Utilization of steelmaking slag at marine environment for coastal revegetation

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Abstract: Due to lack of nutrient elements supply such as iron for the multiplication of photoplankton and seaweeds, recently barren grounds without seaweed in coastal areas present serious environmental problems not only in Japan but also around the world. Because of various oxide constituents such as FeO, SiO_2, CaO and P_2O_5, low cost and abundant quantity, steelmaking slag is regarded as one of the best suitable candidate materials for providing nutrient elements for restoring seaweed beds. Ferrous ion is the obligatory nutrient element for growth of seaweed. However it is easy to be oxidized to form ferric hydroxide colloid in the presence of dissolved oxygen in seawater. It is well known that the dredged soil contains various kinds of organic acid such as fulvic acid and humic acid, and these organic acids can chelate iron ion to stabilize it and improve its solubility.

For effective utilization of steelmaking slag at marine environment for coastal revegetation, in the present study, the shaking experiment of synthesized steelmaking slag and dredged soil mixture was conducted to investigate the dissolution of Ca, Si, Al, Fe and P. The dissolution of Ca from slag-soil mixture results in increasing the pH of the shaking solution. Mg provides a buffering action when pH reaches a certain extent. Simultaneously soil also provides a buffering action on the whole pH increasing process. The dissolved iron is estimated to equilibrate with Fe_2O_3 phase, since the oxidation - reduction potential (ORP) value of solution is in the condition of the Fe_2O_3 stable area in the potential-pH diagram.

Key words: Steelmaking slag, seawater, dissolution mechanism, slag-soil mixture, potential-pH diagram

1. Introduction

Steelmaking slag is the by-product of ferrous metallurgy processes. Usually it is used as the raw material of road bed, civil engineering, fertilizer and so on. However, still 1.0 % of converter slag and 7.6 % of electric furnace slag is stocked without any utilization in Japan [1]. Owing to the restricted use of the CaF_2 as an additive and increasing degraded iron ore in Japan, the amount of steelmaking slag is increasing, and hence the steelmaking industry prefers to develop more effective and valuable ways for using steelmaking slag. On the other hand, recently barren grounds without seaweed in coastal areas present serious environmental problems not only in Japan but also around the world. One of the main reasons is the lack of supply of the dissolved nutrient elements especially ferrous ions for the multiplication of photoplankton and seaweeds. Measures for recovering the marine environment is urgently necessary to be taken.

Because of various oxides such as FeO, SiO_2, CaO and P_2O_5, low cost and abundant quantity, steelmaking slag is regarded as one of the best suitable candidate materials for restoring seaweed beds. It is believed to be able to provide the nutrient elements such as Fe, P, Si and so on. In previous researches [2-9], the effect of the mineral phases of slag on the dissolution mechanism of elements, the dissolution behavior of nutrient elements such as Si, P and Fe, and environmentally regulated elements such as F and Cr from slag into seawater have been investigated.

Ferrous ion is the obligatory nutrient element for the photosynthesis of seaweed. However, it is prone to be oxidized to ferric ion in oxic seawater. The solubility of ferric iron is extremely low at the normal pH of seawater because ferric ion readily hydrolyzes to form insoluble colloidal hydrous ferric oxides. It is particularly notorious that the humus soil contains various kinds of organic acid such as fulvic acid and humic acid, and these organic acids can chelate ferrous ion to stabilize it and improve its solubility. In some previous studies [10, 11], the effect of humic substances and slag mixtures on restoration of seaweed beds has been conducted, their researches show a significant improvement effect on iron concentration in seawater and on establishing kelp bed. In another study [12], the influence of mixture of steelmaking slag and dredged soil on the growth of seaweeds was investigated in a marine area. The positive effect of steelmaking slag and dredged soil mixture on the growth of brown seaweed was also paid attention.

In the present study, in order to utilize steelmaking slag effectively at marine environment for coastal revegetation, the effect of dredged soil on the dissolution behavior of Ca, Si, Al, Fe and P from steelmaking slag is investigated by shaking experiments. The shaking time and the CaO/SiO_2 ratio of slag were chosen as the variable parameters. The pH and oxidation - reduction potential (ORP) changing trend and the dissolution behavior of Ca, Si, Al, P and Fe were also monitored and analyzed.

