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UPDATE OF IRON AND STEEL SLAG IN JAPAN AND CURRENT DEVELOPMENTS FOR VALORISATION

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Abstract

After rapid economical growth in the 1970s, the production of iron and steel slag in Japan did not greatly change. The way of slag usage, however, changed to meet social demand and requirement. In order to continue effective use of slag in the future, we realise the necessity of development for new applications and market reclamation to create the stable demand, while both investment in construction and public works decrease. This report describes the situation of iron and steel slag in Japan, quantity of production and usage, legal regulations, and besides the development of new applications of slag, particularly the activities around the sea area.

Introduction

Iron and steel are basic materials that support modern civilisation, and iron and steel slag (ferrous slag) is also used as a material in various sectors owing to many years of research. Slag enjoys stable quality and properties that are difficult to obtain from natural materials, and is drawing attention now and in the future as an environmentally friendly material, from the perspectives of resource and energy conservation, and CO_2 reduction.

Table 1: Materials named 'slag' in Japan and annual production (2011)

from metal manufacture			Million tonnes
ferrous slag[1]	blast furnace slag	granulated BF slag	19.5
		air-cooled BF slag	4.7
	steelmaking slag	BOF slag	11.3
		EAF slag	2.9
non-ferrous slag[2]	copper-, ferronickel slag, *etc*		5.3
from waste treatment, *etc*			
heat-treated, melted/fused waste, sewage sludge[3]			0.8

Nippon slag association (NSA) was established in 1978 based on the Japan Slag Society that had promoted slag usage, and merged a part of the slag related function of the Japan Iron and Steel Federation (JISF) in 1984. The members of NSA are steel companies (both BF-BOF and EAF), slag processing companies and several cement companies as the slag user.

The scope of NSA is focused on ferrous slag, which is generated from the manufacturing of iron and steel (Table 1), though the word 'slag' embraces several slags such as non-ferrous and waste treatment slag.

Slag production and applications

Since 1970s, the annual production of iron and steel slag in Japan is constant, thereby showing the same trend as observed for the production of steel, and maintains approximately 37 million tonnes (Figure 1). The mechanical/chemical characteristics, however, have been persistently modified to meet customer satisfaction and social requirements.

The primary constituents of slag are lime (CaO) and silica (SiO_2), and their chemical compositions are similar to those of regular sedimentary rock and Portland cement (Table 2). Both the chemical composition and physical properties are quite stable, because the slag is produced from iron and steel making processes in which operational conditions are managed and controlled. Additionally, slag contains no organic substance, which is removed at a temperature higher than 1200°C.

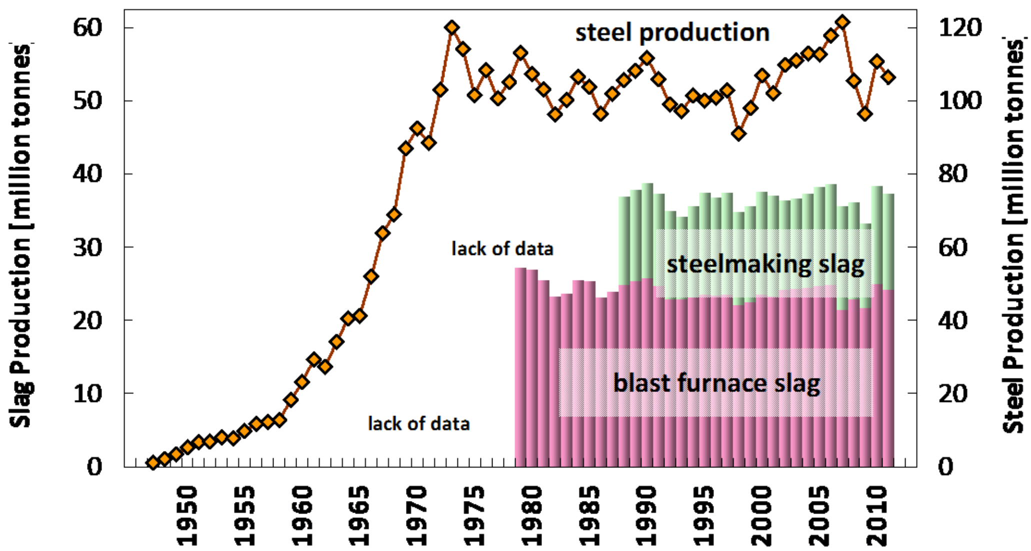

Figure 1: Annual production of slag[1] and steel[4] in Japan

The range of ferrous slag use is not limited to civil engineering, the slag is also recognised as an important material to reduce the environmental load, to conserve the natural resources and to reduce CO_2 emission.

