

KATHOLIEKE UNIVERSITEIT
LEUVEN

Proceedings of the **SECOND INTERNATIONAL**
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

18-20 April 2011
Leuven, Belgium

Editors: Peter Tom Jones, Yiannis Pontikes, Jan Elsen, Özlem Cizer, Luc Boehme,
Tom Van Gerven, Daneel Geysen, Muxing Guo, Bart Blanpain

Organisers:



Utilisation of steelmaking slag for improvement of coastal environment

Xiaorui ZHANG, Hiroyuki MATSUURA, Fumitaka TSUKIHASHI

Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoka, Kashiwa, Chiba 277-8561 JAPAN

*zhangxrui@moon.k.u-tokyo.ac.jp, matsuura@k.u-tokyo.ac.jp,
tukihasi@k.u-tokyo.ac.jp*

Abstract

The improvement and rehabilitation of the coastal environment is a critical issue in Japan. The mixture of steelmaking slag and soil is a candidate material for this purpose. Ferrous ion contained in the slag dissolves in seawater and plays an important role in promoting the growth of various sea plants. Shaking experiments were conducted at room temperature with various synthesised slags and different mass ratio of slag/seawater to understand the dissolution behaviour of various elements from slag into seawater. The slag basicity influences the dissolution behaviour of elements to a greater extent than the slag/seawater ratio. The dissolution mechanism of ferrous ion is discussed by using the solubility diagram.

Introduction

Approximately 100 million tonne of crude steel is produced annually in Japan, thereby consuming enormous amounts of resources and energy. Environmentally-friendly and harmonised steelmaking processes are required for the sustainable development of steel industries. Many by-products such as slag, sludge, dust, exhaust gas and waste heat are generated during steel production. Especially, about 22 and 10 million tonne of, respectively, blast furnace and steelmaking (converter and electric furnace) slags are annually generated in Japan¹ and the development of slag utilisation technologies is of significant importance. In the case of blast furnace slag, almost 100% of slowly-cooled and water-quenched slags are recycled. Although most of the converter slag is recycled, about 1% of converter slag is still dumped without any utilisation.¹ Therefore, the utilisation of converter slag must be further developed.

It is known that the mixture of steelmaking slag and soil improves the coastal environment by enhancing the growth of various sea plants. Sea desertification along the coast has become a serious issue in the world and has caused a decrease in fishery. Although the mechanisms of sea desertification are not completely understood yet, a deficiency in seawater of nutrition elements, especially ferrous ion,

for sea plants seems to be one of the critical mechanisms, . Steelmaking slag is therefore one of the best candidate materials for supplying nutrition elements into seawater because of its ionic nature, proper mineral composition and cost effectiveness.² Enhancement of phytoplankton breeding by the addition of steelmaking slag into seawater has been confirmed by many studies.^{3,4} Several projects with respect to utilisation of a mixture of steelmaking slag and soil for coastal environment improvement have been conducted and the positive effects have been phenomenologically confirmed. Therefore, there is a possibility to use steelmaking slag as a rehabilitation material for coastal environments.

However, the reaction and dissolution mechanisms of steelmaking slag, and/or those of the mixture of steelmaking slag and soil, into seawater have not been understood comprehensively. Mechanisms for coastal environment rehabilitation such as nutrition element dissolution, or enhancement of sea plant growth by dissolved elements must be clarified for the development of a more effective use of steelmaking slag in coastal environments.

The *Iron and Steel Institute of Japan (ISIJ)* has started a new innovative 3 year program for advanced technology development in 2010, in which the whole mechanisms for the recovery and rehabilitation of coastal environments are clarified through four approaches, *i.e.* (1) dissolution mechanisms of various elements from steelmaking slag into seawater, (2) dissolution mechanisms of nutrition elements from the mixture of steelmaking slag and soil into seawater, (3) the mechanisms of the enhancement for the growth of sea plants by utilising steelmaking slag, and (4) evaluation of the impact of the utilisation of steelmaking slag in coastal environments. The dissolution behaviour of various elements from steelmaking slag into seawater is investigated in the present research.