2. Experimental

2.1 Sample preparation

In an electric furnace, the slags were prepared by melting a mixture of produced CaO and FeO, and reagent grade SiO_2 and $Ca_3(PO_4)_2 \cdot xH_2O$ in an iron crucible (outer diameter 40 mm, inner diameter 32 mm, height 115 mm) at 1723 K for 50 minutes, subsequently decreasing temperature at a rate of 10 K/min to 1073 K and keeping for 60 min before quenched by blowing Ar gas. During the whole synthesized process, the reaction tube of the electric furnace was flushed by Ar flow with a rate of 1 L/min. The synthesized slag was ground and sieved to powder with particle diameter of less than 150 μm. The compositions of slags are shown in Table 1.

Table 1 Compositions of synthesized slags. (mass%)

slag	FeO	CaO	SiO_2	P_2O_5	Al_2O_3	CaO/SiO_2
C-1.0	30	31.3	31.2	2.5	5.0	1.0
C-1.5	30	37.5	25.0	2.5	5.0	1.5
C-2.0	30	41.7	20.8	2.5	5.0	2.0

The artificial seawater is made by mixing a measured amount of instant artificial seawater powder (from BizScience company) and 20 L distilled water in a polyethylene bottle, and its pH is controlled to around 8.20 by 0.13 mol/L alkali solution. The composition of artificial seawater is shown in Table 2. The concentrations of Ca and Mg in the normal artificial seawater are calculated as 419 ppm and 1328 ppm respectively.

Table 2 Chemical composition of artificial seawater.

Constituent	Concentration (mg/L)
NaCl	24534.0
$MgCl_2 \cdot 6H_2O$	11111.5
Na_2SO_4	4094.0
$CaCl_2 \cdot 2H_2O$	1535.0
KCl	694.5
$NaHCO_3$	201.0
KBr	100.5
$SrCl_2 \cdot 6H_2O$	42.5
H_3BO_3	27.0
NaF	3.0

The dredged soil is taken from an inner harbor in Japan and the ratio of contained water to soil is 3.4.

2.2 Shaking experiments

One gram of synthesized slag was mixed completely with approximate 8 g of dredged soil in a 250 mL polyethylene bottle and kept in a fume cupboard for 1 day. Then the mixture was put with 100 mL artificial seawater and shaken for 1 hour to 4 days at the room temperature. After shaking, the solution was filtrated by the membrane filter with 0.45 μm pore diameter, and pH and ORP were measured immediately. The concentrations of Ca, Mg, Si and Al were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), and concentrations of Fe and P were measured by 1, 10-phenanthroline spectrometric method and molybdenum blue spectrophotometric method respectively.

3. Results

3.1 Variation tendency of pH and ORP

The change of pH of shaking solution with slag-dredged soil mixture is shown in Fig.1. During the shaking process, pH of seawater is stable around 8.20, while that of the shaking solution with dredged soil decreases quickly in the initial shaking period and then keeps 7.0 after two days. The pH of shaking solution with slag-dredged soil mixture also decreases slightly in the initial period and keeps stable after 12 hours. Consequently, addition of dredged soil can provide a buffering action on the whole pH increasing process. Moreover, pH increases with increasing the CaO/SiO_2 ratio of slag. As it is well known that increase of pH is resulted from the dissolution of Ca from slag, the dissolution behavior of Ca is given in Fig.2.

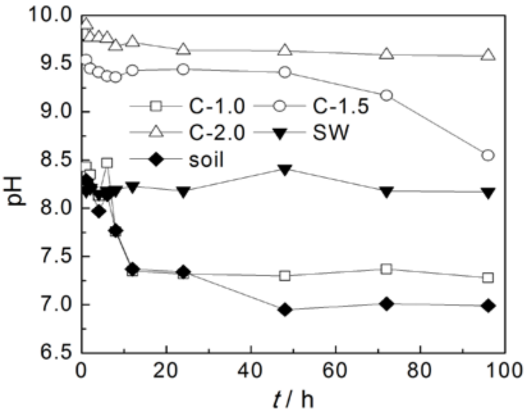

Fig.1 pH change of solutions with time.

