Dissolution Behavior of Environmentally Regulated Elements from Steelmaking Slag into Seawater

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Steelmaking slag contains nutrition such as Si, P and Fe for acceleration of phytoplankton growth. Phytoplankton can fixate carbon dioxide more than any other creatures on the earth. Hence, suppression of CO₂ can be achieved by educating the potential of steelmaking slag as the nutrition for their propagation.

When it is considered to supply nutrition from steelmaking slag to seawater, we must avoid hazardous elements dissolution from steelmaking slag into seawater. In the present work, the dissolution behavior of Ca, Mg, Mn and F from steelmaking slags into artificial seawater was studied continuously with our previous paper. The dissolution mechanism of elements from steelmaking slags was discussed again by using stability diagram in seawater.

KEY WORDS: steelmaking slag; CO₂ fixation; seawater; marine phytoplankton; solubility; thermodynamics; stability diagram; environmentally regulated elements.

1. Introduction

More than 13 million tons of steelmaking slags are produced and about 0.5 million tons of steelmaking slags are landfilled each year in Japan. Utilization of steelmaking slag is indispensable for sustainable growth of steelmaking industry. Large amount of carbon dioxide is discharged from steelmaking industries and it is threatening the global environment every minute. Therefore, immediate action for CO₂ suppression is required.

When it is considered to supply nutrition from steelmaking slag to seawater, we must avoid hazardous elements dissolution from steelmaking slag into seawater. In the present work, the dissolution behavior of Ca, Mg, Mn and F from steelmaking slags into artificial seawater was studied continuously with our previous paper. The dissolution mechanism of elements from steelmaking slags was discussed again by using stability diagram in seawater.

2. Experimental

Hot metal pretreatment slags and converter slags were supplied from six steelmaking companies in Japan. The supplied slags were identical with that used in the previous work. Chemical analysis of the samples was done with the wave length dispersion type Electron Probe Micro Analyzer (EPMA) and the dissolution experiment of steelmaking slags into artificial seawater was conducted in the same manner with the previous work. The concentrations of Ca, Mg and Mn in solutions were determined by the Induction Coupled Plasma Spectroscopy (ICP). The concentration of F was determined by F-ion electrode method. The pH of solution was periodically adjusted to 8, which is the pH of natural seawater, by adding adequate amount of reagent grade of HCl.

Calculation of stability diagram was carried out as the same manner as the previous work. In the present work, formation of complex ions was considered. Concentrations of complex ions were evaluated using stability constant, K'. The reaction for formation of complex ion, MI, and stability constant can be expressed as Eqs. (1) and (2).

\[ \text{M} + \text{I} = \text{MI} \] ....................................... (1)

\[ \log K' = \log a_M - \log a_I - \log a_c \\
= \log \gamma_M + \log \gamma_I - \log \gamma_c \\
\] ............................................... (2)

where, a is activity, γ is activity coefficient, and c is mole concentration in aqueous solution (mol·L⁻¹). The activity...
is referred to pure substance coexisting with seawater. Concentration of 1 mol·L⁻¹ was chosen as a standard state for species dissolving in seawater.

Standard potential, activity coefficient, and stability constant at 298 K used in the present work are listed in Tables 1 to 3. Estimation of activity coefficients in seawater was conducted by the same manner as the previous work.

3. Results and Discussion

3.1. Morphology of Fluorine in Steelmaking Slag

Figures 1 and 2 show typical examples of fluoride, calcium and phosphorus mapping images observed by EPMA for slags of P9 and P11. The total compositions of steelmaking slag used have been reported in the previous work. Fluorine co-existed with calcium and no fluorine was observed in the phosphorus concentrated phase in slag P11, which had high calcium content. Fluorine speculated to exist mainly as CaF₂ in this slag. On the other hand, in slag P9, which had low calcium content, fluorine co-existed with both calcium and phosphorus. Therefore, fluorine in this slag was presumed to exist mainly as apatite phase. It was deduced from these results that the morphology of fluorine would change with the composition of steelmaking slag.

