Improvement of Function and Utilization of Steelmaking Slag

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Abstract: Steelmaking slag is one of the main by-products of steelmaking process, and it has to be efficiently utilized. In Japan, approximately 10 million tons of converter slag is generated annually and most of them are recycled for various purposes. Nevertheless, about 1 % of generated slag is dumped without any utilization. Since the demand of steelmaking slag as construction material is expected to decrease, the stock of steelmaking slag is expected to increase. Two schemes should be considered to solve the issue of steelmaking slag utilization, first is to decrease volume of slag generation and second is to find the new future utilization of steelmaking slag in other fields by developing or adding new functions of steelmaking slag. To decrease the volume of slag generation, it is required to increase the utilization efficiency of solid CaO remaining in the slag to reduce the amount of slag. In Japan, the utilization of solid phase during refining processes, so called "multi-phase flux" has been developed and the condensation behavior of P_2O_5 into the solid phase during CaO dissolution into $FeO–CaO–SiO_2–P_2O_5$ slag has been intensively studied. From the view point of innovative utilization of steelmaking slag, the improvement and rehabilitation of coastal environment in Japan by steelmaking slag have been proposed. The mixture of steelmaking slag and soil is one of the candidate materials for the recovery of coastal environment. Ferrous ion contained in the slag dissolves from steelmaking slag into seawater and plays an important role in promoting the growth of various seaweeds.

Key words: slag, ironmaking, steelmaking, hot metal pretreatment, refining, utilization, multi-phase flux, marine environment, dissolution

1. Introduction

Modern ironmaking–steelmaking process via blast furnace and converter route inevitably produces slag as a by-product. Because enormous amount steel is produced in the world, a vast amount of slag is also generated. Therefore, the various treatment and utilization methods of slag have been examined for a long time. However, development of the new application area of slag as a resource has been required since serious competition against various materials generated from other departments of industry becomes severe at various fields where slag has been traditionally utilized as a resource. In this paper, researches for development of new functional slags are discussed from viewpoints of reduction of ironmaking and steelmaking slag emission, and exploitation of new application fields.

2. Slag Generation and Its Utilization

Figure 1 shows the change in annual steel production of the world.[1] Annual change in slag emission in Japan is shown in Fig. 2.[2] The amount of blast furnace slag and steelmaking slag are approximately 300 kg/t-pig iron and 100 kg/t-steel, respectively. As a result of 100 million tons of annual steel production in Japan, 21 million tons of blast furnace slag, 10 million tons of converter slag, and 2.3 million tons of electric furnace slag have been generated in 2009.

Figures 3 to 6 show the amount of slag utilized in various fields regarding whole ironmaking and steelmaking slag, blast furnace slag, converter slag, and electric furnace slag.[3] Blast furnace slag has been comprehensively utilized, while small portion of converter and electric furnace slags has been still dumped without any application.

Slag generated by steel production is required to be utilized for establishment of sustainable society. Two strategies are conceivable for slag generation. One is the development of highly efficient smelting and refining processes with less slag generation, resulting reduction of environmental load. Slags have been researched and designed to increase the refining capacity as a function of slags so far. However, new designs of slags or processes with original concept to decrease slag generation additional to sufficient refining capacity must be conducted, and thus the various researches and developments have been conducted with such viewpoints. The other is the development of new methods utilizing slag as a resource, because slag is a by-product inevitably generated as long as steel is produced from iron ore and coal as resources. Epochal applications of slags as a resource with newly created functions must be explored, in addition to traditional applications of slags.

Amount of crude steel production in China for the last decade and is more than 700 Mt/year. Situation of ironmaking and steelmaking slags in China have not been statistically clarified. However, Chinese modern ironmaking and steelmaking processes produce almost the same amount of slags and thus it is expected that severalfold amount of ironmaking and steelmaking slags are generated compared to Japan and most of those have been recycled as various resources such as cement production. In Chinese universities, many researches regarding slag are ongoing, such as the recovery of valuable metals such as Ti and V.

