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Invited Review

Recycling of ironmaking and steelmaking slags in Japan and China

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Abstract: The mass production of steel is inevitably accompanied by large quantities of slags. The treatment of ironmaking and steelmaking slags is a great challenge in the sustainable development of the steel industry. Japan and China are two major steel producing countries that have placed a large emphasis on developing new technologies to decrease slag emission or promote slag valorization. Slags are almost completely reused or recycled in Japan. However, due to stagnant infrastructural investments, future applications of slags in conventional sectors are expected to be difficult. Exploring new functions or applications of slags has become a research priority in Japan. For example, the utilization of steelmaking slags in offshore seabeds to create marine forests is under development. China is the top steel producer in the world. The utilization ratios of ironmaking and steelmaking slags have risen steadily in recent years, driven largely by technological advances. For example, hot stage processing of slags for materials as well as heat recovery techniques has been widely applied in steel plants with good results. However, increasing the utilization ratio of basic oxygen furnace slags remains a major challenge. Technological innovations in slag recycling are crucial for the steel industries in Japan and China. Here, the current status and developing trends of utilization technologies of slags in both countries are reviewed.

Keywords: ironmaking; steelmaking; slag; recycling; seawater; stabilization

1. Introduction

Steel is the most important engineering material in the global economy. In 2020, over 1.9 billion tons of crude steel were produced [1], despite challenges from the COVID-19 pandemic. As the backbone of modern society, the steel industry continues to strengthen its innovative capabilities by offering advanced steel products to meet rapidly rising market demands. Concurrently, the steel industry has been working to reduce environmental impacts, i.e., CO_2 gas emission, and to develop and maintain environmentally harmonized processes.

Various byproducts are created from steelmaking, one of which is slag. Gangue phases, e.g., SiO_2 in iron ore, additives, e.g., CaO and MgO, and iron oxide form the basis of ironmaking and steelmaking slags, which become byproducts after molten steel is poured from the furnace. Due to enormous slag volumes, it is necessary to repurpose slags for energy or materials recycling applications. Energy recycling from hot slags can help reduce CO_2 emissions, which is an urgent task for most industrial countries in the world. Although most slags can be recycled efficiently at present, these current technologies may not be applicable in the future due to advancements in industrial structures. Therefore, it is necessary to explore new slag recycling technologies based on the distinct physical or chemical properties of the slag.

Japan and China are two leading steel producing countries. The mass production of crude steel is accompanied by large quantities of slags. Great efforts have been made in both countries to decrease slag emission or promote slag recycling. Here, we review fundamental research as well as current technologies for recycling ironmaking and steelmaking slags in Japan and China as representative examples. Experiences from both countries can be used as a point of reference for other countries.

2. Recycling of ironmaking and steelmaking slags in Japan

2.1. Overview

Table 1 lists typical compositions of different types of slags. Blast furnace (BF) slags are mainly composed of CaO and MgO, which are added as flux agents to decrease liquidus temperatures and to maintain fluidity in the furnace,

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and SiO_2 and Al_2O_3, which enter as iron ore gangue and coke ash, respectively. Since blast furnaces provide highly reducing conditions, the iron oxide content in BF slags is small. In contrast, basic oxygen furnace (BOF) slags contain significant amounts of CaO as a refining flux to absorb impurities, e.g., S and P, in hot metals, as well as iron oxide due to the oxidizing conditions of the BOF needed to convert hot metal to molten steel and to remove impurities via blowing oxygen. Electric arc furnace (EAF) slags also contain iron oxide and CaO, which are introduced during the melting of steel scraps and other iron sources and the refining of molten steel in the furnace. Approximately 20.1 million tons of BF slags and 9.5 million tons of BOF slags were generated in Japan in 2020 (Fig. 1) [2]. The decrease in slag quantities compared with 2019 was largely due to the impact of the COVID-19 pandemic on steel production. The treatment of slags is summarized in Fig. 2 [2]. Around 77% of BF slags are treated by water-quenching, and the obtained BF slag sands are used in cement production. The remaining slags are treated by slow-cooling in slag yards, and the obtained hard slag rocks are crushed, classified in suitable size ranges, and used as road-bed and concrete aggregate materials. In contrast, approximately 25% of BOF slags are recycled within ironmaking or steelmaking plants as various materials, e.g., flux agents in sintering processes to partially replace CaO or in hot metal pretreatment processes as iron oxide sources. The remaining slags are mostly treated by slow-cooling in slag yards and subsequently used in civil engineering as alternative materials for natural rocks.

Table 1. Typical compositions of blast furnace (BF) slags, basic oxygen furnace (BOF) slags, and electric arc furnace (EAF) slags wt%

Slag type	T.Fe	CaO	SiO_2	P_2O_5	MgO	Al_2O_3
BF slag	0.4	41.7	33.8	0.1	7.4	13.4
BOF slag	17.4	45.8	11.0	1.7	6.5	1.9
EAF slag	29.5	22.8	12.1	0.3	4.3	6.8

Note: Data source, Nippon Slag Association.

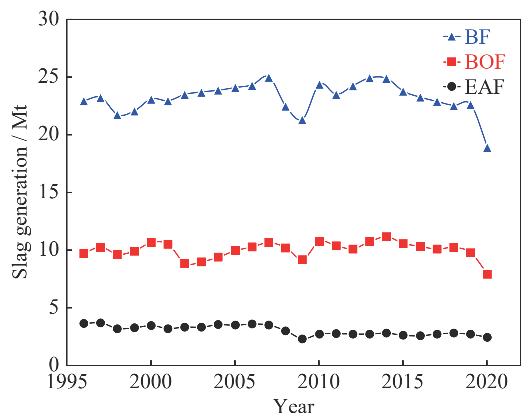

Fig. 1. Slag generation in Japan in recent years [2].

