Dissolution Behavior of Nutrition Elements from Steelmaking Slag into Seawater

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Suppression of CO₂ and waste such as slags discharged from iron- and steelmaking processes are some of the typical biggest issues for the protection of global environment and sustainable growth of steelmaking industry. Utilization of active phytoplankton growth will be one of the best options to stabilize and suppress carbon dioxide at high-efficiency.

Inorganic minerals such as C, O, N, Si, P and Fe are necessary for phytoplankton multiplication. It is crucial for supply of nutrition into seawater effectively for phytoplankton multiplication to understand the dissolution behavior of some elements from steelmaking slags into seawater. Firstly, the morphology of the precipitated phases in steelmaking slags during cooling period was investigated in the present work. Secondary, the dissolution behavior of some elements from steelmaking slags and pure substances such as 4CaO·P₂O₅ (8.5 mass% P), 3CaO·P₂O₅ (10.0 mass% P) and 2CaO·SiO₂–3CaO·P₂O₅ (2.8 mass% P) solid solution phase into artificial seawater has also been studied. Thirdly, the dissolution mechanism of elements from steelmaking slags was discussed by using stability diagrams of Si, P and Fe in seawater.

KEY WORDS: steelmaking slag; CO₂ fixation; seawater; marine phytoplankton; solubility; thermodynamics; phase diagram; nutrition.

1. Introduction

Suppression of CO₂ and waste such as slags discharged from iron- and steelmaking processes are some of the typical biggest issues for the protection of global environment and sustainable growth of steelmaking industry. Utilization of active phytoplankton growth will be one of the best options to stabilize and suppress carbon dioxide at high-efficiency because phytoplankton can fixate more than 2 kg/m² of carbon per year. If active phytoplankton multiplication in the ocean can be achieved for an area of 10000 km², almost the same area with Aomori-Prefecture of Japan or half of the State of New Jersey, 20 M tons of carbon will be stabilized. This is equivalent to the required reduction amount of greenhouse gases that Japan has committed in the Kyoto Protocol at the United Nations Framework Convention on Climate Change (COP3).

Inorganic minerals such as C, O, N, Si, P and Fe are necessary for phytoplankton multiplication. It has been reported by Nakamura et al.1) that some kinds of phytoplankton can grow quite rapidly if Fe, Si, P and N are supplied into seawater in the adequate proportion. One of the best candidates as a source of such minerals is steelmaking slag because of its cheap cost, sufficient quantity, adequate mineral concentration and its ionic nature. On the other hand, steelmaking companies are now seeking for a new technology to reduce the amount of steelmaking slag and new demand of the slag as valuable resources.2)

It is crucial for supply of nutrition into seawater effectively for phytoplankton multiplication to understand the dissolution behavior of some elements from steelmaking slags into seawater.3) Firstly, the morphology of the precipitated phases in steelmaking slags during cooling period was investigated in the present work. Secondly, the dissolution behavior of some elements from steelmaking slags and pure substances such as 4CaO·P₂O₅ (8.5 mass% P), 3CaO·P₂O₅ (10.0 mass% P) and 2CaO·SiO₂–3CaO·P₂O₅ (2.8 mass% P) solid solution phase into artificial seawater has also been studied. Thirdly, the dissolution behavior of elements from steelmaking slags was discussed by using stability diagrams of Si, P and Fe in seawater.

2. Experimental

2.1. Chemical Analysis of Steelmaking Slags

Composition of hot metal pretreatment slag and converter slag supplied from six steelmaking companies in Japan is shown in Tables 1 and 2. Since the specification of steel products and operating conditions are widely different in each plant, slag composition such as basicity (CaO/SiO₂ in
mass ratio), FeO content and P₂O₅ content is different in the range of 1.79–9.67, 1.3–42.2 mass% and 0.68–16.9 mass%, respectively. The concentrations of minor components such as Al₂O₃, MnO, F and S are also different. Slag samples were mounted in the mold with resin and polished, and then carbon was deposited on the polished surface. Concentration of each element in samples was analyzed with the wave length dispersion type Electron Probe Micro Analyzer (EPMA).

For some slag samples, re-heating experiment was conducted to examine the effect of cooling rate on the morphology of the precipitated phases in steelmaking slag during the cooling period. Two small iron crucibles containing approximately 5 g of slag were kept at 1 623 K for 1 or 5 h in the hot zone of vertical electric resistance furnace under Ar atmosphere. After the aimed holding time, one of the crucibles were withdrawn from the upper part of the reaction tube in the furnace and quenched by jetting He gas, and another was cooled from 1 623 K to room temperature in the furnace with the constant slow cooling rate of 1 K/min. Both morphology and contents of each element in slag samples were also analyzed by EPMA.