The concentration of Ca during shaking of dredged soil and mixture of slag C-1.0 and dredged soil has approximately the same concentration of Ca as that of seawater. The dissolution behavior of Ca from the slag-soil mixtures shows a similar variation tendency with pH change, namely the concentration of Ca is larger when the CaO/SiO_2 ratio of slag is larger. Though the concentration of Ca in the case of mixture of slag C-2.0 and soil is much larger (near 1760 ppm) than that in the case of mixture of slag C-1.5 and soil (817 ppm at largest), pH of mixture of slag C-2.0 and soil is merely a little larger than that of mixture of slag C-1.5 and soil.

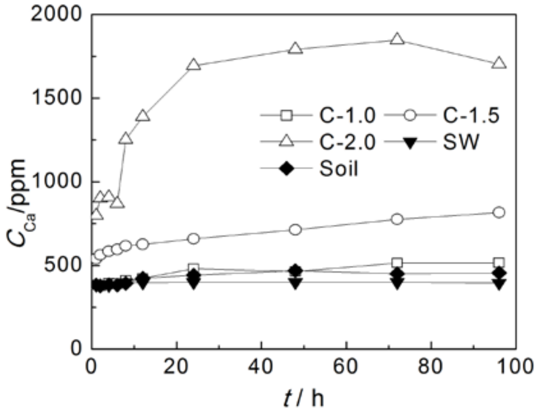

Fig.2 Dissolution behavior of Ca.

Compared with the dissolution behavior of Ca, the concentration change of Mg has an opposite variation tendency according to the CaO/SiO_2 ratio of slag. When the CaO/SiO_2 ratio of slag is larger, the concentration of Mg in the shaking solution is lower. For instance, the concentration of Mg of mixture of slag C-2.0 and soil is lowest which is 550 ppm after shaking for one day.

Fig.3 gives the variation tendency of ORP of shaking experiments with time. Compared with seawater having 430 mV of ORP, shaking solution with slag-soil mixture or soil has a much smaller ORP value. All of them changes from 250 mV to 350 mV.

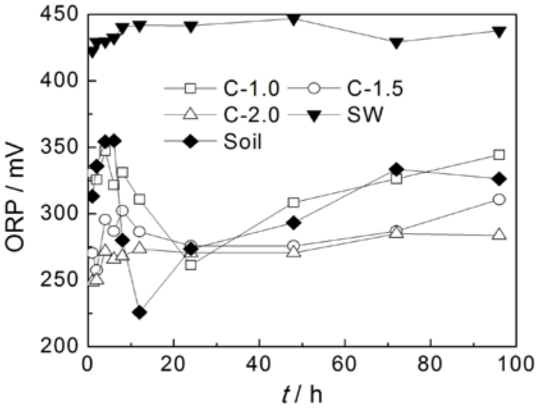

Fig.3 Variation tendency of ORP with time.

3.2 Dissolution behavior of Al, Si, P and Fe

The dissolved concentration of Al increases with increasing the CaO/SiO_2 ratio of slag and shaking time. After 4 days shaking, the concentrations for soil, mixture of slag C-1.0 and soil, C-1.5 and soil and C-2.0 and soil is 2.92, 3.77, 4.96 and 7.98 ppm respectively.

The concentration of Si is high in the beginning of shaking and subsequently it decreases in the initial time of shaking briefly. The concentration of Si for slag-soil mixture is larger than that for soil shaking. The dissolution of Si for mixture of slag C-2.0 and soil decreases monotonously with shaking time. The dissolution of Si for mixture of C-1.5 and soil appears a maximum value at shaking for 8 hours, while that of mixture of slag C-1.0 and soil reaches a minimum value when shaking for 6 and 8 hours, and then it gradually increases in the following shaking time. Generally, the concentration of Si for mixture of slag C-1.5 and soil is largest compared with others.

The dissolved concentration of P was detected only in the shaking solution of mixture of slag C-1.5 and soil. The concentration of P is stable but greatly increases at the fourth day. The largest concentration of P is 1.668 ppm.

The dissolved Fe is not detected in seawater but in some of the shaking solutions with an extremely low concentration. The effect of dredged soil on the dissolution of Fe is indistinct and ambiguous.