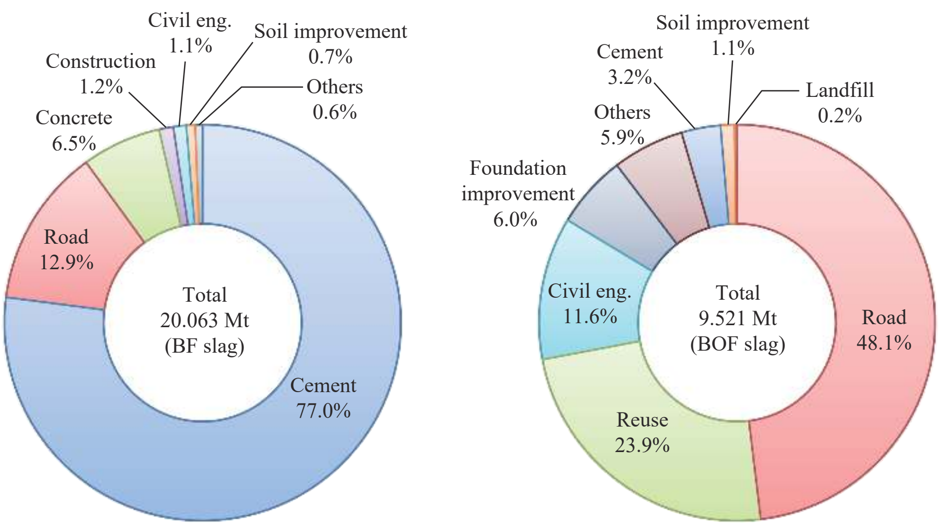

Fig. 2. Utilization of BF and BOF slags in Japan in 2020 [2].

In general, complete recycling routes for BF slags have been established. However, recycling BOF slags is not straightforward due to unreacted or precipitated CaO phases. Furthermore, due to the reduction of investments in Japanese infrastructure, extended applications of BOF slags in conventional sectors are unlikely.

The Iron and Steel Institute of Japan (ISIJ) has conducted research to minimize the generation of ironmaking and steelmaking slags, as well as to effectively utilize and recycle those industrial byproducts. Recent research activities by the ISIJ in the last two decades are listed in Table 2. These research programs were operated by both academic researchers and industrial engineers, who investigated targeted research topics with fundamental scientific and practical engineering viewpoints, respectively. Beneficial results obtained via these activities have been widely shared by all individuals and corporate members of the ISIJ and further disclosed through presentations at ISIJ annual meetings and publications in journals published by the ISIJ (ISIJ International and Tetsu-to-Hagané).

As shown in Table 2, there has been a focus on the preparation of novel functional materials from ironmaking and

Table 2. Recent research activities on steel slag by the ISIJ

Project period	Research project
2004–2007	Utilization of byproducts from steel manufacturing processes by hydrothermal synthesis
2005–2008	Innovative development of refining processes in steelmaking by multi-phase fluxes
2008–2010	Process simulation for the dephosphorization of pig iron by multi-phases
2010–2012	Utilization of steelmaking slags in coastal environments
2012–2014	Rehabilitation of field areas on the coast damaged by the tsunami
2013–2015	Optimal slag formation to promote lime dissolution
2016–2018	Control of the solidification microstructure of steelmaking slags for the suppression of alkali component elution
2017–2019	Production of highly clean Cr-alloyed steel by controlling slags and inclusion
2018–2021	Artificial phosphorus ore originating from slags
2019–2021	Effective utilization of phosphorus oxide in steel slags

steelmaking slags, the development of new refining processes for slag generation reduction, the control over physical and chemical properties of slags, and the innovative application of slags to maximize the utilization of chemical constituents. Since ironmaking and steelmaking slags can be considered as a stably supplied local resource with well-controlled physical and chemical properties, the full-scale application of slags would lead to conservation of natural resources, and thus a reduction of global greenhouse gas emission.

Recovery of thermal energy associated with ironmaking and steelmaking slags is an important issue, and various technologies have been developed to address this issue. Recently, a novel method was reported from the COURSE50 national project conducted by Japanese steel producers [3]. A twin roll method for slag solidification and a packed bed method for heat exchange from slags to air were combined for the efficient recovery of sensible heat from slags [4]. Molten slags were shaped into thin sheets to enhance heat transfer from slags to the heat recovery equipment. This method recovered more than 30% of the thermal energy from BOF slags. However, due to the limited value of recovered thermal energy from 300 to 850 K, the application of this method is yet to be determined.

In order to enhance the utilization ratio of BOF slags, new technologies are being developed by researchers in Japan. One solution is to reduce the generation of BOF slags by optimizing refining processes. We have reported a resource and energy-saving process for dephosphorization using a multi-phase flux. This multi-phase flux dephosphorization reaction has been studied from a variety of viewpoints [5−18], e.g., the reaction behavior of phosphorus [5−10], phase relationships [11−14], and thermodynamics [15−17]. This novel refining process using multi-phase flux is expected to have less CaO consumption and slag emission, and energy-saving effects.

Another solution for BOF slag issues is to explore new applications. Recently BOF slags have been recognized as an effective source of nutrient elements for the recovery of the coastal environment from desertification. BOF slags can be processed into underwater fertilizers, which can release soluble nutrients to improve the growth of seaweed (Fig. 3). We have recently conducted fundamental studies to clarify the dissolution behavior of Si, P, and Fe from BOF slags into seawater to develop a new method of utilizing BOF slags in seawater [19−20]. We studied the enhancement effects of adding gluconic acid [21−23], blending with dredged soil [24], and slag carbonization [25−26] on the dissolution of elements. Long-term dissolution behaviors of steelmaking slags and slag-additive mixtures in seawater were also studied [27]. Here, we briefly discuss the major findings of these studies.

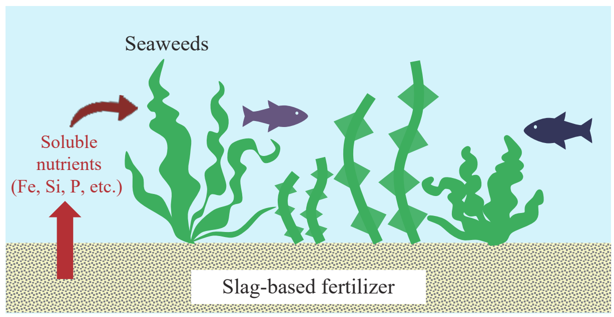

Fig. 3. Utilizing BOF slags in seawater to improve seaweed growth.

