Xu Gao, Shin-ya Kitamura

Utilization of steelmaking slag in Japan and the recent progress towards soil amendment

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan.

Abstract

In Japan, about 40 million tons of slags are generated during iron and steelmaking process annually, thus investigations into the effective utilization of such large amount of by-product always attract attentions. In this paper, the production, chemical characteristics and recent utilization of slag in Japan, especially steelmaking slag, were reviewed. Both converter slag and electric arc furnace slag are mainly utilized for road and civil construction, ground improvements and reuse in the steel plant. Other utilization purposes in marine environment such as preventing the eutrophication of phosphorus or suppressing the activity of sulfate reducing bacteria have been investigating. On the other hand, with the perspective of extracting valuable elements, research has also been conducted on the recovery of Mn and P from slag. After the great Tohoku earthquake and subsequent Tsunami happened in 2011, the requirement for the reconstruction of roads and ports, as well as for the recovery of damaged farmland, has greatly drawn attention to the utilization of the slag. In particular, the application of steelmaking slag as fertilizer and soil improvement agent during the recovery of damaged paddy fields has been studied actively.

1. Survey of slag production and utilization in Japan

In Japan, almost 100 million tonnes of steel are produced every year, and along with this production, about 40 million tonnes of various slags are generated [1]. For iron making, about 300 kg of blast furnace slag are generated when producing 1 tonne of iron. For steel making, about 100 to 150 kg/tonne-steel converter slag is discharged, and this by-product contains not only the converter slag but also the slag generated during hot metal pretreatment. When scrap is used as the main raw material for steelmaking, about 120 kg/tonne-steel of electric arc furnace slag is generated.

The main chemical compositions of classified ironmaking and steelmaking slag are listed in Table 1 [1]. For the slags that have been used under reducing atmosphere during refining, such as blast furnace slag and the reducing slag of electric furnace slag, the compositions of the slag mainly consist of CaO-SiO_2-Al_2O_3 ternary system. On the other hand, for the slags used under oxidizing atmosphere, the slag mainly consists of CaO-SiO_2-FeO_x ternary system.

Table 1: Typical chemical compositions of slag in iron and steel industry of Japan [1]

Type / Com- -ponent	Blast furnace slag (mass%)	Converter slag (mass%)	Electric arc furnace slag (mass%)	
			Oxidizing slag	Reducing slag
CaO	41.7	45.8	22.8	55.1
SiO_2	33.8	11.0	12.1	18.8
T-Fe	0.4	17.4	29.5	0.3
MgO	7.4	6.5	4.8	7.3
Al_2O_3	13.4	1.9	6.8	16.5
S	0.8	0.06	0.2	0.4
P_2O_5	<0.1	1.7	0.3	0.1
MnO	0.3	5.3	7.9	1.0

Normally, blast furnace slag is either quenched by water (granulated slag) or slowly cooled in air. In 2013, nearly 82% of the blast furnace slag was quenched by water [2]. Converter slag and electric arc furnace slag are generally slowly cooled at a slag yard in air.

Almost 72% of blast furnace slag is used as cement, and other main uses are road material and concrete [2]. Similarly, both the converter slag and the electric arc furnace slag are mainly utilized for road and civil construction, ground improvement and reuse within the steel plant. Because overall steel production via electric arc furnaces in Japan is around 23% [2], the generated amount of converter slag is larger than that of electric arc furnace slag.

In Japan, before decarburization, hot metal pretreatment to remove Si, P, and S is widely used. Therefore, “converter slag” represents a general designation for desiliconization slag, desulfurization slag, dephosphorization slag, and decarburization slag. In this paper, these slags referred to as “steelmaking slag”. Figure 1 shows the main chemical compositions of steelmaking slags [3]. The different slags can be distinguished by variations in the iron oxide concentrations and CaO/SiO_2 ratios. Consequently, the chemical compositions of steelmaking slag vary over a wide range; this makes the slag treatment more complex but also leads to more possibilities and larger potentials on the way to valorization.