4. Discussion

4.1 Influence factor on pH increasing process

In the shaking experiments, the increase of pH proceeds with the dissolution of Ca but it does not increase continuously because of Mg contained in the seawater. Fig.4 gives the relationship between concentration change of Ca and Mg. Concentration of Mg has no change in the case of the dissolution of Ca from soil and mixture of slag C-1.0 and soil, while it decreases linearly with the increase of Ca concentration in the case of the dissolution of Ca from mixture of slag C-1.5 and soil and mixture of slag C-2.0 and soil. Therefore, pH of the shaking solution cannot increase unboundedly even though the considerable dissolution of Ca from mixture of slag C-2.0 and soil occurs. Hence, a substitution reaction that Mg ion provides a buffering action when pH reaches a certain extent can be deduced:

$$\mathrm{CaO(in\ slag)+H_2O+Mg^{2+}(in\ seawater)=Ca^{2+}(in\ seawater)+Mg(OH)_2(s)} \quad (1)$$

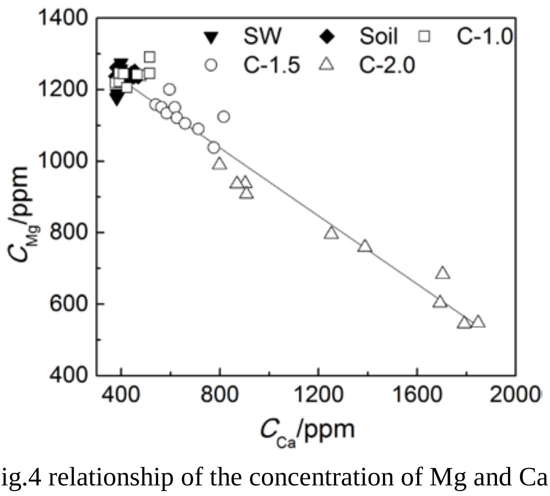

Fig.4 relationship of the concentration of Mg and Ca.

4.2 Dissolution mechanism of Fe

Potential-pH diagram for iron – water system at room temperature is shown in Fig.5 [13] together with the ORP value of shaking experiments. Although the ORP values of the shaking experiments in the case of slag-soil mixture or soil are lower than that of seawater, they are still in the Fe_2O_3 stable region. Therefore the concentration of the dissolved iron is in equilibrium with Fe_2O_3 phase. Owing to the extremely low solubility of Fe_2O_3, the dissolved iron is very little in the shaking solution even with the addition of dredged soil.

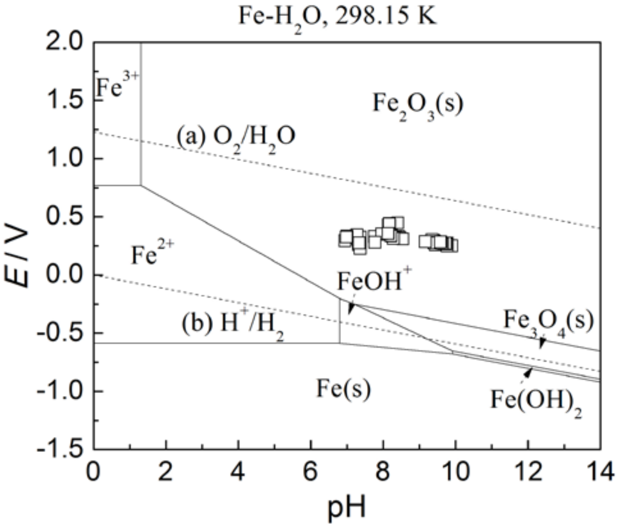

Fig. 5 Potential - pH diagram for iron - water system at 25°C (Concentration of Fe is 10^{-6} mol/L).

5. Conclusions

The effect of dredged soil on the dissolution behavior and mechanism of Ca, Si, Al, Fe and P from steelmaking slag into seawater was investigated by shaking experiments. The pH increases is enhanced by the dissolution of Ca from slag-soil mixture or soil, while Mg contained in the seawater provides a buffering action when pH reaches a certain extent and the dredged soil supplies a slight buffering action on the whole pH increasing process. The ORP value of shaking experiments is lower than that of seawater. The dissolution behaviors of Al, Si, P depend on the CaO/SiO_2 ratio of slag. The dissolved iron is little because the ORP value of shaking in the case of slag-soil mixture or soil is in the Fe_2O_3 stable area, which has an extremely low solubility in the seawater.

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