Experimental

The dissolution behaviour of the steelmaking slag into seawater was studied by shaking experiments with seven kinds of synthesised slags mixed with artificial seawater. The compositions of the slags are shown in Table 1. The synthesised slags were prepared by melting the oxide mixture in an iron crucible at 1723 K in a reaction tube of an electric furnace and quenching the molten slag on a steel plate by an argon flow. Although the CaO/SiO₂ ratio of conventional steelmaking slags is much larger than that of synthesised ones, the smaller CaO/SiO₂ ratio was chosen to synthesise slags with simple slag compositions and lower melting temperature. Shaking experiments were conducted at room temperature with pulverised slags (<150 µm). The mass ratio of slag to seawater was changed between 0.2 g/100 mL and 5.0 g/100 mL, the shaking time varied from 1 to 10 days, and the shaking rate

was about 160 cycles per minute. The composition of seawater is shown in Table 2. After each experiment, the pH was measured and the solution was filtrated by using a membrane filter with 0.45 μm pore diameter. Dilute hydrochloric acid was added to the filtrate before analysis to stabilise the dissolved elements. Subsequently, the concentration of the dissolved elements in the filtrate was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Table 1: Composition of the synthesised slags

Slag	FeO (mass%)	CaO (mass%)	SiO ₂ (mass%)	P ₂ O ₅ (mass%)	CaO/SiO ₂ (mass ratio)
S-1	30.0	45.0	22.5	2.5	2.0
S-2	25.0	36.5	36.5	2.0	1.0
S-3	25.0	38.0	35.0	2.0	1.1
S-4	25.0	44.0	29.0	2.0	1.5
S-5	15.0	41.5	41.5	2.0	1.0
S-6	15.0	43.5	39.5	2.0	1.1
S-7	15.0	50.0	33.0	2.0	1.5

Table 2: Composition of the artificial seawater

Composition	Concentration (mg/L)
NaCl	22100
MgCl ₂ ·6H ₂ O	9900
CaCl ₂ ·2H ₂ O	1500
Na ₂ SO ₄	3900
KCl	610
NaHCO ₃	190
KBr	96
Na ₂ B ₄ O ₇ ·10H ₂ O	78
SrCl ₂	13
NaF	3
LiCl	1
Others	0.12

Results and discussion

Figure 1 shows the change in pH of the solution with time in the case of slag S-1. The pH increased in the first day, and then it became almost constant. An effect of slag mass ratio was not clearly observed and the pH was stable at 10.30 ± 0.05 .

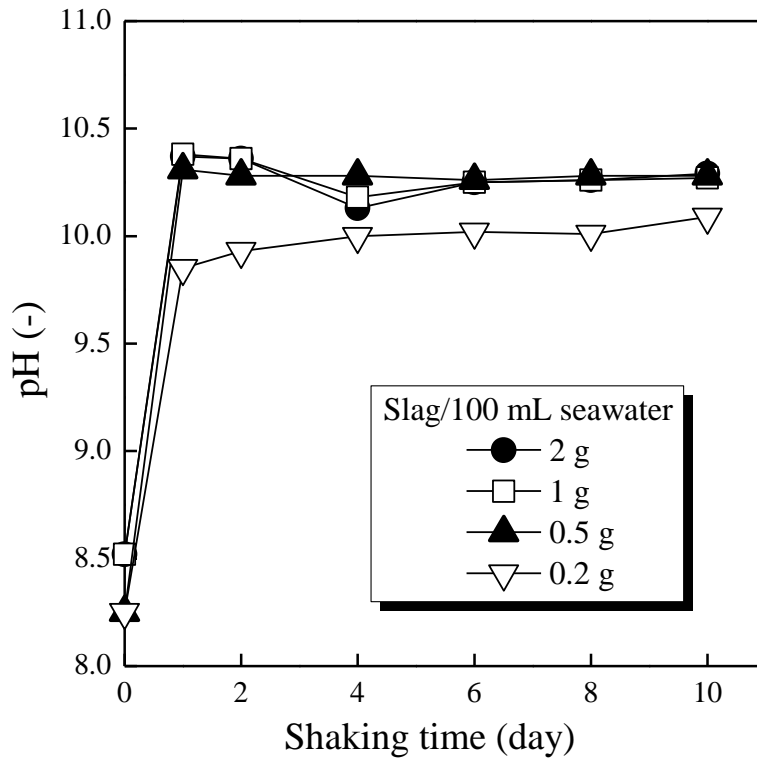


Figure 1: Change in pH of the solution with shaking time for the slag S-1 and seawater mixture