2.2. Utilization of BOF Slags for the rehabilitation of coastal environments

2.2.1. Dissolution behavior of BOF slags in seawater

Shaking experiments were conducted at room temperature controlled by an air conditioner. The shaking speed was 160 cycles·min^{-1} with an amplitude of (20 ± 5) mm, and the shaking duration was varied in the range of 1 to 10 d. A prescribed amount of slag and 100 cm^3 of artificial seawater were put in a 250 cm^3 polyethylene bottle based on the ratio of slag and seawater between 0.2 and 2 g per 100 cm^3. After the prescribed experimental time, the pH, and concentrations of the dissolved elements were measured using inductively-coupled plasma optical emission spectrometry (ICP-OES). Table 3 lists the chemical compositions of a synthesized BOF slag. Table 4 lists the chemical composition of the artificial seawater, which was prepared by dissolving raw seawater material into distilled water. Seawater was aerated prior to the shaking experiment to reach equilibrium with the ambient atmosphere.

The concentration change of Si, P, and Fe versus the shak-

Table 3. Chemical compositions of a synthesized BOF slag wt%

FeO	CaO	SiO_2	P_2O_5	CaO/SiO_2
30.0	33.8	33.7	2.5	1.0

ing time is shown in Fig. 4 [19]. The concentration of Si (C_{Si}) showed a clear trend and increased with both time and slag/seawater ratio. The concentration of P (C_P) increased with an increasing slag/seawater ratio but showed a minimal increase with time after the first day. Similarly, there was no apparent change for the dissolution of Fe after the first day. The experimental results also indicated that the CaO/SiO_2 mass ratio of the slag had a significant impact on the dissolution behavior of the elements.

2.2.2. Effect of adding gluconic acid into seawater

Multiple approaches were considered to improve the dissolution of nutrient elements into seawater from steelmaking slags. Enhanced dissolution of nutrient elements, especially Fe, was expected by creating slag-based composite materials to supply organic acids, which have a chelating effect on the dissolving species. Therefore, the effect of gluconic acid, a biologically essential organic acid, on the dissolution behavior of nutrient elements from slags into seawater was investigated. Gluconic acid, i.e., 2,3,4,5,6-pentahydroxyhexanoic acid or $HOCH_2[CH(OH)]_4COOH$, has a large dissociation constant in water and is extremely water-soluble. Shaking experiments were conducted in batches as previously described. The shaking speed was 160 cycles·min^{-1} with an amplitude of (20 ± 5) mm, and the shaking duration varied from 1 to 96 h (4 d). Artificial seawater containing up to 0.50 g·L^{-1} of gluconic acid was prepared in advance. One gram of slag was added into 100 mL of artificial seawater-gluconic acid solution in a 250 cm^3 polyethylene bottle.

Table 4. Chemical composition of artificial seawater

Constituent	Concentration / (mg·L^{-1})
NaCl	22100
$MgCl_2·6H_2O$	9900
Na_2SO_4	3900
$CaCl_2·2H_2O$	1500
KCl	610
$NaHCO_3$	190
KBr	96
Others	95

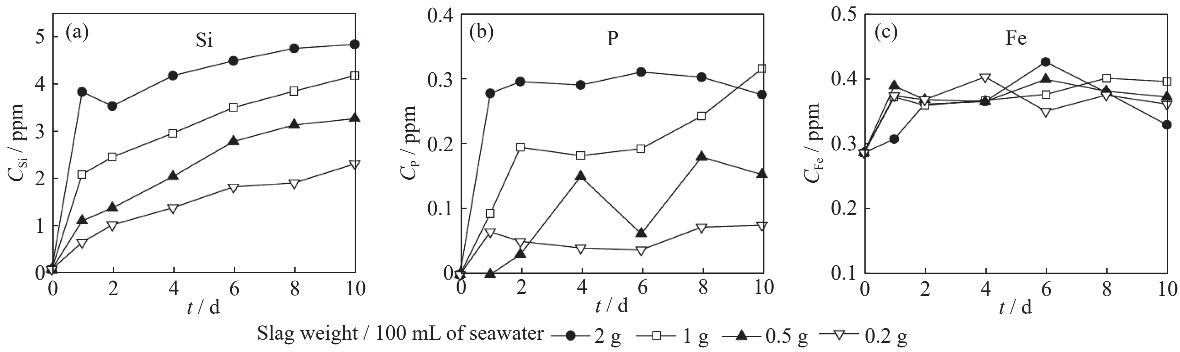

Fig. 4. Concentration change of Si (a), P (b), and Fe (c) versus shaking time for a synthesized slag immersed in seawater [19].

Fig. 5 shows the concentration change of Si and Fe versus shaking time for a synthesized slag (Table 1) immersed in seawater with the addition of gluconic acid [22]. The elements exhibited a similar trend, i.e., the concentration increased monotonically with shaking time. The addition of gluconic acid improved the dissolution of Si and Fe due to the chelating effect. The dissolution rate and amount increased with increasing gluconic acid concentration. The enhancement effect of gluconic acid on Si dissolution is attributed to the formation of silica hydrate, which has a larger solubility, and the effect on the dissolution of Fe is attributed to the formation of iron-gluconate complexes.

2.2.3. Dissolution of BOF slags into fresh water containing gluconic acid

This study aimed to quantitatively evaluate the influence of organic acids on the dissolution behavior of steelmaking slags in aqueous environments. To understand the physical chemistry of the dissolution process, laboratory-scale experiments were conducted using fresh water containing only gluconic acid to eliminate the complex influence of coexisting salts.