3.2. Dissolution of Ca, Mg, Mn and F from Steelmaking Slag into Artificial Seawater

The results on dissolution behavior of Ca, Mg, Mn and F from steelmaking slag into artificial seawater are shown in Figs. 3 and 4. Dissolution behavior of elements from steelmaking slag differs from each other. Calcium contents increased rapidly and the final calcium contents varied from 400 to 1 400 mg/L. In general, concentrations of magnesium from hot metal pretreatment slag did not change and those from converter slag slightly decreased. Rates of manganese dissolution were very slow and the maximum manganese content after the experiment was 2 mg/L. Dissolution behavior of fluorine divided clearly into two groups, whether the rates of fluorine elution were positive or not. Fluorine did not dissolve from some samples while fluorine dissolved more than 15 mg/L from others. This behavior is discussed later.

3.3. Calculation of Stability Diagram in Seawater

The stability diagrams of Ca, Mg, CO₃⁻, Cr, Pb, Cd, As, and would change with the composition of steelmaking slag.

Table 1. Standard chemical potentials of substances at 298 K.

| species    | state     | \( \mu / J \) Ref |
|------------|-----------|-----------------|
| H⁺         | aq        | 0               |
| Ca⁺        | aq        | -553087         |
| Mg⁺        | aq        | -456036         |
| Cl⁻        | aq        | -131157         |
| SO₄²⁻      | aq        | -754202         |
| ̂F⁻        | aq        | -276482         |
| H₂CO₃⁻     | aq        | -623445         |
| HCO₃⁻      | aq        | -587083         |
| CO₃²⁻      | aq        | -528129         |
| H₂SO₄²⁻    | aq        | -1012576        |
| HSO₄⁻      | aq        | -955503         |
| SO₃²⁻      | aq        | -887050         |
| H₂PO₄⁻     | aq        | -1147307        |
| HPO₄²⁻     | aq        | -113173         |
| PO₄³⁻      | aq        | -1094168        |
| CO₃²⁻      | aq        | -776658         |
| H₂CO₃⁻     | aq        | -777926         |
| CaF₂       | s         | -315400         |
| PbF₂       | aq        | -243110         |
| HPO₄⁻      | aq        | -33892          |
| Ca²⁺       | aq        | -77792          |
| Mg²⁺       | aq        | -361600         |
| CaCO₃      | aq        | -607292         |
| Ca₂O₂      | aq        | -350217         |
| H₂O        | l         | -237141         |
| CO₂        | g         | -94089          |
| CaCO₃      | s         | -1128811        |
| Ca(OH)₂(CaO Hyd.) | s | -898421 |
| CaSO₄     | s         | -135904         |
| Ca₂O₂     | s         | -279300         |
| CaO₂PO₄    | s         | -219850         |
| Ca₃PO₄     | s         | -420138         |
| MgO       | s         | -102823         |
| Mg(OH)₂(MgO Hyd.) | s | -833652 |
| MgSO₄     | s         | -1147408        |
| Ca₂O₂     | s         | -1546950        |
| Ca₂O₂       | s         | -312654         |
| CaPO₄      | s         | -384496         |
| Ca₂O₂      | s         | -1175460        |
| PO₄        | s         | -189335         |
| CaO       | s         | -225068         |
| As₂O₃      | s         | -756080         |

Table 2. Activity coefficient of dissolved substances in seawater at 298 K.

