low permeability, thanks to the reduction and densification of $Ca(OH)_2$, NEM-R also has high chemical resistance and hence has been adopted for sewerage facilities (in the Kanto area), which demand superior resistance to sulfuric acid (**Photo 5**).

Photo 3 Arrowhead Tunnels

Photo 4 Repair of irrigation canal

5.2 "Hi-Guard" high-durability surface covering materials utilizing ultrafine-grain blast furnace slag

Utilizing the salt-fixing capacity and dense structure of the blast furnace slag, Hi-Guard (HG) is capable of effectively providing protection against the permeation of chloride ions, and hence it is especially suitable for covering the surfaces of ocean structures. With a 1-mm-thick HG covering, the effective chloride ion diffusion coefficient, which is 2.7×10^{-8} cm^2/s for concrete without HG covering, can be reduced to 1.2×10^{-8} cm^2/s. In addition, the results of an 11-year exposure test of a pier with HG covering in the Kanto area confirmed that the permeation of salts into the base mortar had been restrained effectively, and the airborne salts had been mostly fixed within the HG layer (**Fig. 5**).[14]

The other repair materials of Nippon Steel & Sumikin Cement are "Hi-FLUENT," non-shrink polymer cement mortar for grouting; "High-STUFF," ultrafine-grain slag-based grout for cracks; and "PAVE BLANC," grout for semiflexible pavement.

Photo 5 Repair of sewage facility

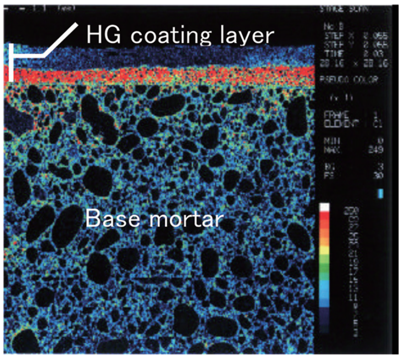

Fig. 5 Distribution of Cl in HG coating and base mortar

6. Special Powders

6.1 "FS Shot" admixture for high-quality spraying concrete

For the Hokkaido Shinkansen, the construction of which started in 2005, the development of a new admixture for spraying concrete utilizing recyclable fly ash and slag powder from the standpoint of ensuring a stable supply of raw materials in Hokkaido, reducing environmental impact, and cost reduction was conducted with the initiative of the Japan Railway Construction, Transport and Technology Agency. As a result, it was possible to offer an admixture that has the prescribed compressive strength and that is superior in workability and ecofriendliness, as compared with the conventional admixture composed of silica fume and limestone powder[15] (**Table 2**).

Nippon Steel & Sumikin Cement supplies a mixture of fly ash and ground granulated blast furnace slag 4000 (mixing ratio 7:3) as the "FS Shot" admixture for high-quality spraying concrete. This admixture was officially adopted by the above agency in 2011 for its guidelines on high-quality spraying concrete design and work execution.

6.2 "Spirits" ground granulated blast furnace slag

"Spirits" is ground granulated blast furnace slag for concrete (compatible with JIS A 6206) that is available in three classes: 4000, 6000, and 8000. It is used to lower the heat generation of concrete, improve the strength, fluidity, and acid resistance of concrete, restrain the alkali–silica reaction, and obtain a smoother surface of finished concrete. The addition of Spirits reduces the $Ca(OH)_2$ concentration of concrete and improves the sulfuric acid resistance of concrete, as shown in **Photo 6**.

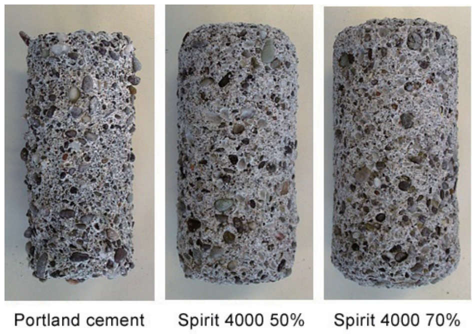

Photo 6 Specimens after sulfuric acid solution (5%) immersion

Table 2 Field test results [15]

Field test results		Unit	Standard value	Current mixture		New mixture	
				Measurements (mean)	Number of sample	Measurements (mean)	Number of sample
Slump		cm	8 ± 2	8.6	451	—	—
		cm	18 ± 2	—	—	18.9	358
Compressive strength	3 hours σ_{3h}	N/mm^2	≧ 1.5	1.75	50	2.21	35
	24 hours σ_{24h}	N/mm^2	≧ 8.0	12.02	50	16.47	35
	28 days σ_{28}	N/mm^2	≧18.0	31.24	50	31.54	35
Dust quantity		mg/m^3	≧ 3.0	2.09	39	2.15	49
Accelerating agent dosage		%	—	6.33	—	6.5	—
Spraying efficiency		%	—	88.4	4	90.8	25
Machine trouble		time/day	—	0.26	—	0.18	—

Recently, in view of improving the reliability of concrete structures, studies on the self-healing of admixtures have been conducted, and the self-healing performance of ground granulated slag has been reported.[16)]

7. Conclusion

Beginning with the introduction of the Nittetsu Colloid for the Seikan Tunnel in 1971, Nippon Steel & Sumikin Cement has developed and sold high-performance products such as the cement-based solidifier, ultrafine cements, and concrete repairing material utilizing the advantageous properties of blast furnace slag and advanced pulverizing technology. Through the development of new products utilizing blast furnace slag, the company intends to continue contributing to the improvement of social infrastructure, implementation of disaster prevention/reduction measures, stable supply of energy, prolongation of infrastructure life, and reduction of CO_2 emissions.

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