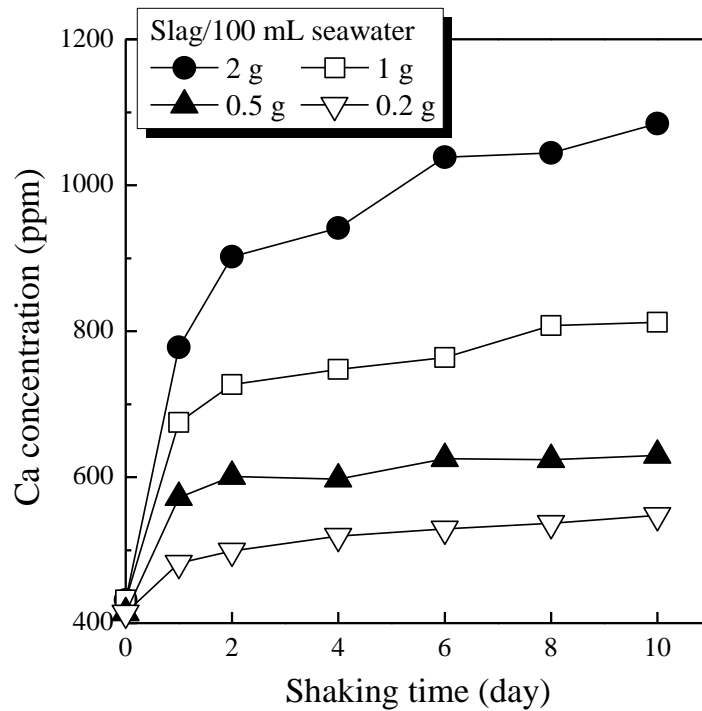


Figure 2: Change in Ca concentration in the solution with shaking time for the slag S-1 and seawater mixture.

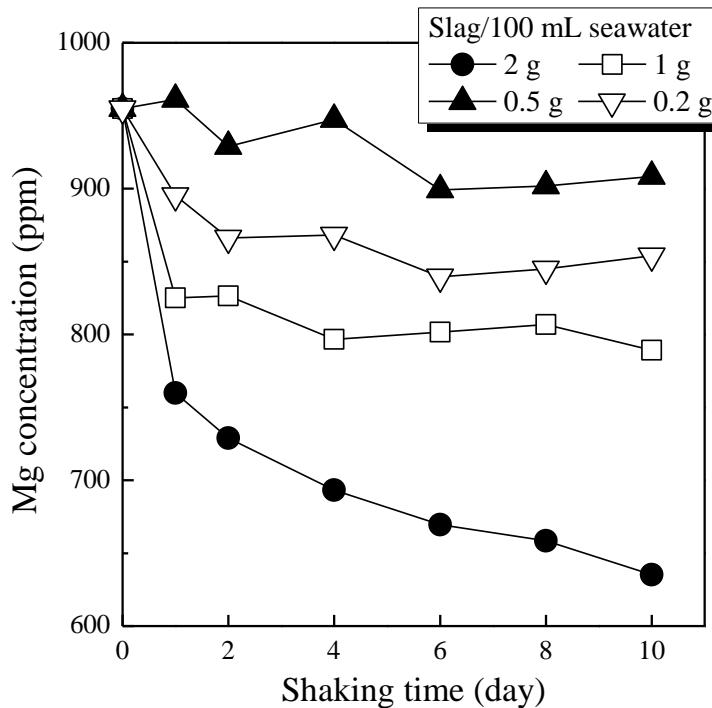


Figure 3: Change in Mg concentrations in the solution with shaking time for the slag S-1 and seawater mixture.