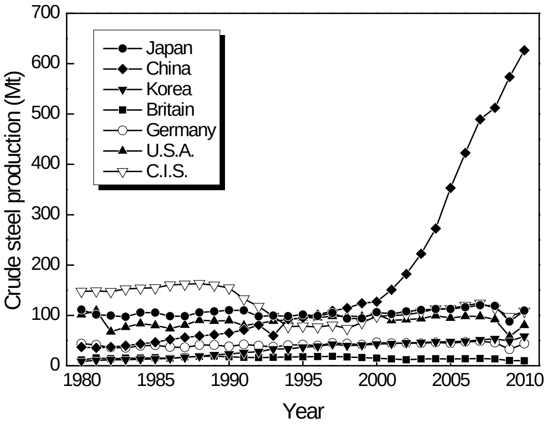


Figure 1 Change in annual steel production of the major steel-producing countries.

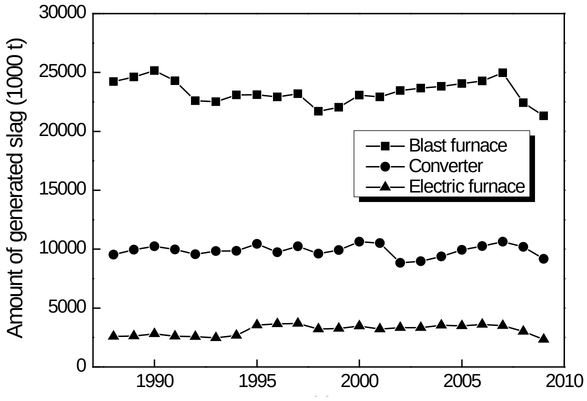


Figure 2　Change in annual slag emission in Japan.

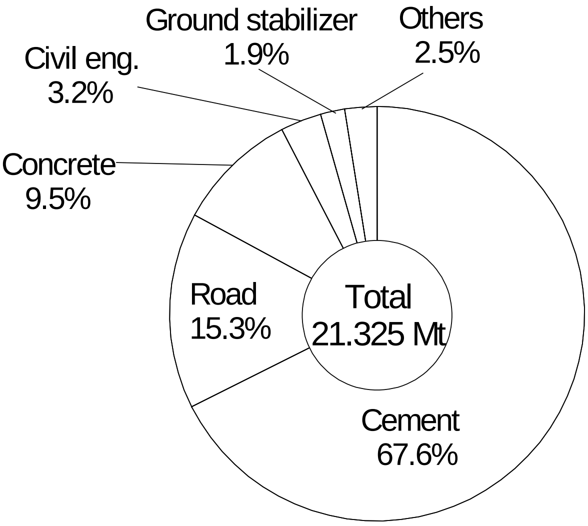


Figure 3　Recycling of blast furnace slag for various purposes in Japan (2009).

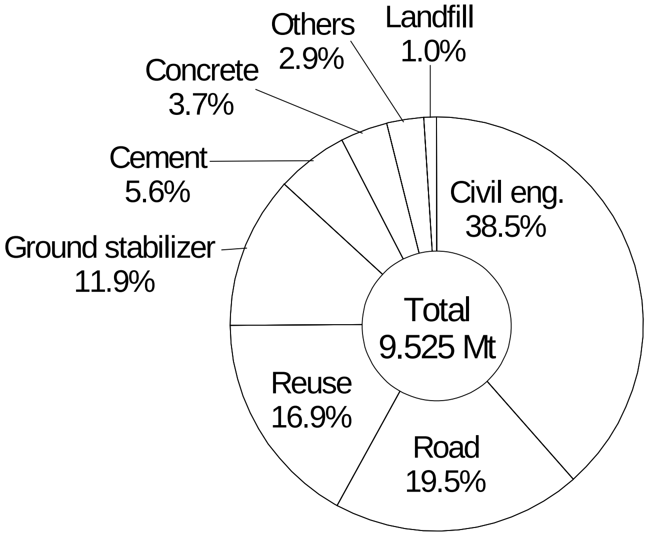


Figure 4　Recycling of converter slag for various purposes in Japan (2009).