Shaking experiments were carried out using a 100 cm^3 gluconic acid aqueous solution and 1 g of artificial glassy slag powder. Three kinds of artificial glassy slags were prepared from reagent grade chemicals, and all slags contained 3wt% FeO, and the CaO/SiO_2 mass ratio was 1. Sample A and sample P contained 5wt% Al_2O_3 and 5wt% P_2O_5, respectively, while sample O was composed of only CaO, SiO_2, and FeO. After the prescribed experimental time, the pH and ORP of the solution were immediately measured, followed by filtration with a 0.45 μm pore membrane filter, and the concentrations of the dissolved elements were quantitatively analyzed.

The change in concentration of Fe dissolved from an artificial glassy slag is shown in Fig. 6 [23]. The effect of gluconic acid on the enhancement of Fe dissolution was clearly demonstrated. The change in concentrations of other elements showed a similar trend, i.e., the concentration increased monotonically with increasing gluconic acid concentration. The effect of gluconic acid addition was particularly significant on the increase of Fe concentration.

As explained in our and others' previous studies, gluconic

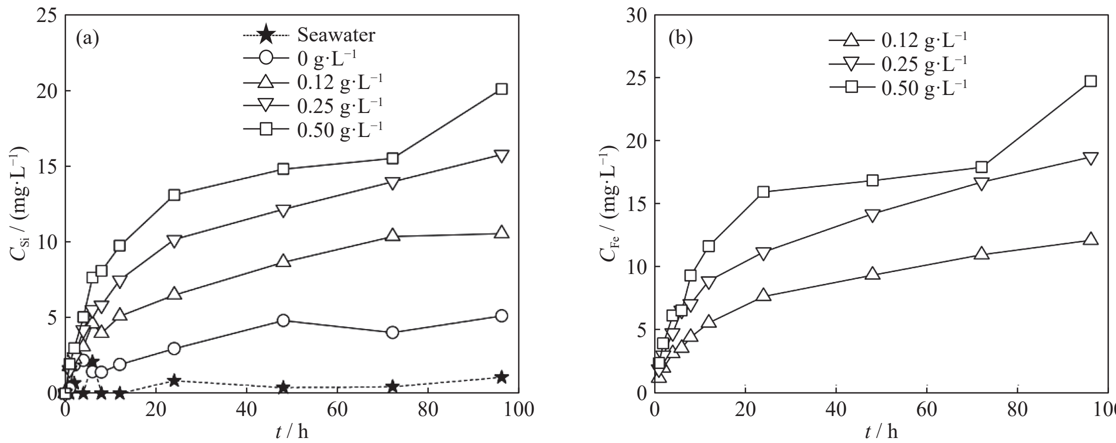

Fig. 5. Concentration change of Si (a) and Fe (b) versus shaking time for a synthesized slag immersed in seawater with the addition of gluconic acid. Reprinted by permission from Springer Nature: *J. Sustain. Metall.*, Enhancement of the dissolution of nutrient elements from steelmaking slag into seawater by gluconic acid, X.R. Zhang, H. Matsuura, and F. Tsukihashi, Copyright 2015.

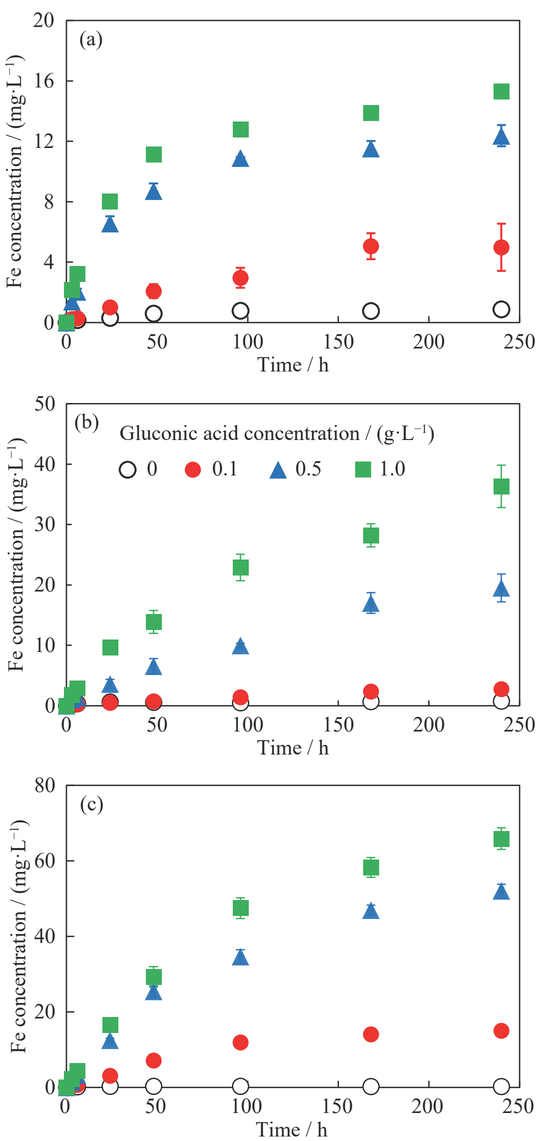

Fig. 6. Change in concentration of Fe with time: (a) sample A; (b) sample P; (c) sample O [23].

acid is well known as a strong chelating agent, and the increase in Fe concentration by adding gluconic acid is due to this effect. However, a quantitative analysis of the dissolution behavior is necessary to understand the dissolution mechanism of steelmaking slags in aqueous environments and to control the dissolution behavior to adequately maximize steelmaking slag used as a rehabilitation material. Thus, the dissolution mechanism was discussed by estimating dissolved species.

Fig. 7 shows the change in the mass ratio of dissolved FeO to dissolved CaO with time [23]. In the absence of gluconic acid, the elution ratios of SiO_2, FeO, Al_2O_3, and P_2O_5 to CaO were smaller than those of the slags, particularly the dissolution ratio of FeO. On the contrary, the dissolution ratios changed to be similar to the slag composition, except for Al_2O_3. Oxides were selectively dissolved in fresh water from the slag (preferential dissolution of CaO), while the dissolution behavior changed to congruent dissolution by the addition of gluconic acid.