Figures 2 and 3 show the change in, respectively, Ca and Mg concentrations with time for slag S-1. The Ca concentration increased significantly with increasing mass ratio and shaking time (e.g. + 653 ppm Ca for 2 g/100 mL and 10 days), meanwhile the Mg concentration decreased when the slag S-1 was added into seawater. Since the seawater contains Mg ion, Ca and Mg concentrations changed with time according to the following reaction.



This reaction presents a buffering action due to pH increase. Figure 4 shows the relationship between Ca and Mg concentrations in the case of slag S-1. It shows the tendency of decreasing Mg concentration with increasing Ca concentration in the seawater, and the sum of the concentrations of the two elements is approximately kept constant.

The dissolved Fe concentration was generally very low. Figure 5 shows the change in Fe concentration in the solution with shaking time for slags S-2 to S-7. The Fe concentration increased clearly in the initial period, and after that it became almost constant. The Fe concentration increased with increasing CaO content in the slags (see Table 1 and Figure 5). Figure 6 shows the calculated relationship between solubility of iron into pure water and pH at 298 K. In this figure, Fe concentrations in the shaking solution for slag S-1 are also shown.

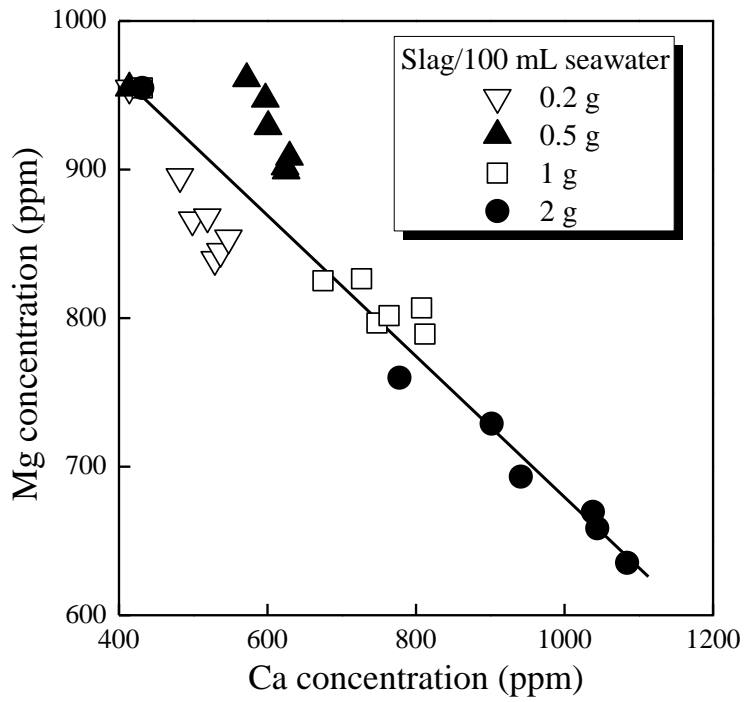


Figure 4: Relationship between Ca and Mg concentrations in the case of slag S-1.