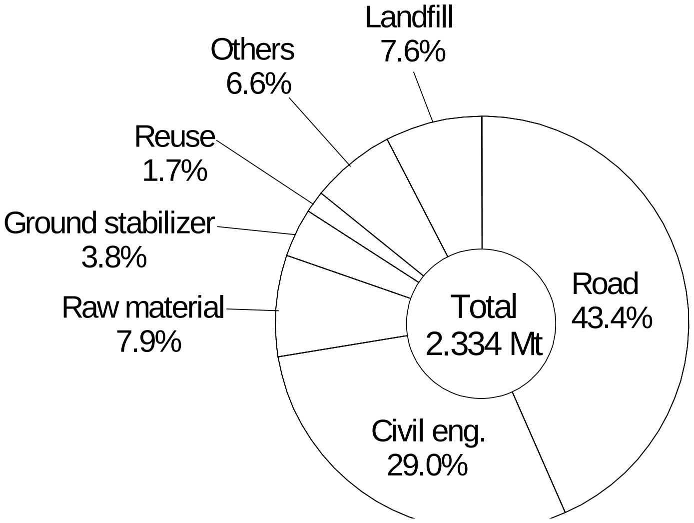


Figure 5 Recycling of electric furnace slag for various purposes in Japan (2009).

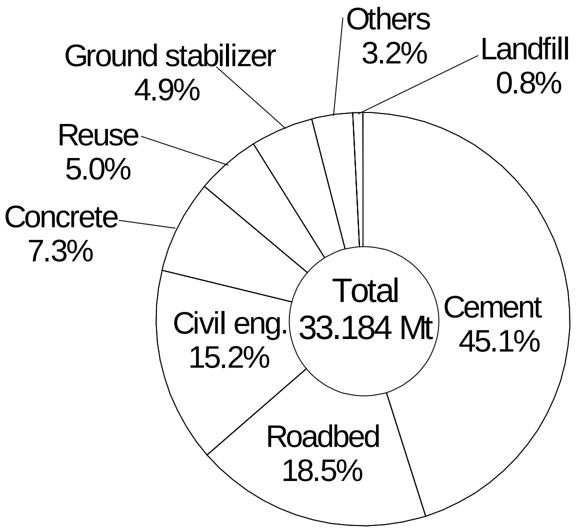


Figure 6 Recycling of ironmaking and steelmaking slag for various purposes in Japan (2009).

3. Increase in Slag Refining Capacity and Cutoff of Slag Emission by Development of Highly Efficient Slags

Increase in various refining capacities of ironmaking and steelmaking slags is an important issue to meet continuous demands, and fundamental researches and technological developments for slags or fluxes have been conducted together with many technological and operational improvements at hot metal pretreatment, converter, or secondary refining processes. Refining process has gradually shifted from hot metal pretreatment process by torpedo cars to refining by converter vessels since around 2000 due to the regulation of fluorspar addition at steelmaking fluxes.[4] In addition, there is a demand to improve not only refining capacities but also various functions of slag from viewpoints of reduced environmental load such as reduction in CO_2 gas emission, regulation of utilization of fluorides, decrease in slag emission and so on. One of such research topics is the development of highly efficient “multi-phase flux” by positive application of heterogeneous slag for refining process, which is introduced in detail in the following section.

3.1 Refining process by the use of “multi-phase flux”

Practically, refining processes with heterogeneous flux composed of solid CaO and related solid compounds, and liquid slag have been operated. However, the roles of solid and liquid phases in fluxes have not been considered well at traditional physicochemical analyses of reaction mechanisms, and thus the solid phases coexisting with liquid slag have not been utilized efficiently at operations so far. Based on above mentioned background, refining fluxes composed of solid and liquid phases or two liquid phases have been expressed as “multi-phase flux” and various researches have been intensively conducted to develop innovative refining processes by utilizing multi-phase fluxes efficiently in the Iron and Steel Institute of Japan.[5-22]

Hot metal dephosphorization process had been operated with highly basic flux saturated with CaO by adding CaF_2. However, current process has been operated with fluxes with large FeO content and small basicity due to the restriction of CaF_2 utilization. In the case of the flux with small basicity, dephosphorization reaction proceeds at the $2CaO{\cdot}SiO_2$-saturated region and phosphorus is removed from liquid phase and concentrated into the solid solution composed of $2CaO{\cdot}SiO_2$ and $3CaO{\cdot}P_2O_5$. Fixation of phosphorus as $3CaO{\cdot}P_2O_5$ into slag is important to progress dephosphorization reaction efficiently and reduce CaO consumption.