| species | Activity coefficient | Ref |
|---------|----------------------|-----|
| H₂CO₃⁻ | 1.13                 | 9   |
| Na₂CO₃ | 1.13                 | 9   |
| Mg₂CO₃ | 1.13                 | 9   |
| CaCO₃  | 1.13                 | 9   |
| MgCO₃  | 1.13                 | 9   |
| Ca₂O₂  | 1.13                 | 9   |
| CO₂    | 0.68                 | 9   |
| Na₂    | 0.76                 | 9   |
| K⁺     | 0.64                 | 9   |
| Mg²⁺   | 0.36                 | 9   |
| Na⁺    | 0.28                 | 9   |
| Cl⁻    | 0.64                 | 9   |
| CO₃²⁻  | 0.20                 | 9   |
| SO₄²⁻  | 0.12                 | 9   |
| F⁻     | 0.61                 | Debye-Hückel eq |
| Cr³⁺   | 0.80                 | Debye-Hückel eq |
| Mg²⁺   | 0.68                 | HCO₃⁻ |
| Ca²⁺   | 0.68                 | HCO₃⁻ |
| MgCl²⁻ | 0.16                 | HPO₄⁻² |
| CaCl²⁻ | 0.16                 | HPO₄⁻² |
| H₂CO₃⁻ | 1.13                 | HCO₃⁻ |
| Cr₂O₄²⁻| 0.16                 | HPO₄⁻² |
| Pb²⁺   | 0.16                 | HPO₄⁻² |
| H₂PO₄⁻ | 1.16                 | H₂PO₄⁻ |
| Ca²⁺   | 0.68                 | H₂PO₄⁻ |
| As₂O₃  | 0.68                 | H₂PO₄⁻ |
| H₂SO₄⁻ | 1.13                 | H₂SO₄⁻ |
| As₂O₃  | 0.68                 | H₂SO₄⁻ |

Table 3. Stability constants log \( K' \) of substances in seawater at 298 K.

| H₂CO₃⁻ | CO₃²⁻ | SO₄²⁻ | F⁻ | Cl⁻ |
|--------|-------|-------|-----|-----|
| 0.96   | 0.72  | 0.68  | 0.72 | 0.2 |
| 0.69   | 0.72  | 0.72  | 0.68 | 0.2 |
| 1.16   | 3.49  | 2.36  | 1.3  | 0.2  |
| 1.16   | 3.49  | 2.36  | 1.3  | 0.2  |
Fig. 1. EPMA mapping image of F, Ca and P in high CaO concentration steelmaking Slag P11.

Fig. 2. EPMA mapping image of F, Ca and P in low CaO concentration steelmaking Slag P9.
Fig. 3. Dissolution behavior of elements into artificial seawater from hot metal pretreatment slags.

Fig. 4. Dissolution behavior of elements into artificial seawater from converter slags.
and F were calculated in order to discuss the dissolution behavior of environmentally restricted elements from steelmaking slag and mechanism of pH increase with calcium dissolution.

The stability diagrams were calculated at 298 K in the present work, because most of the standard potentials of dissolved species were unknown at room temperatures and are applicable to the ocean condition. The contents of objective elements in seawater and pH were chosen as the variables, while concentrations of all the other elements were fixed except for stability diagram of fluorine. Bold lines in the stability diagrams are the solubility limits of each element and thin lines represent equilibrium concentration of various kinds of dissolved species. Substances in square bracket show the solid species that precipitates in cooled slag and become stable in seawater on each condition. Dissolved substances are represented in parenthesis.

To understand the nature of the sea, it is important to know the equilibrium among Ca, Mg and CO₂ in seawater. Hence, the stability diagrams of Ca, Mg and CO₂ were determined.

Stability diagram of calcium in seawater at 298 K is shown in Fig. 5. In the present work, CaCO₃, Ca(OH)₂, CaO, and CaSO₄ were considered as possible solid substances that could equilibrate with seawater. Ions such as, Ca²⁺, CaSO₄⁻, CaF⁻, CaHPO₄, CaHCO₃⁻, CaCO₃⁻ were also taken into account as dissolved species. Calcium content that equilibrates with CaSO₄ is extremely high, and thus the calcium solubility to CaSO₄ saturation is not shown in the figure. Concentrations of Ca²⁺ that equilibrates with Ca(OH)₂ and CaO are always approximately 10⁻⁸ times larger than that equilibrating with CaCO₃. Therefore, CaCO₃ would precipitate before Ca(OH)₂ when calcium solubility to CaCO₃saturation is more basic region. Predominant dissolving species is Ca²⁺ at lower pH than 9.7, while CaCO₃⁻ is the predominant one when pH is higher than 9.7.