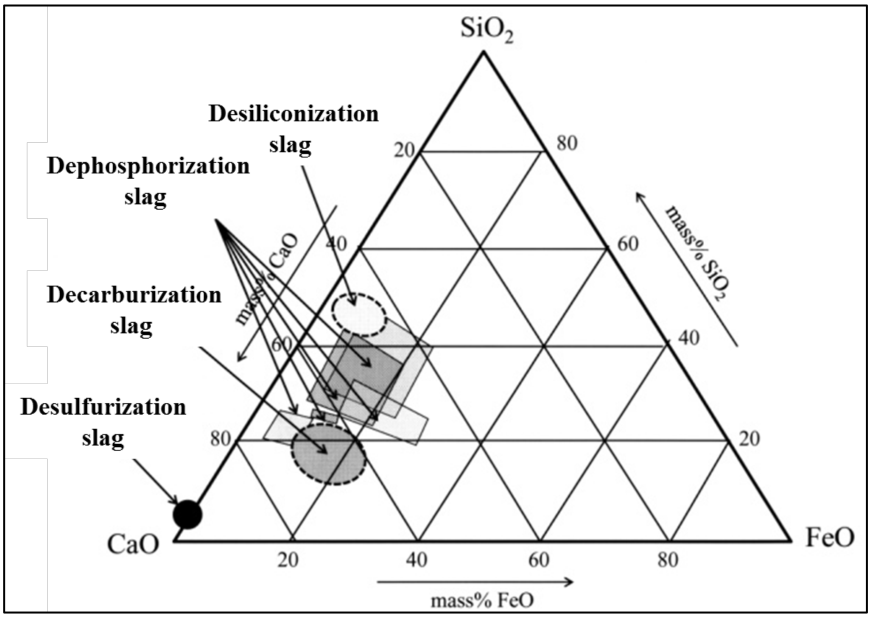

Figure 1: Variations on slag compositions via different refining processes [3]

In order to utilize the steelmaking slag, the characteristic of each slag should be understood firstly. Except slag of desulphurization which is carried out in a reducing atmosphere, the slags after desiliconization, dephosphorization and decarburization contain iron oxides. For desiliconization slag, traditionally the CaO/SiO_2 ratio is around unity. For dephosphorization slag, as in normal practice, a $2CaO \cdot SiO_2$ saturated slag is used, $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ solid solution forms during the process, and phosphorus is mainly concentrated in this solid solution [4-8]. For the decarburization slag, a high CaO/SiO_2 ratio is required to suppress the phosphorus recovery during the process. Thus solid CaO and $2CaO \cdot SiO_2$ coexist in the slag. In many cases, as the content of phosphorus in this slag is very low [6], the decarburization slag is reused in the dephosphorization process or sintering process. The CaO/SiO_2 ratio is extremely high in the desulfurization slag due to the low SiO_2 content as desulfurization is a reduction reaction [9]. After refining, the desulfurization slag can be reused in the sintering process [10].

Because of the high CaO/SiO_2 ratio and the shortened refining time, free lime is normally present in decarburization and dephopshorization slag after cooling. In addition, MgO is often added to the slag during refining to protect the refractory lining which leads to the presence of free MgO. Both the free lime and free MgO react with moisture in air and this leads to volume expansion. Thus, the slag cannot be directly utilized as material for construction without steam aging treatment. On the other hand, some valuable elements such as Fe, P, and Mn, etc., are present in the steelmaking slag. Therefore, the development of utilization techniques that can exploit these chemical characteristics of steelmaking slag may offer more reuse possibilities.

2. Several new techniques for utilizing the steelmaking slag

One innovative utilization method for steelmaking slag involves using it to provide a source of iron-ions in the marine environment to stimulate phytoplankton to absorb CO_2 [11-12]. In conjunction with this utilization method, there is a need to suppress pH increases after slag application in seawater, and to achieve this purpose, carbonation treatments for stabilizing steelmaking slag have been applied [13]. Investigations of these marine application of steelmaking slag are still in progress, and others are now underway. For example, researchers have been exploring ways to treat dredged soil with steelmaking slag and apply this slag-soil material to sea shore to improve the supply of nutrients for plankton [14-16]. Other application in marine environment, such as using slag to prevent the eutrophication caused by phosphorus enrichment and to suppress the activity of sulfate reducing bacteria, have also been investigated [17].
Additionally, with the aim of extracting valuable elements, efforts have been made on the recovery of P from slag. Methods that have been proposed for extracting P include the use of magnetic separation techniques to separate the phases containing iron oxides from the nonmagnetic phosphate rich phase [18]; additionally, the selective leaching by controlled pH show promise for extracting P because there are differences in the solubility between phosphate-rich and phosphate-poor phases [19-20].
Studies have also been done on finding ways to recover Mn from steelmaking slag in order to to produce ferro-manganese alloys, which contain extremely low levels of phosphorus [21-22].