Figure 7 shows the estimate of specific CaO consumption in the case of dephosphorization from 0.1 mass% to 0.01 mass%.[23] When phosphorus is completely fixed into solid calcium compounds of multi-phase flux, specific CaO consumption could be dramatically reduced in principle.

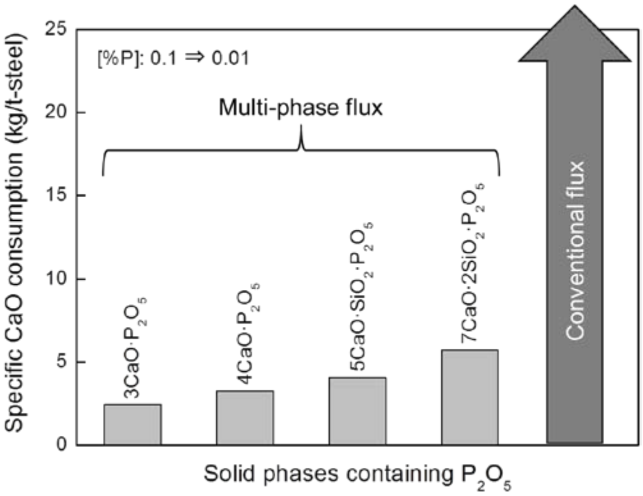


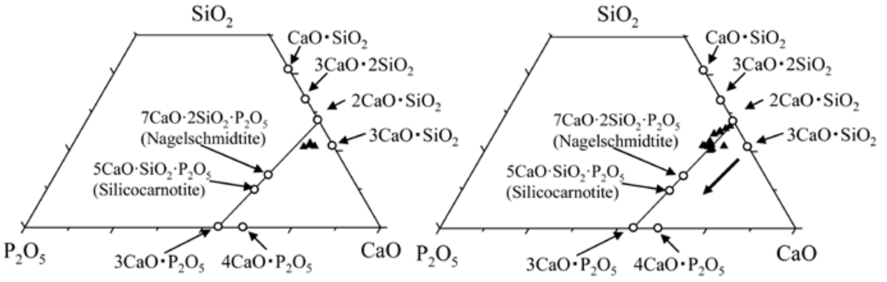
Figure 7 Estimate of specific CaO consumption at dephosphorization process by concentrating P_2O_5 into various solid phases, change in phosphorus content from 0.1 to 0.01 mass%.

3.2 Mechanisms of dephosphorization reaction by multi-phase flux

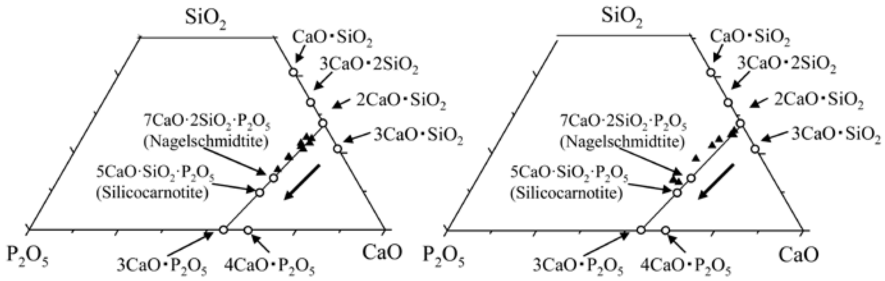
Regarding the dissolution behavior solid CaO into molten slag, dramatic increase of CaO dissolution rate with increasing FeO content of the $FeO–CaO–SiO_2$ slag is reported.[24] The CaO dissolution rate is also affected by additives such as CaF_2, $CaCl_2$, Al_2O_3 or B_2O_3, and by CaO particle size.[25,26]