The average calcium content and pH in natural seawater are shown as a solid circle, and it lies on the saturation line of CaCO₃. Since the major constituent of shell and coral that exist in the sea is CaCO₃, it is reasonable that actual seawater is saturated with this phase. This fact supports the stability diagram calculated in the present work.

When the steelmaking slag is added to the ocean, and if the CaO phase exists on the surface of steelmaking slag, CaO will easily dissolve into seawater. As the result, both pH and Ca²⁺ concentration will increase as the arrow in Fig. 5, with the following reaction.

\[
\text{CaO} + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{OH}^- \quad \text{(3)}
\]

The concentration of Ca²⁺ ion saturated with 3CaO·SiO₂ or 2CaO·SiO₂ in seawater, is shown in Fig. 5. Calcium content in equilibrium with 4CaO·P₂O₅ is extremely high, and thus the calcium solubility to 4CaO·P₂O₅ saturation is not shown in the figure. Dissolution of these phases into seawater results in the increase of Ca²⁺ concentration and pH as well as CaO dissolution.

If CaO, 3CaO·SiO₂, 2CaO·SiO₂, or 4CaO·P₂O₅ phase is added to fresh water, the pH and Ca²⁺ concentration will increase to solubility limit of each substance. Fortunately, there are huge amount of Mg²⁺ ion in seawater and the buffering action will take place to prevent more increase of pH. This will be explained later.

Stability diagram of magnesium in seawater at 298 K is shown in Fig. 6. In the present work, MgCO₃, MgO, Mg(OH)₂, and MgSO₄ were considered as possible solid substances that could equilibrate with seawater. Ions such as, Mg²⁺, MgSO₄⁻, MgCl⁻, MgF⁻, MgHPO₄⁻, MgHCO₃⁻, MgCO₃⁻ were also taken into account. As magnesium content that equilibrates with MgSO₄ is extremely high, the magnesium solubility to MgSO₄ saturation is not shown in the figure. Concentration of Mg²⁺ that equilibrates with MgO and Mg(OH)₂ are always about 1000 times larger than that equilibrating with MgCO₃. Therefore, magnesium solubility in seawater is governed by MgCO₃ saturation.

The bold line shows the sum of the solubility of magnesium containing species. The solubility of magnesium decreases with increase of pH and the solubility will be constant at higher pH than approximately 10. Predominant dissolving species is Mg²⁺ at lower pH than 9.5, while MgCO₃⁻ is the predominant when pH is higher than 9.5. Magnesium content and pH in actual seawater are in the stable region of MgCO₃ in Fig. 6. This is reasonable be-
cause coral in the sea contains MgCO₃, and seawater should be saturated with MgCO₃.

If the pH of seawater increases beyond 9.4 by dissolution of CaO, Mg(OH)₂ will precipitate, and the buffering action of Mg²⁺ in seawater will take place to avoid further pH increase accordingly to Eq. (4).

\[
\text{CaO} + \text{H}_2\text{O} + \text{Mg}^{2+} = \text{Ca}^{2+} + \text{Mg(OH)}_2 \quad \text{(4)}
\]

Buffering action to pH increase in seawater by Mg ion has also been observed by Masuda. Hence, drastic change of pH will not occur unless massive amount of CaO containing steelmaking slag is added to the sea. The buffering to pH increase will also take place if 3CaO · SiO₂, 2CaO · SiO₂, or 4CaO · P₂O₅ containing steelmaking slag is added to seawater.

Stability diagram of carbon dioxide in seawater at 298 K is shown in Fig. 7. Partial pressure of CO₂ in air, P_CO₂, was set at 0.0003/10⁵ (Pa) in the present work. H₂CO₃, HCO₃⁻, MgHCO₃⁻, NaHCO₃, CaHCO₃⁻, CO₃²⁻, MgCO₃, NaCO₃, CO₃²⁻, and CaCO₃ were considered as dissolved species. The bold line shows sum of the solubility of carbon containing species. The solubility of carbon is constant when pH is lower than 6, and it increases with pH at higher pH condition. The predominant ion on the conditions where pH is lower than 6.7, between 6.7 and 8.9, and higher than 8.9 are H₂CO₃, HCO₃⁻, and MgCO₃, respectively. Average carbon content and pH in actual seawater are very close to the bold line.