Table 2: Typical chemical compositions (wt%) of slag[5]

Slag	CaO	SiO_2	Al_2O_3	MgO	FeO	S	P_2O_5	Remarks
Blast furnace	**42**	**34**	**13**	**7.4**	**0.4**	**0.8**	**<0.1**	CaO/SiO_2=1
BOF/steelmaking	**46**	**11**	**2**	**6.5**	**17.4**	**0.1**	**1.7**	CaO/SiO_2=4
Pre de-S	*50*	*10*	*2-10*	*2*	*7*	*1.5*	*<0.5*	
Pre de-P	*35*	*25*	*5*	*5*	*15-25*	*<0.2*	*2.0-5.0*	*Ref.*
BOF	*45*	*15*	*3*	*5*	*15-20*	*<0.1*	*2.0*	*JFE*
LF	*30-40*	*10-15*	*15-35*	*5-10*	*10-25*	*<0.1*	*<0.5*	
EAF/steelmaking	**23**	**12**	**7**	**4.8**	**29.5**	**0.2**	**0.3**	Oxy/melting
	55	**19**	**17**	**7.3**	**0.3**	**0.4**	**0.1**	Red/refining
Andesite (rock)	6	60	17	2.8	3.1	-	-	
Portland Cement	64	22	6	1.5	3.0	2.0	-	

Blast furnace (BF) slag

BF slag mainly consists of gangue of iron ore and coke ash, melted together with limestone for easy separation of molten iron from inorganic oxides. The chemical composition of BF slag is shown in Table 2. The production of BF slag is approximately 24 million tonnes a year in Japan, that is ca. 290 kg of BF slag generated for every ton of hot metal.

The slag is processed in two different methods: air-cooling in the slag yard, into which the molten slag is discharged to obtain crystallised slag, with moderate water spraying if necessary. The slag then undergoes crushing, sieving and removing magnetic matters.

Air-cooled BF slag is used for roadbed because its favourable bite and hydraulicity promise high bearing capacity. The use of recycled construction material as roadbed is growing, and composite roadbed materials with admixtures of ferrous slag to improve their physical properties are also in use. Air-cooled BF slag that hardly shows alkali-aggregate reaction due to low SiO_2 content is also used as a coarse aggregate for concrete.

In granulation equipment, on the other hand, a high-pressured water jet is injected to blow off the molten slag, and then quenched granulated BF slag is produced. The granulated slag consists of glassy particles less than ca. 5 mm in diameter, and has strong latent hydraulicity. With the increased consumption of Portland BF slag cement as a means of energy saving and resource conservation, granulation facilities have been upgraded to satisfy quantity and quality requirements of customers.

Granulated BF slag is pulverised finely, and the pulverised slag is used as constituent of Portland BF-slag cement, extender of Portland cement and concrete admixture due to the latent hydraulicity promised by pulverising. Concrete employing Portland BF-slag cement further offers superiority in long-term mechanical properties and chemical stability as well.

The merit of BF slag cement is not only its mechanical performance, but also environmental aspects: both conservation of natural materials through the use of a by-product, and reduction of CO_2 emission during cement production (Table 3). Compared to ordinary Portland cement, it is estimated that 40% reduction of CO_2 emission in production of Portland BF-slag cement type B, which is widely used in Japan, because of the decrease in dissociation of CO_2 from limestone and in emission from the fuel during de-carbonation.[6]

Table 3: Effect of slag cement on CO_2 emission[6] (kg-CO_2/ton)

	OPC	**BFS cement**	**Reduction**	
electricity	77	55	22	29%
de-CO_2 / limestone	510	294	216	42%
combustion / fuel	271	159	112	41%
delivery, transportation *etc.*	38	18	20	
total CO_2 emission (kg-CO_2/ton)	**896**	**526**	**370**	**41%**

Granulated BF slag is directly used as well for civil engineering work, such as backfilling and covering, due to its large angle of internal friction in sandy form and its lightweight.