Partition of P_2O_5 between $2CaO{\cdot}SiO_2$–$3CaO{\cdot}P_2O_5$ solid solution and liquid slag is the key factor to fix phosphorus contained in hot metal or molten steel into $2CaO{\cdot}SiO_2$–$3CaO{\cdot}P_2O_5$ solid solution efficiently.[27–30] Ito *et al.*[29] and Hirosawa *et al.*[30] measured phosphorus partition ratio between solid $2CaO{\cdot}SiO_2$ and molten CaO–SiO_2–FeO_x–P_2O_5 slag at hot metal temperatures. P_2O_5 was condensed inside $2CaO{\cdot}SiO_2$ phase of steelmaking slag after solidification. Inoue and Suito found that the mass transfer of phosphorus from $2CaO{\cdot}SiO_2$-saturated slag to the $2CaO{\cdot}SiO_2$ particles was fast and a uniform CaO–SiO_2–P_2O_5 solid phase was formed within 5 s.[28]

Pseudo binary phase diagram for the $2CaO{\cdot}SiO_2$–$3CaO{\cdot}P_2O_5$ system indicates the wide solid solution range around 1573 K and the formation of phosphorus-containing compounds such as Silicocarnotite ($5CaO{\cdot}SiO_2{\cdot}P_2O_5$) and Nagelschmidtite ($7CaO{\cdot}2SiO_2{\cdot}P_2O_5$). Therefore, efficient hot metal dephosphorization process with the use of multi-phase flux containing solid CaO could be operated if P_2O_5 in liquid slag is concentrated into solid $2CaO{\cdot}SiO_2$ phase. Authors have so far clarified the reaction mechanisms between solid CaO and molten CaO–FeO–SiO_2–P_2O_5 slag, formation mechanisms of P_2O_5-containing solid phases at the interface between solid CaO and molten slag, and mechanisms of P_2O_5 concentration at the interface between solid $2CaO{\cdot}SiO_2$ and molten slag.[15,16,31] Figure 8 shows the influence of FeO content on the composition of solid solution phase at the reaction between molten slag and solid CaO at 1573 K for 10 s. Phosphorus is absorbed into solid $2CaO{\cdot}SiO_2$ phase as $3CaO{\cdot}P_2O_5$ and the reaction is promoted with larger FeO content.



(a) FeO_x=25.0mass%   (b) FeO_x=30.0mass%



(c) FeO_x=35.0mass%   (d) FeO_x=40.0mass%

Fig. 8 Influence of FeO content on the composition of $2CaO{\cdot}SiO_2$–$3CaO{\cdot}P_2O_5$ solid solution formed by the reaction between solid CaO and molten FeO–CaO–SiO_2–P_2O_5 slag at 1573 K for 10 s.

The phase formation mechanisms by the reaction between solid CaO and liquid slag are explained as follows, which is schematically illustrated in Figure 9.[31]

(a) Dissolution of CaO into the slag resulting the increase of CaO content in the melt,