It is found from the calculated stability diagrams of calcium, magnesium, and carbon that CO₂ in air atmosphere is in equilibrium with seawater, and also calcium and magnesium are in equilibrium with CaCO₃ and MgCO₃. Even if calcium and magnesium contents and pH in seawater change drastically by slag addition, calcium and magnesium contents and pH in seawater will return to its initial value defined by equilibrium among CaCO₃, MgCO₃, and CO₂ in air atmosphere.

Since steelmaking slag contains some elements, which are regarded as harmful to the environment and human-being, dissolution of these elements from steelmaking must be prevented. In the following, the stability diagrams of these elements were calculated at 298 K.

Stability diagram of chromium in seawater at 298 K is shown in Fig. 8. In the present work, Cr(OH)₃, Cr₂O₃, Cr(OH)₆⁺, Cr(OH)₅⁻, Cr₂O₇⁻ and H₂O were considered as possible solid substances that could equilibrate with seawater. Trivalent chromium ions, Cr³⁺, Cr(OH)²⁺, Cr(OH)₅⁻, and Cr₂O₇⁻ were taken into account in the calculation. The predominant trivalent chromium species are Cr³⁺, Cr(OH)²⁺, Cr(OH)₅⁻, and Cr₂O₇⁻, on the condition where, pH is lower than 4.0, between 4.0 and 6.8, between 6.8 and 8.5, and higher than 8.5, respectively. Solubility of chromium increases when the equilibrium with solid substances change from Cr(OH)₃, Cr₂O₃ to Cr(OH)₅, Cr₂O₇⁻.

Due to the change of predominant ionic species with pH, the solubility of chromium takes the minimum value at pH of 8.5 in seawater and chromium content of seawater is less than 0.05 mg/L. This value depends on the kind of solid substance. However, hexavalent chromium ions are more stable than trivalent ions in air. Stability diagram involving hexavalent chromium ions and Cr(OH)₆⁺, Cr₂O₃, Cr(OH)₅⁻, H₂O is shown in Fig. 9. Oxygen partial pressure, P_O₂, was set at 0.21/10⁵ (Pa). HCrO₄⁻ and CrO₄²⁻ were considered as hexavalent chromium ions in the calculation of stability diagram. Solubility of chromium ions is tremendously high and exceeds the environmental regulation limit of 0.05 mg/L. The equilibrium hexavalent chromium ion concentration will be lower than the environmental regulation...
limit, when the activity of \( \text{Cr(OH)}_3 \) is lower than approximately \( 10^{-6} \).

The stability diagrams of lead, cadmium and arsenic in seawater are shown in Figs. 10 to 12. For lead and cadmium, solubility has a minimum value caused by the change of predominant ionic species with pH. The concentrations of these elements equilibrating with pure oxides in seawater exceed the environmental regulation limit in the whole pH region. Environmental regulation will be satisfied when the activity of \( \text{PbO} \), \( \text{CdO} \) and \( \text{As}_2\text{O}_3 \) are lower than \( 10^{-7}, 10^{-7} \) and \( 5 \times 10^{-6} \), respectively. Therefore, steelmaking slags that contain certain amounts of chromium, lead, cadmium and arsenic should not be added into seawater without immobilizing these elements.