The usage of granulated BF slag to fine aggregate for concrete has been expanded significantly due to its little contamination of saline and other inhibitory substances. In 2006, sea sand mining has been comprehensively banned from the viewpoint of environmental conservation policy, and this prohibition stimulated demand for the granulated slag as a sand substitute.

The ingredients of BF slag such as CaO, SiO_2 and MgO are used for fertiliser and soil improvement as well.

The production of granulated slag was replaced by air-cooled slag and increased to 80% of total BF slag (Figure 2), in order to meet the demand for BF slag with higher performance. And approximately 70% of BF slag is used for the cement industry (Figure 3), though the half of the granulated slag is exported at the moment.

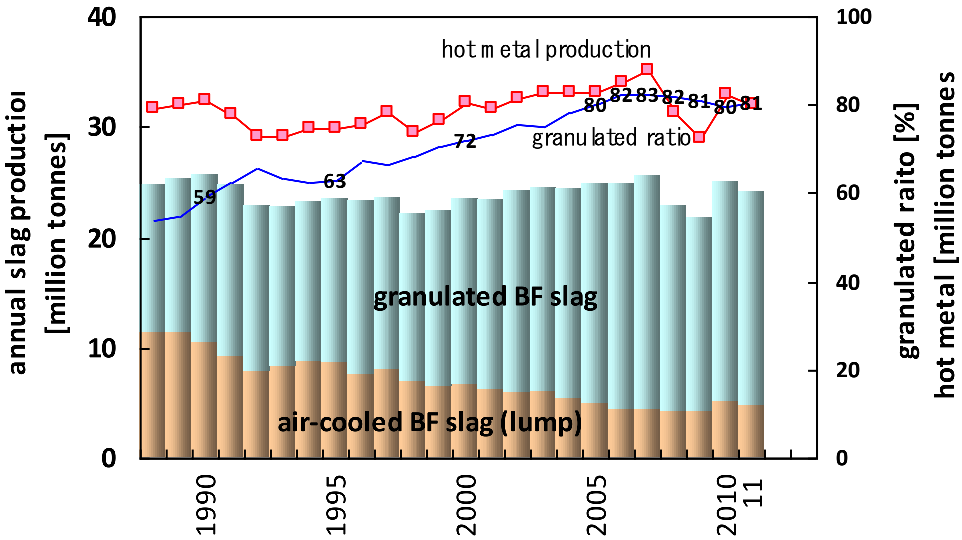

Figure 2: Change of granulation ratio of BF slag[1]

Steelmaking slag

In the steelmaking process, molten metal is refined and converted into steel, either in a basic oxygen furnace (BOF) or an electric arc furnace (EAF), and the molten steel is additionally refined to high grade steel when necessary; about 75% of the steel in Japan is produced via BF-BOF process, in which BF and BOF slag are produced, while the EAF process produces only steelmaking slag. CaO, the primary refining agent, is the main component of steelmaking slag as shown in Table 2.

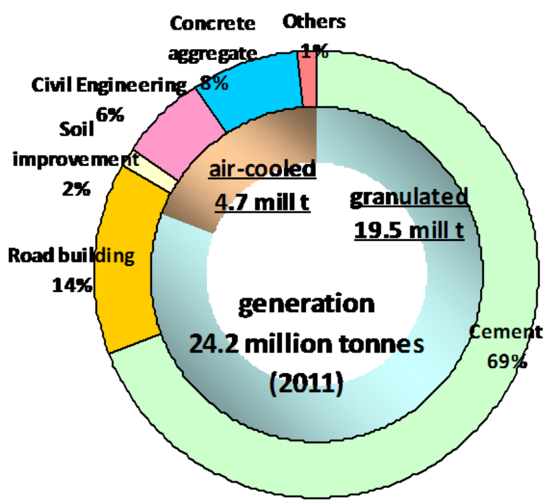

Figure 3: Breakdown of BF slag usage, total generation and the ratio of granulated and air-cooled (2011)[1]

In Japan preliminary hot metal treatment processes are widely adopted for effective steel production. In each pre-treatment process, the operational conditions, such as the oxygen potential, the temperature of the system and the way of refining flux addition are practically optimised for de-sulphurisation and de-phosphorisation reactions, thereby reducing the generation of steelmaking slag. All the pre-treatment slags (de-S, de-P), BOF/EAF slag and secondary refining slag, are categorised as steelmaking slag, of which the main component is CaO as well. The total amount of steelmaking slag is approximately 120 kg per ton of crude steel, and is mostly independent of steel grade produced.