2.2. Dissolution Experiment of Steelmaking Slags into Seawater

One gram of steelmaking slag (270 mesh under) was put in the tefron vessel together with 0.500 L of artificial seawater and kept for the given period under the constant oscillation mode (oscillation width 40 mm, 80 cycles per minute). Temperature of the seawater was kept constant at 293 K with the aid of isothermal circulator. At the aimed period, seawater was filtrated to remove solid substances and supplied for chemical analysis. The contents of Si, P and Fe in solutions were determined by the Induction Coupled Plasma Spectroscopy (ICP). By adding adequate amount of reagent grade of HCl, pH of the solution was periodically adjusted to 8, which is the pH of natural seawater.

The dissolution behavior of elements from 4CaO·P₂O₅ (8.5 mass% P), 3CaO·P₂O₅ (10.0 mass% P) and 2CaO·SiO₂–3CaO·P₂O₅ solid solution phase (2.8 mass% P) into artificial seawater was also investigated. Substances 4CaO·P₂O₅ and 3CaO·P₂O₅ (biomaterial research grade) was supplied from pharmaceutical company, and 2CaO·SiO₂–3CaO·P₂O₅ solid solution was synthesized by ourselves by mixing CaCO₃, SiO₂, CaHPO₄·2H₂O and sintering at 1 773 K in air for 24 h. Each substance was confirmed using X-ray diffraction that the sample was desired phase.

2.3. Stability Diagram of Elements in Seawater

Estimation of stability diagram was carried out using the reaction involving water and hydrogen ion as Eq. (1).

\[ aA + nH₂O = bB + nH⁺ \].................(1)

where, \( a, b, m, \) and \( n \) are coefficients, \( A, B \) are ionic species or substances coexists with seawater. Equilibrium constant, \( K \), of Eq. (1) can be expressed as follows.

Table 1. Composition of hot metal pretreatment slag supplied from steelmaking companies.

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<tr>
<th></th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>MgO</th>
<th>MnO</th>
<th>F</th>
<th>S</th>
<th>Al₂O₃</th>
<th>CaO/SiO₂</th>
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<td>0.028</td>
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<td>47.2</td>
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<td>4.3</td>
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<td>2.6</td>
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<td>3.54</td>
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Table 2. Composition of converter slag supplied from steelmaking companies.

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<th></th>
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<th>Fe₂O₃</th>
<th>CaO</th>
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<th>P₂O₅</th>
<th>MgO</th>
<th>MnO</th>
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<th>Al₂O₃</th>
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<td>0.04</td>
<td>4.81</td>
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Here, $DG^\circ$ is Gibbs free energy of Eq. (1), $R$ is gas constant, and $T$ is absolute temperature. Equilibrium constant and Gibbs free energy can be expressed as Eqs. (3) and (4).

$$\log K = \frac{-\Delta G^\circ}{2.303RT} \quad \text{(2)}$$

In Eq. (4), $a$ is activity, $\gamma$ is activity coefficient, $c$ is molar concentration in aqueous solution (mol·L$^{-1}$), and $\mu^0$ is standard chemical potential of ions and substances. The activity is referred to pure state for substances coexisting with seawater. For species dissolved in seawater, concentration of 1 mol·L$^{-1}$ was chosen as a standard state. The activity of hydrogen ion and pH has the following relationship.

$$\text{pH} = -\log a_{H^+} \quad \text{(5)}$$

Combined Eqs. (3) to (5) and assumed the activity of water as unity, solubility of species or concentration ratio of species in seawater can be determined as follows.

$$b \log c_A - a \log c_A = \log K + n \log H^+ - b \log \gamma_A + a \log \gamma_A \quad \text{(6)}$$

Standard potential and activity coefficients at 298 K used in the present work$^{4-11}$ are listed in Tables 3 and 4. The activity coefficients of dissolved substances, $i$, in seawater that had not been reported were estimated using Debye–Hückel theory.

$$\log \gamma_i = -\frac{A z_i^2 \sqrt I}{1 + B d_i^0 I} \quad \text{(7)}$$

where, $A$ and $B$ are constants which depend on temperature and solvent, $z_i$ is valency of dissolved substances, $d_i^0$ is ion-size parameter (Å), and $I$ is ionic strength of the solvent. The values of $A$, $B$, and $I$ applied in the present work were 0.509, 0.329, and 0.676, respectively. The values for ion-size parameter reported by Klotz were used in the present work. For ion species which ion-size parameter is unknown, the activity coefficient was assumed to be equal to those of species which have the same valency as a first approximation.