3. Application of steelmaking slag for the recovery from the earthquake and tsunami

After the enormous tsunami triggered by the 2011 great Tohoku earthquake receded, about 13-28 million tonnes of debris were deposited on the land surface along with large amounts of thick sludge [23]. After removing the large debris, efforts have been made to improve the soil strength for reconstructions by using steelmaking slag.
Within the damaged areas, about 23,600 ha (2360km^2) of farmland along the northeastern coast were impacted [23]. This means, a large area of fertile granary, as we so remembered, was gone. Since a large part of this farmland consisted of paddy

field, the value of steelmaking slag as a fertilizer and soil improving agent has been considered and evaluated more intensively.

Figure 2 shows the changes in the chemical status of paddy soil after the tsunami [3]. The sodium content was much higher than normal levels, whereas the calcium content was lower than normal level. This caused many problems such as increases in the electrical conductivity of soil and depravation of drainage condition. Together, these changes finally inhibited the growth of paddy.

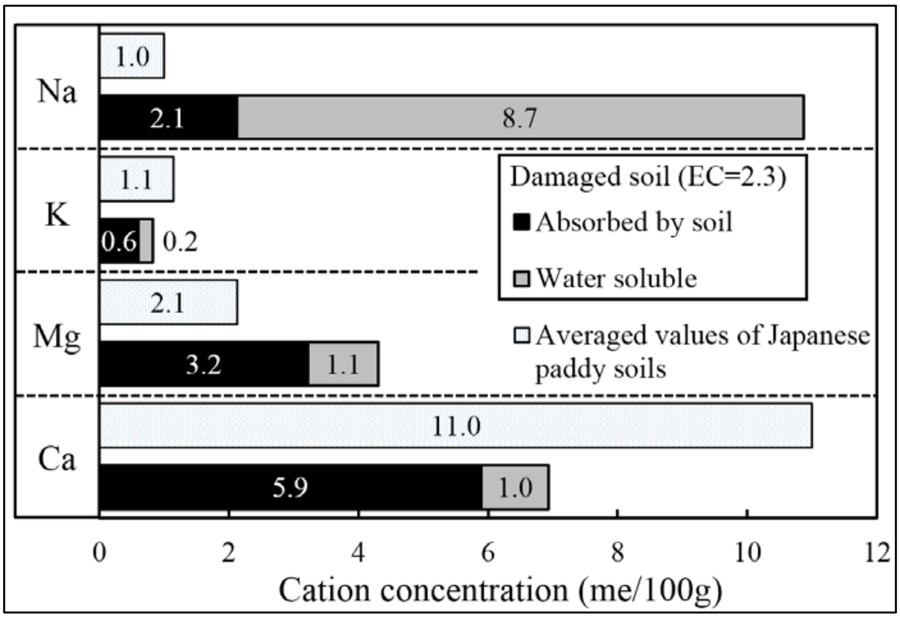

Figure 2: Chemical status of damaged paddy soil comparing to normal condition [3]

Although the water dissolvable sodium can be washed out of soil by rain, the content of sodium in the damaged areas has remained higher than normal value. Thus, the sodium absorbed by the soil cannot be simply removed by irrigation or rainfall alone. Instead, the addition of calcium ions holds the key. As shown in Figure 3 [3], after the addition of calcium ions to the paddy soil, the sodium ions could be exchanged and finally washed away by rainfall. The operation for desalting of paddy fields has been recommended by the Ministry of Agriculture, Forestry and Fisheries (MAFF) of Japan has also specified the requirement for calcareous material [24]. In addition to Ca, supplements of silicate, which is an important nutrient for paddy, were also found to be necessary since the losses of silica were significant after the desalting operations took place.