Molten slag from these processes is discharged to a cooling yard or a slag ladle, and then cooled in atmosphere or by moderate spraying. The crystallised rocky slag then undergoes crushing, sieving and recovering of metallic iron, to obtain the appropriate granularity for the intended application of the slag.

As shown in Table 2, a distinctive characteristic of the steelmaking slag is the high CaO content compared to BF slag. The ratio of CaO content to SiO_2 is normally above 2 to 3, thus the steelmaking slag possibly contains free lime. Because free lime in steelmaking slag in service may expand in contact with water, a stabilisation treatment of the slag is applied depending on the application. One of the stabilisation methods is 'natural ageing' where the slag is cured outdoors, whereas another possibility is 'steam ageing' in which high temperature water vapour, at atmospheric pressure or pressurised, is employed.

In the stabilisation process, free lime in the slag is efficiently hydrated and/or partly carbonated, thus possible expansion of the treated slag is practically suppressed and controlled. Stabilised steelmaking slag is used for roadbed, and its high bearing capacity promised by its hydraulic properties gets good evaluation. Taking advantage of its properties of having a greater mass per unit volume and greater angle of internal friction than natural sand, it is used as a substitute for sand in port and harbour construction works to improve the soil material, *e.g.* sand compaction pile. Its hardness and abrasion resistance is suitable for aggregate of asphalt concrete as well.

Steelmaking slag is also used for cement clinker as a source of iron oxide, and as raw material for fertiliser as a source of CaO, SiO_2, MgO, FeO and P_2O_5.

As a result of the development of applications, the reclamation ratio that used to be 40%, became 2% of the total amount of steelmaking slag as shown in Figure 4.

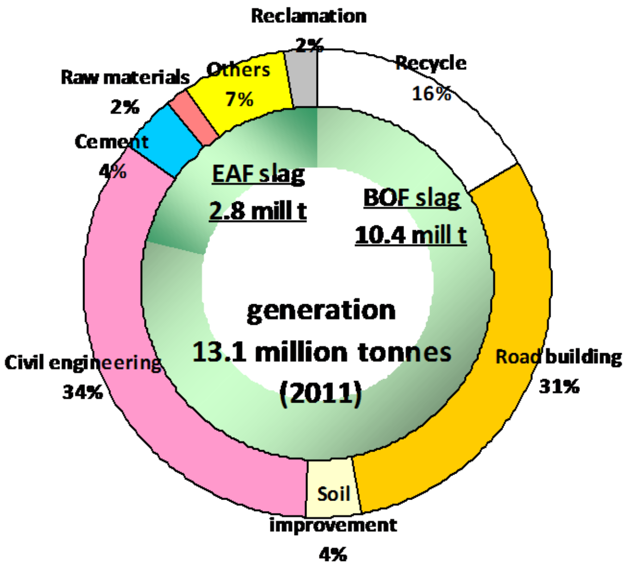

Figure 4: Breakdown of steelmaking slag usage, total generation and the ratio of BOF and EAF slag (2011)[1]

Promotion of utilisation of Slag

The history of effective usage in Japan is long; production of Portland BF slag cement began in 1910, and the Japanese national standard for Portland BF-slag cement was formulated in 1926. Extensive use in reclamation and land formation was conducted successively for steelworks projects at the waterfront, and use as roadbed material began in the late 1960s.

The traditional use as landfill material approached its limit with the massive expansion of the steel industry until 1970 when the rapid economic growth calmed and significant civil engineering diminished. From then on, the environmental consciousness started growing. The recognition of the importance of the conservation of resources and energy actively forced slag recycling towards the development of application.

Certification and authorised specifications

The steel companies have recognised the development of technology for the production and quality management of ferrous slag products and the acquisition of authorised certifications for these products as important managerial challenges in order to expand slag applications.

JISF and NSA have promoted the institution and adoption of Japan Industrial Standards (JIS). The following products related to iron and steel slag have been defined: 1) ground BF slag (JIS A 6206) itself and its application to Portland cement

(JIS R 5210), BF slag cement (JIS R 5211), and ready-mixed cement concrete (JIS A 5308), 2) BF and EAF slag for slag aggregate for cement concrete (JIS A 5011-1 and -4), and 3) iron and steel slag for road building material (JIS A 5015).