The types and concentrations of dissolved species were estimated using formation reactions of the metal chelates in solution. The equilibria of hydration and chelation reactions of Ca, Si, Al, Fe, and P with gluconic acid (hereafter denoted as HGH_4) were calculated at 298 K using the analyzed concentrations of the solutions. Equilibrium between the inorganic ions and hydration reactions is expressed by Eqs. (1) to (3). The chelation reaction equations of Ca, Al, and Fe with gluconic acid and the equilibrium constants (K) of those reactions are shown in Eqs. (4) to (9). The dissolution reaction of gluconic acid in water and the acid dissociation constant is shown in Eq. (10). Equilibrium constants were calculated using standard Gibbs free energies of formation. Detailed calculation procedures and necessary physicochemical data are reported elsewhere [23].

$$A^{n+} + mH_2O = A(OH)_m^{(n-m)+} + mH^+ \quad (1)$$

$$BH_m^{n-} = B^{(n+m)-} + mH^+ \quad (2)$$

$$H_mXO_4^0 = H_{(m-n)}XO_4^{n-} + nH^+ \quad (3)$$

$$Ca^{2+} + GH_4^- = Ca(GH_4)^+, \lg K_{(4)} = 1.22 \quad (4)$$

$$Al^{3+} + GH_4^- = Al(GH_4)^{2+}, \lg K_{(5)} = 1.98 \quad (5)$$

$$Al(GH_4)^{2+} = Al(GH_3)^+ + H^+, \lg K_{(6)} = -2.87 \quad (6)$$

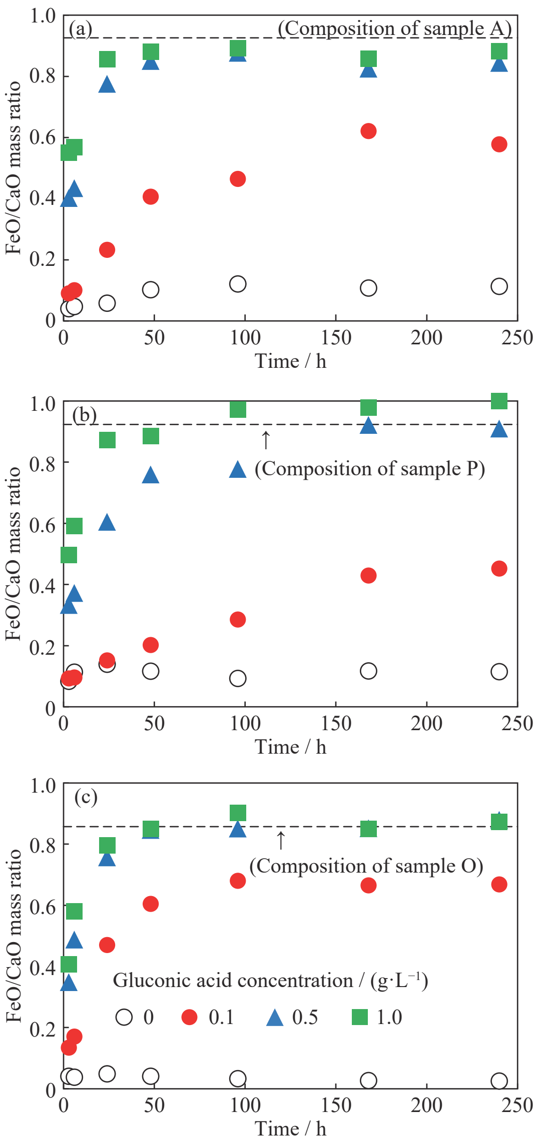

Fig. 7. Change in ratio of dissolved FeO to CaO with time: (a) sample A; (b) sample P; (c) sample O [23].

$$Al(GH_3)^+ = Al(GH)^- + 2H^+, \lg K_{(7)} = -9.29 \quad (7)$$

$$Fe^{2+} + GH_4^- = Fe(GH_4)^+, \lg K_{(8)} = 1.0 \quad (8)$$

$$Fe^{3+} + GH_4^- + 4OH^- = Fe(G)^{2-} + 4H_2O, \lg K_{(9)} = 37.2 \quad (9)$$

$$HGH_4 = H^+ + GH_4^-, \lg K_{(10)} = -3.60 \quad (10)$$

The calculated ratio of existing forms of gluconic acid is shown in Fig. 8. Even after 240 h of dissolution experiments, more than 90% of gluconic acid is in the gluconate ion (GH_4^-) form, which indicates that the dissolution of FeO is not limited by the concentration of gluconic acid.

Fig. 9 shows the relationship between the ratio of chelated Fe ions and pH. The ratio significantly increased with increasing pH. Our recent study comparing different types of organic acids revealed that the influence of solution pH on the chelation ratio of Fe depends on the type of organic acid. Therefore, understanding the characteristics of organic acids is crucial for using organic acids effectively to enhance the dissolution of elements from steelmaking slags since the pH of aqueous solutions of steelmaking slags mostly increases

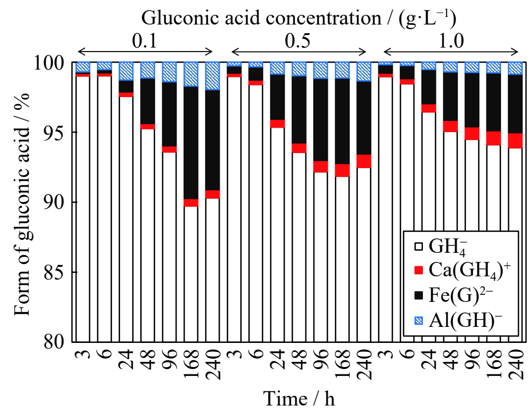

Fig. 8. Forms of gluconic acid after the dissolution of sample A [23].

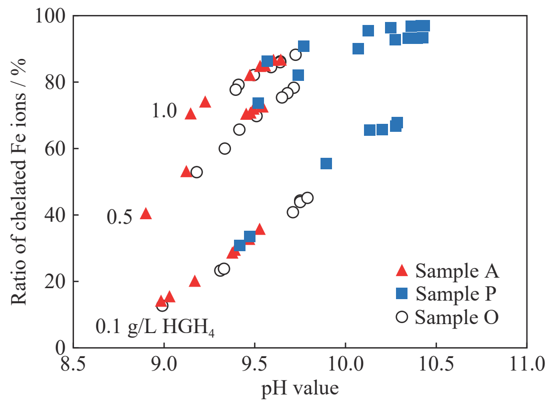

Fig. 9. Relationship between the ratio of chelated Fe ions and pH [23].

due to the dissolution of CaO.