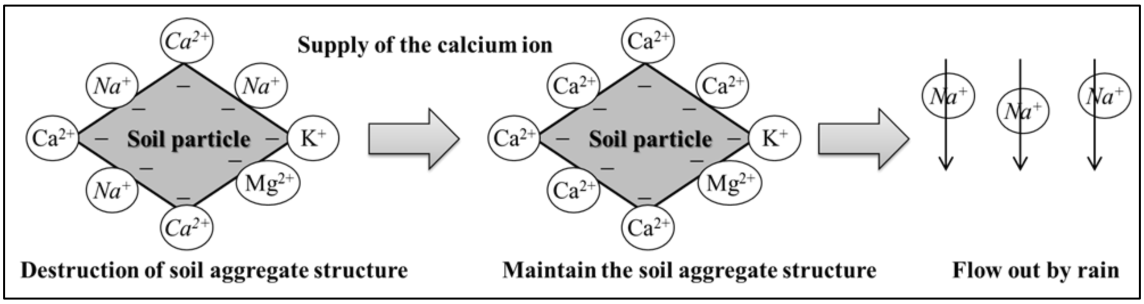

Figure 3: Desalting process by feeding calcium ion [3]

In addition to the problems described above, the damaged paddy soil also suffers from acidification as a result of the formation of hydrogen sulfide (H_2S), due to sludge accumulation. As shown in Figure 4 [3], the sludge left by the tsunami contains FeS_2, which is stable in sea water. However, it is easily oxidized in air and forms sulfate (SO_4^{2-}). Then, sulfate-reducing bacteria convert the sulfate to H_2S, which acidifies the soil and causes the detrimental changes in the paddy fields. To stabilize the H_2S, the addition of iron ions is effective as this lead to the formation of stable FeS.

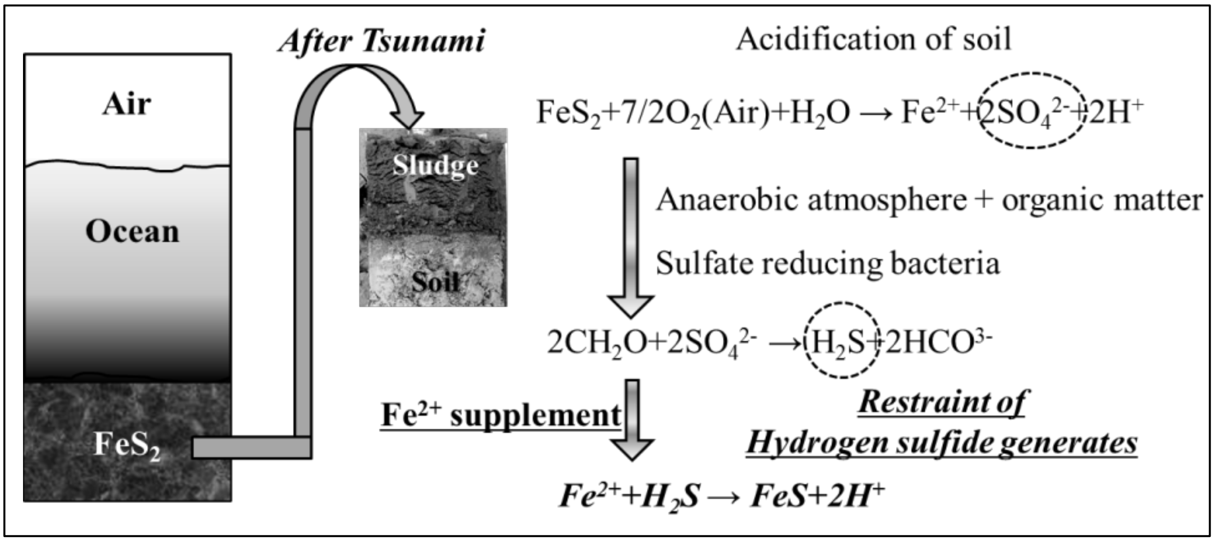

Figure 4: Restraint on the generation of hydrogen sulphide [3]

To summarize these findings, adequate supplies of Ca, Si and Fe are necessary for the recovery of paddy field. Importantly, soil amendments composed of steelmaking slag can provide an effective way to supply the required elements for soil recovery at low cost.