Ferrous slag products are incorporated in national specifications related to ports and harbours, housing, railway, expressway and civil engineering works. MLIT stated in their policy, 'Industrial waste such material as ferrous slag, coal ash and nonferrous metal slag, and where these are employed as useful materials for such purposes as concrete material, roadbed material and civil engineering material, they shall not constitute waste under the terms of the Waste Management Law.' *(MLIT: Ministry of Land, Infrastructure, Transport and Tourism)*

Relevant academic societies and industrial associations which have incorporated slag products into their guidelines and policies are for example: Architectural Institute of Japan, Japan Society of Civil engineers, Japan Road Association, NSA, the Japan Port & Harbour Association, Coastal Development Institute of Technology and Council on promoting recycling at ports, harbours and airports for port and harbour construction and infrastructure.

Both BF slag and BOF slag have also been incorporated as fertiliser by law in 1955 and 1981 respectively.

Legal position

The legal system in Japan that controls slag handling and usage is based on 'Basic Environment Law' and 'the Basic Law for Establishing the Recycling-based Society.' Slag is possibly categorised as industrial waste as listed in 'Waste Management Law', though almost all ferrous slag is adequately processed and utilised as useful material in public facilities. The one per cent ferrous slag that is isolated from this stage of processing is appropriately controlled and managed as waste.

Meanwhile, 'the Law for Promotion of Effective Utilities of Resources' nominates the steel industry as a designated resource-saving industry and expects from them to suppress the production of slag as a by-product and to promote the usage of this by-product as a recyclable resource.

'The Law on Promoting Green Purchasing' further instituted an extensive list of 'qualified procurements' that national and local governments actively seek to include in their procurements.

With comprehensive consideration, NSA emphasises that ferrous slag is not a waste as far as it is utilised effectively and environmentally correctly.

Conformance to environmental standards

The quality of ferrous slag has been already specified in JIS as a civil engineering material, and the vast majority of slag is effectively used. Given the lack of quality standards addressing environmental safety, however, the Ministry of Environment states ‘While soil environmental standards and measurement methods are invoked for safety evaluations, evaluations must be performed that are appropriate and suited to their current form and the context of their use.’

Heavy metals and harmful elements

Test methods for chemicals in slag were instituted in JIS. The work required to incorporate ferrous slag for road building and other specific ferrous slag products into the additions, has been completed, but is waiting for publication. The environmental sections in JIS standards were revised.

The environmental safety of soil has been conventionally evaluated by elution testing in accordance with environmental quality standards and the ‘Soil Contamination Countermeasures Law.’ The slag products used in land environment are confirmed to meet the necessary standards. When using ferrous slag products in marine environments or reclaimed land, environmental safety is evaluated with ‘the elution standard for harbour application’, which is derived from the dredged soil standards in accordance with the ‘Marine Pollution Prevention Law.’

Alkalinity

Lime, the major component of ferrous slag, may cause a higher pH in contact with water, because it dissolves in water to form Ca^{2+} and OH^- and produces slaked lime. When the slag is applied in marine construction, however, pH measurements confirmed that it hardly influences the pH of the surrounding marine waters, even though granulated BF slag has been used in large volumes in port and harbour construction works. The excess of OH^- ions is consumed and the pH is mitigated by the formation of magnesium hydrate in seawater.

Air-cooled BF slag and steelmaking slag which are primarily used on land, show a pH around the level of 11 and 12 in contact with water, which is equivalent to or below those of recyclable roadbed material and cements, which are often used for ground improvement. Generally speaking, as the soil in Japan is mild acidic, it can neutralise the alkaline eluate from the slag and automatically absorb it. Artificial neutralisation will be necessary when the water shows an exceptionally high alkalinity and directly flows out to a body of water without being absorbed by the soil.

Influence during work execution

Ferrous slag products are traded as valuable resources at the local market value on the basis of negotiations with customers. NSA released a new edition of the 'Guidelines on Control of Iron and Steel Slag Product' in 2006 (latest revision in 2012) from a perspective of ensuring the appropriate utilisation of ferrous slag product and preventing problems arising from it, and these are now being incorporated into corporate manuals. The guide line includes: 1) members' obligations, 2) quality control of the products, 3) sales management of prior order acceptance, delivery and work execution, 4) follow up surveys subsequent to completion of execution, 5) products handling and 6) verification of the manual and correction.