2.2.4. Effects of blending BOF slags with dredged soil

In a study by Hayashi *et al.* [28], a positive effect of blending steelmaking slags with dredged soil on the rehabilitation of coastal environments was observed. The growth of seaweed can be enhanced from the supply of nutrient elements from the mixture of steelmaking slags and dredged soil. In the present study, synthesized steelmaking slags were mixed with dredged soil collected from an inner harbor in Japan [24]. The dried soil was composed of SiO_2 and NaCl phases according to X-ray diffraction (XRD) characterization. Approximately 0.5 to 3 g of slag was mixed with 8 g of dredged soil in a 250 cm^3 polyethylene bottle. After curing in a fume cupboard for 24 h, 100 cm^3 of seawater was added to the bottle and mixed until it was completely turbid. The conditions of the shaking experiments were identical to previous sections.

A positive effect of soil addition on the dissolution of Si was observed compared with the results without soil addition. Since the dissolution of Si from slags or soil is negligibly small, the enhanced Si dissolution was likely due to the blending. A similar trend was observed for P, yet the improvement was not as apparent as that of Si. The concentration of P also increased with the increase of slag amount in the mixture. In the case of Fe, the blending effect was also apparent. The concentration increased during the initial shaking period and decreased gradually after reaching a maximum at ca. 12 h.

2.3. Summary

Developing new functions of BOF slags is crucial to establishing sustainable steel production in Japan. BOF slags have the potential to be utilized for the rehabilitation of coastal environments. Laboratory-scale experiments to understand the dissolution behaviors of Si, P, and Fe into fresh water and seawater were conducted using synthesized slags. Positive effects of adding gluconic acid and blending slag with dredged soil on the dissolution of Si, P, and Fe were observed. These results indicate that the rehabilitation of coastal environments using steelmaking slags is promising.

3. Recycling of ironmaking and steelmaking slags in China

3.1. Overview

Fig. 10 shows the recent output of BF and BOF slags in China [29]. Slag quantities are rising steadily along with the fast growth in crude steel production. In 2019, the outputs of BF and BOF slags in China reached 283 and 149 million tons, respectively [29–31]. Fig. 11 shows the change of valorization ratios of slags in recent years [29]. Here the percentage of slags reused as a resource or material after dressing steel particles and iron oxides is defined as the valorization ratio. The ratios for both BF and BOF slags rise year after year, driven largely by technological advances. For BF slags, the valorization ratio increased from 65% in 2006 to 85% in 2018. For BOF slags, despite a lower value, the valorization ratio also rose and tripled from 10% in 2006 to 30% in 2018. However, both ratios are still far below the initial set targets. Recently, along with intensified government-led efforts to tackle environmental and resource issues, a series of technical routes, management modes, valorization standards, and environmental regulations for the utilization of BF and BOF slags have been established. Fundamental studies and technological innovations are conducted at different scales by research institutes, universities, and steelmakers, with expected breakthroughs in the near future. In this section, current technologies and ongoing research on slag valorization in China are discussed.

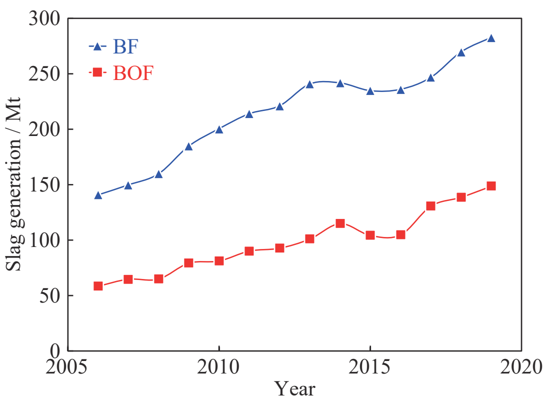

Fig. 10. Slag generation in China in recent years [29].

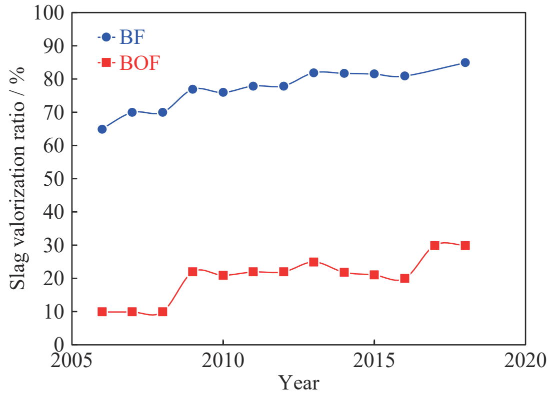

Fig. 11. Change of valorization ratios of BF and BOF slags in China in recent years [29].

3.2. Hot stage processing of BF slags in China

3.2.1. Processing BF slags by water quenching

Different processes have been developed to granulate BF slags. The common feature of these methods is that molten BF slags are poured through a high-pressure water jet or a rotation drum close to the blast furnace. After accelerated water cooling, BF slags turn into vitreous solidified slag sands. A slag granulation technology called INBA or modified INBA developed by Paul Wurth at the beginning of the 1980s is the most popular process for hot stage slag treatment of large-scale BFs. Due to high reliability, low sulfur emissions, and limited water consumption, the first INBA process in China was introduced by Baosteel for the No. 2 blast furnace (4063 m^3) in 1991 [32]. Subsequently, Wuhan Steel, Ma'anshan Steel, Benxi Steel, and Taiyuan Steel also introduced the INBA process.