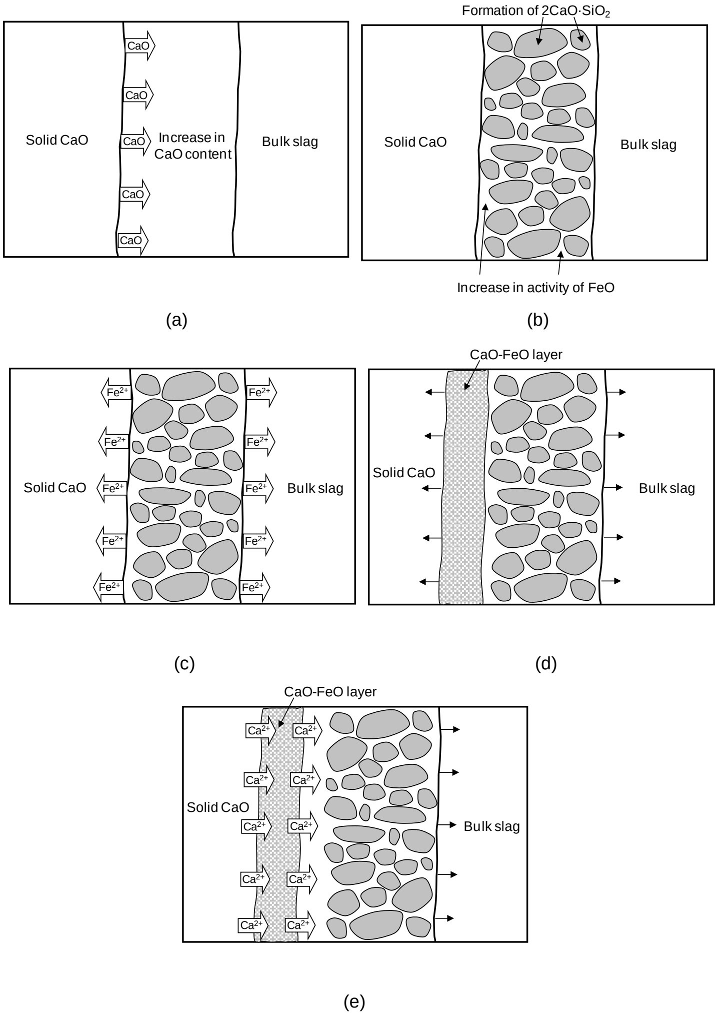
(b) Formation of $2CaO \cdot SiO_2$ phase from liquid slag, decrease of CaO and SiO_2 contents in the liquid, and relatively increase of FeO content,

(c) Diffusion of FeO from FeO-rich phase to both solid CaO and bulk slag,

(d) Formation of CaO–FeO phase adjacent to solid CaO,

(e) Continuous diffusion of CaO to bulk slag through formed CaO–FeO layer.

Considering the practical conditions at refining processes in which slag becomes multi-phase flux, an elaborated model simulating refining reactions of molten iron based on competing reaction model has been developed by taking the effect of dissolution of $3CaO \cdot P_2O_5$ into $2CaO \cdot SiO_2$ solid phase into account.[22] Characteristics of this program are the modeling of reaction progress of hot metal dephosphorization reaction with formation of solid solution at multi component system and multi-phase conditions, and the user interface specialized for the intended use.



(a) (b)

(c) (d)

(e)

Fig. 9 Schematics of reaction mechanisms between solid CaO and molten CaO–FeO–SiO_2 slag.

4. Beneficial Utilization of Slag as a Resource

Since major components of slag are those of stone, enormous amount of slag have been used as a resource for constructional materials such as roadbed, or cement resource by taking physical advantages of slag such as physical strength. In addition, some slags have been used as fertilizer because slag contains useful constituents such as iron or phosphorus. Further, trial application for construction of seaweed field by utilizing the effect of promotion of seaweed growth by steelmaking slag at marine environment due to the dissolution of various ions into seawater has been conducted.

4.1 Materials for rehabilitation of marine environment

Conventionally, iron ion essential for growth of various plants at marine environment has been supplied by flowing in through rivers from terrestrial forests as iron ion chelated by humic acids. However, seaweed beds have been disappeared at coast due to the environmental change of forests and rivers resulting change in marine environment. Recently, the utilization of ironmaking and steelmaking slags has been promoted at harbors and seashores as a supply source of various ions such as iron ion to regenerate seaweed beds and rehabilitate marine environment. Furthermore, it has been confirmed that iron ion plays an important role on the promotion of growth of various sea plants at marine regions. The above circumstances have enhanced the possibility of aggressive utilization of ironmaking and steelmaking slags as a rehabilitation material for marine environment to recover seaweed bed, prevent degradation of seaweed, and fix CO_2 gas by formation of seaweed bed. Traditionally, slags have been used at harbors and seashores as a foundation and construction material by utilizing the strength of slag as a well-known physical property. Additionally, utilization of slags as a rehabilitation material expecting chemical functions of compounds contained in slags has been forwarded for various usages such as seaweed beds or fish reef. Various researches have been conducted to clarify dissolution behaviors of steelmaking slags into seawater, multiplication of phytoplankton, beneficial use of products, or estimation of influence on the ecological system.[32–53] Previous projects for slag utilization at marine regions have also demonstrated that the existence of iron ion dissolved from steelmaking slag is effective for the growth of marine plants.