Development of new applications

Although the way to the safe and stable usage of blast furnace slag has been established in the cement industry, the steelmaking slag, which is mainly used for construction, is facing a decrease in demand because of the economical situation of Japan and the competition with other recyclable materials.

In order to promote new applications of steelmaking slag and to obtain better understanding of the slag as a recyclable material as well, the characteristics of the slag are investigated to meet social demands, such as the promotion of a recycling-based society and the improvement and restoration of the environment. As a result of this intensive research, we found that both the amount of production and the nature of steelmaking slag meet the conditions required for marine restoration materials; vast amount of material, which is safe to aquatic live and stable in quality, can be continuously supplied without additional consumption of natural resources. The observed pH increase is not significant because the area and duration of the change are relatively small. The experimental results showed that the pH of the area is immediately mitigated by the formation of magnesium hydrate.
Steel industry has been intensively promoting development of safe usage of steelmaking slag for restoration of marine environment, and succeeded in several applications.

Blocks using ferrous slag for marine environments have been developed and their application in actual marine environments has begun. Another development is the use of ferrous slag as a water and bottom-sediment decontaminant. The development of the technology as a means of marine environment remediation continues with such efforts as to proliferate oceanic phytoplankton and fix CO_2. Some large-scale tests have been conducted and are brought into practice.

Figure 5: Frontier rock^{TM} (left) and restoration of quay (right) with Frontier rock^{TM}

'Frontier Stone^{TM}' and 'Frontier Rock^{TM}' are made of steelmaking slag hydrated matrix, developed as a substitute of cement concrete block (Figure 5). They have been already applied to practical marine engineering by JFE (JFE steel) and NSSMC (Nippon Steel & Sumitomo Metal Corporation) with authorised report and manual for practical application.

'Marine block^{TM}', developed by JFE, is another marine product that is chemically bound through the carbonation of CaO in the slag. As Marine block^{TM} is covered with calcium carbonate, which is similar to the component of seashells and coral, it has a high affinity to marine life. Several conducted and ongoing experiments in actual sea areas found that Marine block^{TM} is effective for remediation of marine environment such as coral and algae with seaweeds.

'Vivary^{TM} series' of NSSMC, is a products line up of marine materials with the advantage of iron containing steelmaking slag, which artificially regulates the balance of ion in seawater with the help of organic acid. Several experiments in actual marine area proved the positive effect of steelmaking slag on remediation of fertile marine resources.

JISF has been promoting technology for on site construction of shoals in the sea and restoration of depression at the seabed with a mixture of steelmaking slag and soft dredged clay. As dredged clay is hardened by steelmaking slag, it can this way be handled as engineering material without being wasted. Steelmaking slag, additionally, contributes to the improvement of the marine environment; it absorbs dissolved phosphorus, which causes eutrophication when it exists excessively, and suppresses the generation of hydrogen sulphide, which consumes oxygen necessary for aquatic lives. JFE conducted field experiments to examine the effect of steelmaking slag on the suppression of hydrogen sulfide at a secluded part of a harbour in Japan, where often complaints of odour were reported. They reported that the iron ion in steelmaking slag, ferrous and/or ferric, plays a key role in reducing sulfide ions by fixing sulphur as an iron sulphide[7].

The authority also promotes the restoration of the marine environment through effective use of dredged soil and recycled materials, and through the technical development of safety verifications for techniques where steelmaking slag is used in sea and site work.

Our activity now and in the future

The application of slag and the corresponding development of technology in Japan have been focused on civil engineering for one century. However, in order to continue effective use of the slag in the future, we realise the necessity to develop new applications and reclaim market shares to create a stable demand based on social needs, while the investments in construction and civil engineering decrease. The following points are significant activities for NSA to contribute to sustainable growth:

1. Maximisation of the effect on energy saving, resource conservation and reduction of CO_2 emission through the usage of iron and steel slag,

2. Promotion of slag applications to remediate the environment, especially for marine applications. Development of seashore and prevention of disasters were the principal objectives, but the restoration of lost sea area environment will be an important theme in future as well, and

3. Investigation of the hybrid effects by a different combination of steel slag and by the combination with other materials. It produces various good characteristics that were not provided by the simple substance, thereby enabling its utilisation in many aspects.

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