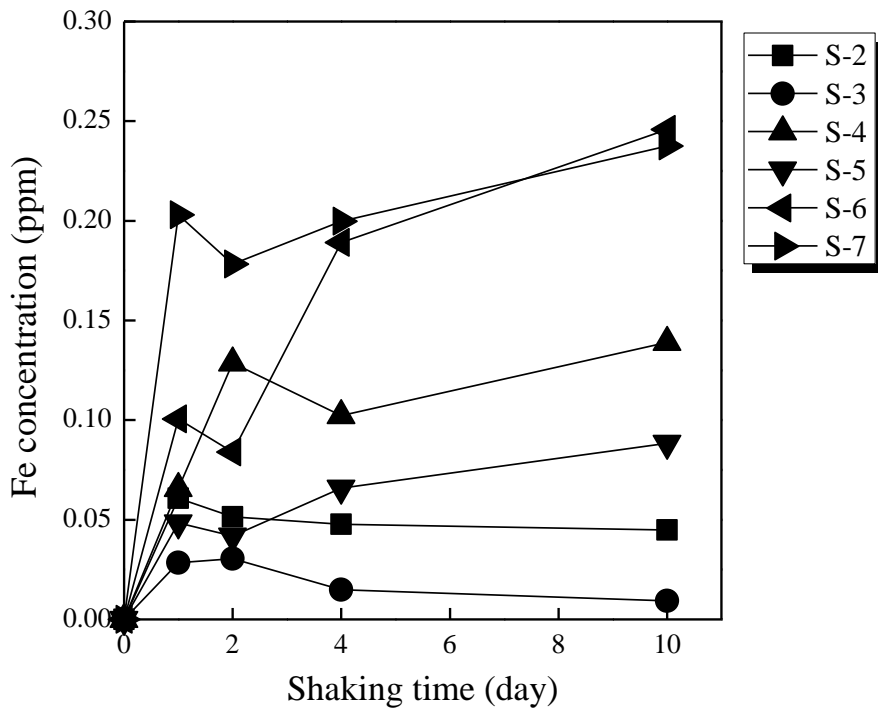


Figure 5: Change in Fe concentration in the solution with shaking time for the slags and seawater mixture.

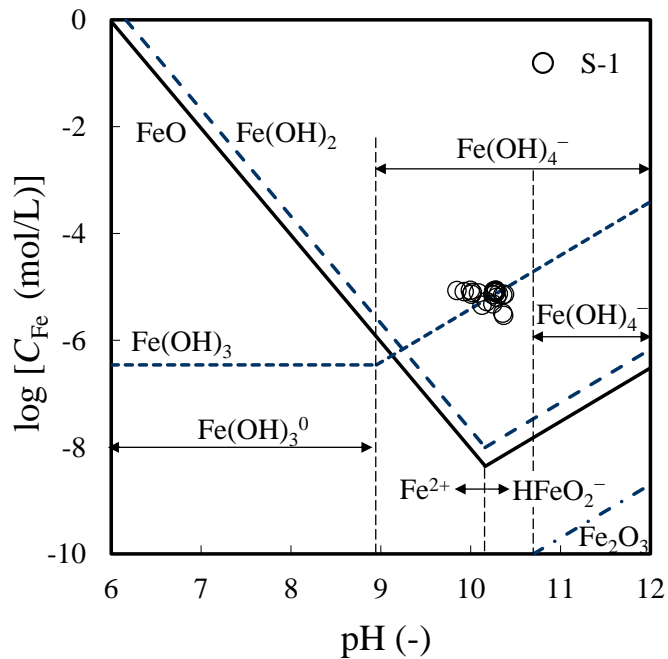


Figure 6: Calculated solubility diagram of Fe in pure water at 298 K, with Fe concentration after shaking the slag S-1 and seawater mixture (0.2 ~ 2 g slag/100 mL seawater, from 1 to 10 days).

Conclusions

The dissolution behaviour of Ca and Fe from various types of the slags into seawater was studied by shaking experiments with different synthesised slag and artificial seawater mixtures. When the pH of the solution increased up to a certain extent by the dissolution of CaO from the slag, Mg^{2+} ions initially contained in seawater form $Mg(OH)_2$ and a further increase in pH was not observed. The Fe concentration was generally very low. It increased clearly in the initial period, and after that it became almost constant. The Fe concentration increased with increasing CaO content in the slags. The effect of dissolved Fe on the promotion of sea plants growth is being studied by another group. The improvement and rehabilitation of coastal environments by the utilisation of steelmaking slag will be clarified in the future study.

References

1. Nippon Slag Association, *Annual Statistical Report of Iron and Steelmaking Slag FY 2009*, Nippon Slag Association, Tokyo, 2-7 (2010).
2. M. Hino, "Enhancement of Photosynthetic CO₂ Fixation by Marine Phytoplankton with Steelmaking Slag as a Nutrient Source", *Tetsu-to-Hagané*, **89** (4) 381 (2003).
3. Y. Nakamura, A. Taniguchi, S. Okada and M. Tokuda, "Positive Growth of Phytoplankton under Conditions Enriched with Steel-making Slag Solution", *ISIJ Int.*, **38** (4) 390-98 (1998).
4. K. Arita, Y. Umiguchi and A. Taniguchi, "Availability of Steelmaking Slag as a Source of Essential Elements for Phytoplankton", *Tetsu-to-Hagané*, **89** (4) 415-21 (2003).