WISDRI Engineering & Research Incorporation Limited developed a modified INBA process. The distance from the granulation box to the process tank was lengthened by a 7-m long channel to allow a complete reaction of the hot slag with the water stream. The filtering capacity of the drum was improved and was suitable for 10 $t \cdot min^{-1}$ to a maximum of 14 $t \cdot min^{-1}$. The steam condensing ability was also enhanced to minimize the outside emission of steam. The water flow rate for slag granulation was 2000 $m^3 \cdot h^{-1}$. Granulated BF slags contained less than 15% water and more than 95% vitreous phases compared with dried slags. Until June 2012, there were nine sets of modified INBA units employed in six blast furnaces with sizes ranging from 1800 to 5800 m^3. In 2019, the newly built Shougang Jingtang No. 3 BF (5500 m^3) adopted a drum-type slag treatment technology based on the INBA principle. The size of the drum was ϕ5 m × 8.34 m, and the structure of the filter was improved. The driving power was enhanced to eliminate the potential running breakdown of the drum under extreme conditions. The slag granulation water was circulated, and thus the heat was recovered from the steam. Combined with other measures, the operation efficiency of slag granulation systems has been improved greatly [33].

3.2.2. Heat recovery from BF slags by dry granulation

Even though certain parts of slags can be valorized as resources, the sensible heat in all kinds of molten slags is almost always wasted. The energy consumption of the steel industry accounts for around 10% to 15% of the total energy consumption in China. An estimation showed that 2.7×10^8 GJ heat, i.e., 9.2 million ton coal equivalent (CE), was wasted in BF slags in 2010 [34]. Therefore, the heat recovery of BF slags is necessary for energy saving and emission reduction in the Chinese steel industry.

Different from the technology developed by steelmaking companies in Japan [4], Dry slag granulation (DSG) is a popular technology to recover heat from BF slags in China [35]. The process produces slag granules suitable for cement making and hot air for heat recovery. DSG shows multiple advantages over water quenching method in saving energy and reducing emissions [36]. Duan *et al.* [37] reviewed the research progress of centrifugal granulation of BF slags. A landmark agreement between the CSIRO and the Beijing MCC Equipment Research & Design Corporation was signed in March 2015 to promote the implementation of the DSG process. So far, this project has progressed well, and the below sub-projects have been completed: (1) core technology of rotation disk dry granulation and heat recovery for BF slags, (2) main equipment design and manufacturing, (3) core control units, and (4) industrial tests and demonstrations of the process [38]. A Strategic Cooperation Agreement on dry granulation of BF slags and waste heat recovery was signed between the Beijing MCC Equipment Research & Design Corporation and Anyang Iron and Steel Group Co., Ltd. on July 16th, 2021.

There are also alternative technologies under development. Chen *et al.* [38] reported a molten slag dry granulation and heat recovery process, which was verified by the Chongqing Saidi Smelting Equipment System Integrating Engineering and Technology Research Center with their pilot scale test. This pilot scale process combined a centrifugal granulation unit and a self-flow packed bed waste heat boiler. The advantage of this process is that no air blowing or direct water cooling is used. After recovering heat, the remaining residue can be recycled in a cement plant. The pilot scale test demonstrated the considerable economic and environmental benefits of this molten slag granulation and heat recovery process.

3.3. Hot stage processing of BOF slags

3.3.1. Pyrolytic self-slaking process

There are seven main technological routes for BOF slag stabilization in China [39]. The pyrolytic self-slaking process developed by Jingye Eng. Corp. Ltd. is the most widely employed method. In this process, molten slags are poured into a sealed tank, followed by water spray to generate steam, which reacts with free lime and magnesia to stabilize the slag. The stabilized slag can be recycled in different ways after size reduction. Due to the good stability, wide suitability of the treated slags, and the high recovery yield of steel grains from residual slags, the pyrolytic self-slaking process is well accepted by steelmakers in China. With consistent research and innovation, this technology has evolved into its fourth generation. The working pressure in the reaction chamber is approximately 0.4 MPa. The whole process takes around 1.5 to 3 h. The capacity of treated slags for one pool is approximately 200 to 250 t during this time period. The content of free CaO in the treated slags is less than 2.5wt%, and the immersion expansion ratio is less than 1.5%. More than 70% of the treated slag grains are smaller than 20 mm. The fume concentration of the emitted gas is less than 10 $mg \cdot m^{-3}$, which satisfies environmental requirements and regulations. Since water steam is also generated, the pilot scale experiment demonstrated the possibility to generate a power of 3 to 5 $kW \cdot h \cdot t^{-1}$. From 2012 to 2019, 54 sets of the fourth generation "pressurized pyrolytic self-slaking process" were adopted by 26 steelmaking plants in China and abroad.

3.3.2. Baosteel's slag short flow (BSSF) process

Development of the BSSF slag process was initiated by Baosteel in 1995, based on imported technology from the Russian Ural Steel Academe. The first BSSF slag processing system was built in Baosteel's 250 t BOF plant in May 1998 [40]. The BSSF process treats high temperature molten slag in a special rotating cylinder. Under the combined effects of mechanical forces from steel balls and water chilling, the molten slag is rapidly quenched and crushed. The slaking of free CaO and MgO in the slags is completed in a short time. The formed BSSF granulated slags are small in size and stable. Additionally, steel particles can be effectively separated using magnetic separation [41].

The BSSF slag processing technology can be potentially applied to treat stainless steelmaking slags, which is challenging due to environmental issues. High free CaO and MgO content in stainless steelmaking slags cause serious dusting when slags are soaked. Unstable hexavalent chromium in stainless steelmaking slags dissolves easily in water and causes water pollution. Due to the high cooling speed of the BSSF slag process, stainless steelmaking slags can be quickly stabilized, and the free CaO content is reduced, and the formation of hexavalent chromium-containing compounds ($CaCrO_4$) and dusting can be minimized. Industrial experiments treating EAF and stainless steelmaking slags using the BSSF slag process have been conducted with satisfactory performances. No hexavalent chromium was detected in the circulated water [42]. These results demonstrated the efficacy of the BSSF process in treating stainless steelmaking slags.

Due to excellent performances, the BSSF process was introduced to many steelmaking plants in China and abroad, including POSCO, India JSW, and Tata Steel. A total of 54 sets of BSSF equipment are now in operation worldwide, and the treatment capacity is about 9 million tons of steelmaking slags per year.