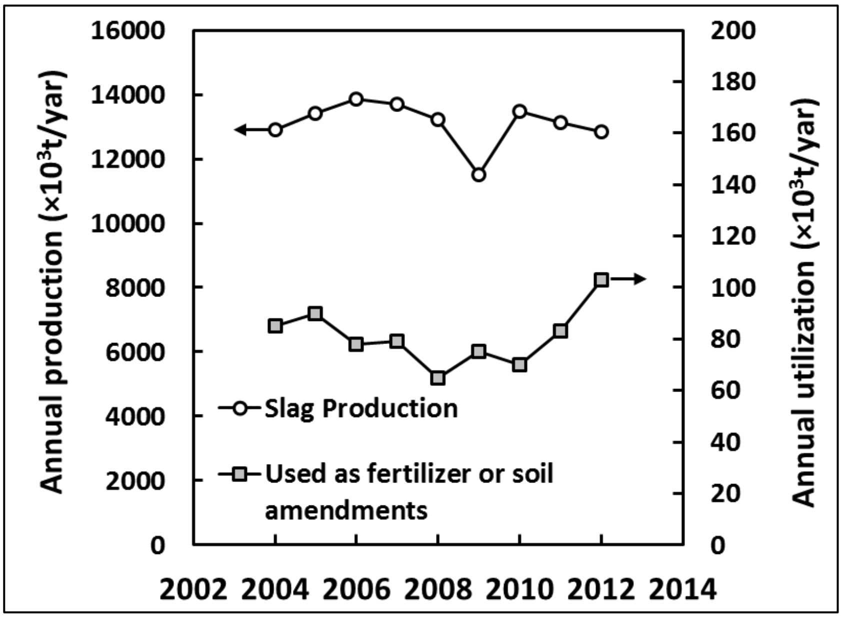

Figure 5: Comparison between the annual utilization as fertilizer and the total production amount for steelmaking slag [26]

Since 1981, steelmaking slag has been permitted for use as lime fertilizer, and now there are three standards (slag silicate, byproduct lime, and slag phosphate) that authorize the use of steelmaking slags as fertilizer [25]. Figure 5 shows the annual utilization amount of steelmaking slag as fertilizer compared to the total production [2, 26]. Although utilization has improved during the last few years, the share of agricultural utilization to the total slag production is still very low.

Based on these backgrounds, the Iron & Steel Institute of Japan (ISIJ) launched the project entitled “Recovery of paddy field damaged by Tsunami by the use of steelmaking slag” as the ISIJ innovative program for advanced technology in 2012. For this project, the current authors have studied the dissolution behavior of Ca, Si, Fe and other elements from various commercial fertilizers made of steelmaking slag in both aqueous solution with controlled pH and actual soil environment [27, 28]. Furthermore, with the cooperation of agricultural experts, the effects of applying one kind of commercial fertilizer made of steelmaking slag in the actual damaged paddy field were confirmed. The yield of rice increased by about 8 to 14% in the area where the fertilizer made of steelmaking was applied. Improvements in pH and silicate content and decreases in sodium content of the soil water were also confirmed.

4. Conclusion

In this paper, the production, chemical characteristics and recent utilization of slag in Japan, especially steelmaking slag, were reviewed. Both converter slag and electric arc furnace slag are mainly utilized for road and civil construction, ground improvements and reuse in the steel plant. Other utilization purposes in marine environment such as preventing the eutrophication of phosphorus or suppressing the activity of sulfate reducing bacteria have been investigating. On the other hand, with the perspective of extracting valuable elements, research has also been conducted on the recovery of Mn and P from slag. After the great Tohoku earthquake and subsequent Tsunami happened in 2011, the requirement for the reconstruction of roads and ports, as well as for the recovery of damaged farmland, has greatly drawn attention to the utilization of the slag. In particular, the application of steelmaking slag as fertilizer and soil improvement agent during the recovery of damaged paddy fields has been studied actively.

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