Stability diagram of fluorine in seawater at 298 K is shown in Fig. 13.\(^{14}\) The variables were selected as pH, calcium and magnesium contents for the calculation of stability diagram of fluorine. The increase of pH with Ca dissolution, and buffering action to pH increase by Mg ions were taken into account. \( \text{CaF}_2 \) was considered as fluorine containing solid substance and \( \text{F}^- \), \( \text{MgF}^+ \), and \( \text{CaF}^+ \) were taken into account as fluorine containing ion species in the present work. The pH and \( \text{Ca}^{2+} \) content of seawater would increase when \( \text{CaO} \) containing steelmaking slag is added, because \( \text{CaO} \) would dissolve into seawater according to Eq. (3). pH and log(a\(\text{Ca}^{2+}\)) increments in the proportion of 2 : 1 during the CaO dissolution into seawater. Hence, fluorine solubility at \( \text{CaF}_2 \) saturation would decrease with increase of pH, because the solubility product of \( \text{CaF}_2 \) is constant. Since \( \text{Ca}^{2+} \) content is much larger than \( \text{OH}^- \) content in natural seawater, the effect of \( \text{Ca}^{2+} \) content increase on fluorine solubility is discreet when pH is lower than 11. \( \text{Mg(OH)}_2 \) precipitates when pH is higher than 9.4, and the equilibrium content of \( \text{MgF}^+ \) decreases with pH increase, and it results in the decrease of total fluorine concentration in seawater.

Seawater will be saturated with \( \text{Ca(OH)}_2 \) where pH is over 12.2 as shown in Fig. 5, because precipitation rate of \( \text{Ca(OH)}_2 \) is faster than that of \( \text{CaCO}_3 \)\(^{15}\) and hence fluorine solubility in seawater in this pH range can be determined by \( \text{CaF}_2 \) and \( \text{Ca(OH)}_2 \) doubly saturated condition shown in the following reaction.

\[
\text{CaF}_2 + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + 2\text{F}^- + 2\text{H}^+ \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)
\]

The fluorine solubility would increase with increasing pH on the condition where pH is higher than 12.2. However, pH increase would cease after \( \text{Ca(OH)}_2 \) is formed in seawater. Hence, fluorine content in seawater would decrease from the initial fluorine content of seawater when steelmaking slag is added.

It is observed that fluorine dissolved from some slag samples in the dissolution experiment of steelmaking slag into artificial seawater. This does not agree with the estimation derived from the stability diagram of fluorine. Relation among fluorine elution behavior from steelmaking into sea-
water and CaO and P2O5 contents of steelmaking slag is shown in Fig. 14. We can roughly say from this figure that fluorine does not dissolve when CaO content of steelmaking slag is low and P2O5 content is high. Two stable apatite phases, Ca₆(PO₄)₆F₂ and Ca₇(PO₄)₄F₂, exist between 3CaO·P₂O₅ and CaF₂ according to the 3CaO·P₂O₅–CaF₂ binary phase diagram. Ca₆(PO₄)₆F₂ is stable and no element will dissolve into seawater from this phase according to the stability diagram of phosphorus in seawater. Hence, it is important to control the CaO and P₂O₅ contents of steelmaking slag in order to precipitate apatite phase during cooling period to avoid fluorine elution.

As the result, fluorine content and pH in seawater would not drastically change by the addition of steelmaking slag. Hence, steelmaking slag may be utilized in seawater without releasing fluorine.

Taniguchi et al. conducted the large-scale dissolution experiment of environmentally restricted elements from steelmaking slag into natural seawater. No significant change of F and As concentrations with time in natural seawater was observed. Hence, dissolution of F and As from steelmaking slag into natural seawater was minute. Other environmentally restricted elements such as Cd, CN, Pb, Cr⁶⁺, Se were not detected through their experiment. Therefore, it was confirmed that environmentally regulated elements in steelmaking slag did not dissolve into seawater during their experimental periods. Dissolution of environmentally restricted elements can be avoided by controlling the composition of steelmaking.

4. Conclusions

Environmentally restricted elements in steelmaking slag do not dissolve into seawater, when concentrations of these elements are relatively low. However, environmentally restricted elements are unstable in seawater. Hence, steelmaking slag, which contains certain amounts of restricted elements, must be immobilized.

The mechanism of buffering action of magnesium ion in seawater can be explained by means of stability diagram. Fluorine content and pH in seawater would not drastically change by addition of steelmaking slag.

Dissolution behavior of fluorine does strongly depend on the composition of steelmaking slag. Control of the slag composition is one of the options to immobilize fluorine in steelmaking slag.

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