3.4. Ongoing researches

Aiming at higher efficiency for the comprehensive utilization of energy and mass of slags, new technologies are under developing. Due to the large quantity of slag emission in China, technologies with the potential capacity of massive treatment are investigated with priority.

Efficient recovery of heat from steelmaking slags is targeted by a few researchers. The dominant technology, pyrolytic self-slaking process, can recover a portion of heat as water vapor, yet the heat recovery ratio is quite low, because water with a low boiling point is not a good medium for heat storage. Sun *et al.* [43–44] proposed a concept of integrating heat recovery with coal or biomass gasification. The heat in the slags can be directly utilized to gasify coal or biomass to generate syngas, with oxide components playing the role of catalysts. It was claimed by the authors that the heat recovery ratio will be much higher. Chen *et al.* [45] proposed a three-stage heat exchange method to treat steelmaking slags. According to theoretical analysis and simulation, the authors estimated that more than 80% heat in molten steelmaking slags can be recovered by this technology. These new proposals or concepts suggest the possibility to realize an efficient heat recovery from steelmaking slag. However, commercial application is still a long way to go. More experimental works or tests are needed to demonstrate the prospect and the technical feasibility.

As mentioned in the previous section, the valorization ratio of steelmaking slags in China is very low (Fig. 11). Therefore, research is more focused on materials recycling technologies from steelmaking slags compared with that on heat recovery. Processing steelmaking slags into bulk commodities is the mainstream direction, reflecting the urgent needs to find a method of massive slag treatment in the country. Steelmaking slags have the potential to be applied in preparing construction materials, if free CaO or MgO in the slag can be stabilized or removed. It is considered that grinding slags into fine powders may mitigate the negative influence of alkali oxides and promote the slag application [46]. Tian *et al.* [47] utilized steelmaking slag powder together with cement to produce road concrete. Fluidity test indicated a good compatibility of the slag powder with other components. Developing a cost-effective process for slag grinding or exploring value-added applications of these slag-derived fine powders are the key issues to be addressed for commercialization. Due to the components of SiO_2 and Al_2O_3, preparing ceramics from steelmaking slags is another technology choice. He *et al.* [48] produced a new type glass–ceramic by melting the mixture of steelmaking slag and SiO_2. The obtained material showed an excellent bending strength and very nice wear resistance. These glass–ceramic materials prepared from steelmaking slags can be used as building and decorative materials. Li *et al.* [49] prepared porous ceramics from steelmaking slags by controlling the composition and sintering temperature without pore-forming agents. These porous ceramics can be used as filtering materials for environment remediation.

Some strategic elements can be found in steelmaking slag. One of these elements is P, which is essential to all forms of life. P fertilizers determine the food production, while P chemicals are indispensable to high-tech devices in modern industry. China is the largest producer of P derivative products. However, the natural resource is depleting. Steelmaking slags containing a certain amount of P are regarded as the potential artificial P mineral. Therefore, recovery of P from steelmaking slag is drawing more attentions. Du *et al.* [50] adopted the method of acid leaching to extract phosphate from dephosphorization slags. The recovery efficiency was reported to be as high as 95.8%. Limitation of this method is that the recycled phosphate fertilizer is not marketable yet due to quality concerns. Yang *et al.* [51] proposed a concept of molten salt processing to recover P from steelmaking slags. Phosphate in the slags can be leached in the molten slat to form soluble ions, which can be converted to elemental P with high added-value by electrochemistry. However, practicability remains to be tested by more in-depth investigations. Combination of both methods (acid leaching and molten salt processing) may formulate a more efficient approach for P recovery.

Although most of these researches are conducted by theoretical estimation or in a bench-scale, and processes with assured application prospect are still lacking, it is highly expected that with sufficient research input in fundamental issues, breakthroughs will be made in a near future.

3.5. Challenges of slag utilization in China

After processing steelmaking slags, large particles containing steel and slag powder with high iron oxide content are generally recycled back into steelmaking plants as raw materials. However, the recycling ratio is not greater than 30%, which means that 70% of steelmaking slag tailings need to be utilized outside of plants. The Chinese government has issued dozens of national standards to improve slag recycling in different industry sectors, including cement, concrete, engineering, road, and other sectors. However, there are still remaining problems and shortcomings. National standards do not match well with industry sectors, and different processing technologies in different steel plants result in different slag properties. Additionally, steelmaking slags are not economical compared with other substitute materials, i.e., slag processing is complex and high cost. Technological innovations and breakthroughs are necessary to solve the slag valorization problem.

3.6. Summary

Heat recovery technology for BF slags in China is progressing gradually toward concurrent materials recycling and energy recovery. The BOF slag pyrolytic self-slaking process has made significant advancements to the industry and is applied in a large number of steelmaking plants in China. Fundamental studies and process developments are still in progress to achieve the comprehensive utilization of slags.

4. Conclusions

Japan and China are leading steel producing countries. The mass production of crude steel is accompanied by large quantities of slags. Both countries have placed a great emphasis on developing new technologies to decrease slag emission or promote slag valorization. Here, we reviewed the current status and developing trends of recycling technologies of slags in Japan and China. Japan has focused on fundamental studies to explore innovative applications of slags, whereas China pays more attention on optimizing existing technologies to advance recycling efficiencies. Processing slags into underwater fertilizers used in offshore areas is an efficient route for long-term and large-scale utilization. Overcoming the engineering barriers of dry granulation of BF slags may lead to simultaneous materials and energy recovery. The newly developed pressurized pyrolytic self-slaking process may solve the problem of free CaO in BOF slags for comprehensive recycling. Communication and collaboration between researchers from Japan and China are expected to significantly advance the field.

In general, the recycling of slags is conducted based on physical properties such as strength. It is necessary to promote recycling by utilizing chemical properties such as slag constituents as well as the thermal energy recovery of slags. The comprehensive utilization of ironmaking and steelmaking slags by technical innovations is essential for sustainable steel production.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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