As mentioned above, the utilization of steelmaking slag at marine environment would rehabilitate the marine environment and promote the growth of various seaweeds. When 1000 thousand tons of steelmaking slag are utilized at Japanese coasts, it is estimated that 75 tons of iron ion would dissolve from steelmaking slag into seawater. If all of the dissolved iron ion are used for photosynthesis of phytoplankton, about 6000 thousand tons of CO_2 would be fixed. In addition, if 8×10^8 m^2 of seaweed bed disappeared for past 30 years are regenerated and various sea plants grow by slag utilization, from 5000 to 10000 thousand tons of CO_2 would be also fixed. It is also expected that the rehabilitation of marine environment results in the positive effects on fishing industry such as increased fish catches.

New innovative program for advanced technology development “Utilization of Steelmaking Slag in Coastal Environment” (The Iron and Steel Institute of Japan (ISIJ), from 2010 to 2013) has studied on the effect of steelmaking slag use at marine environment such as dissolution behaviors of various elements from steelmaking slag or the mixture of steelmaking slag and soil into seawater, assimilation of iron ion into phytoplankton and sea plant, and the estimation of the environmental effect of CO_2 fixation by the growth of plants to clarify the effects of the utilization of steelmaking slag at marine environment academically.

4.2 Dissolution behavior of various elements from steelmaking slag

Figure 10 shows the change in amount of dissolved iron from slag, which indicates the effect of organic acid contained in seawater.[54] The amount of dissolved iron from slag into seawater increased by adding gluconic acid and producing iron gluconate chelate ion. However, concentration of iron ion increased once and then decreased with time, demonstrating the gradual decomposition of iron gluconate ion.

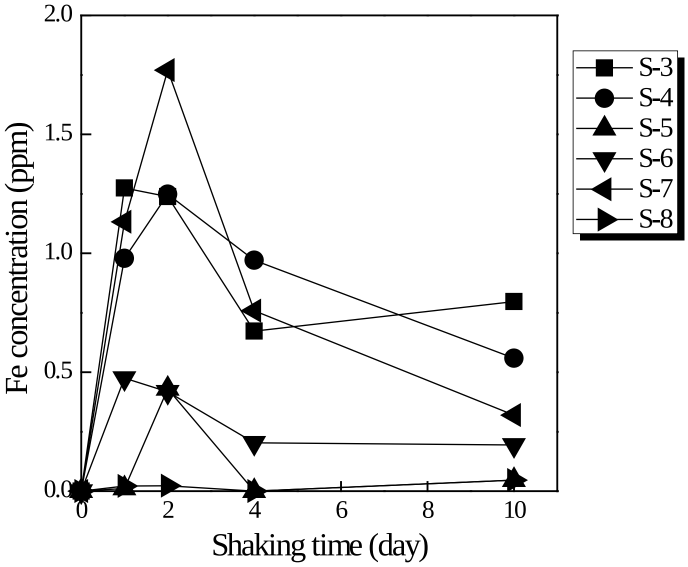


Fig. 10 Variation of Fe concentration in solution with shaking time for slag and seawater mixture

(5 g slag / 100 mL seawater) containing 0.1 g/L gluconic acid.

5. Conclusions

Huge amount of ironmaking and steelmaking slags are inevitably generated from present steel production process from iron ire. Since the degradation of iron ore resource results the increased slag generation, more efficient smelting and refining processes must be developed. Also, the reduction of slag generation by utilizing CaO sufficiently is required.

On the contrary, utilization of ironmaking and steelmaking slags as a resource must be promoted because slag is necessarily generated. It is anticipated that competition with other recycled resources in the use for cement production, roadbed, construction materials and so on would become harder in the future. Therefore, creation of new functions and utilization as innovative ways such as rehabilitation material of marine environment must be developed for the application of slag as a resource.

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