3. Results and Discussion

3.1. Morphology of the Precipitated Phases in Steelmaking Slags

Figure 1 shows typical examples of phosphorus mapping images observed by EPMA for slags of P10 and P11. These slags were supplied from the same steelmaking company and they have different total content of P. In slag P11, which has higher average P content, some phases of which approximately 15 mass% P was concentrated in them. In slag P11, such phase was not observed but other phases, containing 4–5 mass% P, were found to be distributed homogeneously.

Similar observations were also conducted for other slags. It was found from these observations that phases existing in steelmaking slag could be classified into 4 groups. Phase A; the phosphorus concentration was very high (>10 mass%) and containing little Fe and Si, Phase B; the main cations were Ca and Si, and some amounts of P (3–6 mass%) were also included while almost no Fe was included, Phase C;
composition was very close to pure FeO, and phase D; others. Grain sizes of phase B and D were very small and they seemed to be consisted of some crystal phases. Phase D contained very low P. Compositions of phases A and B and those of phases C and D could be approximated to the CaO–SiO2–P2O5 ternary system, as Figs. 2 and 3.

It could be seen from Fig. 2 that the composition of the phosphorus concentrated phase was very close the composition of 4CaO·P2O5 and that of phase B were around the composition of 2CaO·SiO2 or 3CaO·SiO2 compound phases. Compound 4CaO·P2O5 is known to form solid solution, and 3CaO·P2O5 and 2CaO·SiO2 are reported to form silicophosphate solid solution in almost entire composition range at steelmaking temperature. It is found from Fig. 2 that composition of phases A and B corresponds to the mixture of these compounds and CaO.

Fig. 2. Composition of phase A and B in as-supplied steelmaking slags regarded as CaO–SiO2–P2O5 ternary system.

Among the plots in Fig. 3, phases that have extremely high FeO content would be wüstite phase precipitated during solidification. Phase D is suggested to contain the first solidified phase during cooling period.

Some slags were supplied for reheating experiment in order to examine the effect of cooling rate on the morphology of phosphorus concentrated phase. Phosphorus mapping images of P11 slag sample are shown in Fig. 4 for (a) quenched after keeping at 1,623 K for 5 h and (b) slowly cooled with 1 K/min after keeping at 1,623 K for 5 h. In both samples, phosphorus concentrated phase 4CaO·P2O5 was observed. From the comparison of Figs. 4(a) and 4(b), very fine 4CaO·P2O5 phase of approximately 2–3 μm was distributed in the quenched sample, while the morphology in slowly cooled sample seemed to be similar to that of the as-supplied slag. That is, slow cooling of slag resulted in the growth of phosphorus concentrated phase size.

Composition of phases A and B and that of phases C and D can be expressed on the CaO–SiO2–P2O5 and CaO–SiO2–FeO ternary systems, respectively, as Figs. 5 and 6. It shows that the compositions and kinds of existing phases were essentially the same as as-supplied slag, while size distribution was different strongly depended on the cooling rate.

3.2. Dissolution Experiment of Steelmaking Slags into Seawater

Nakamura et al.1) examined the propagation ability of 12 species of phytoplankton in seawater enriched with steel
They reported that enhancement of phytoplankton propagation could be achieved if some elements had been enriched in seawater from steelmaking slags. Dissolution behavior of elements from steelmaking slags into seawater was investigated according to their findings in the present work. The results are shown in Figs. 7 and 8.

Dissolution behavior of elements from steelmaking slags differs from each other. Dissolution rate of iron was very slow and the maximum dissolved iron content in seawater was 0.1–0.2 mg/L even after 30 d. Concentration of silicon and phosphorus increased up to 15 and 4.8 mg/L, respectively. It was interesting that the final phosphorus content in seawater at 30 d seemed to be independent of the total phosphorus content in the steelmaking slag. For instance, solution of P1 slag (4.6 mass% P2O5) had 3.4 mg/L of phosphorus while that of P11 slag (8.0 mass% P2O5) had only 0.4 mg/L at 30 d. This fact indicated that dissolution rate of phosphorus from steelmaking slag into seawater depended on the kind of crystal phase in which phosphorus is contained.

Dissolution behavior of elements from 4CaO·P2O5 (8.5 mass% P), 3CaO·P2O5 (10.0 mass% P) and 2CaO·SiO2–3CaO·P2O5 (2.8 mass% P) solid solution phase in artificial seawater was investigated to confirm that dissolution rate of phosphorus depends on the kind of crystal phase.

The dissolution behavior of phosphorus, calcium and silicon from pure substances to seawater is shown in Fig. 9. The final phosphorus content dissolved from 4CaO·P2O5, 3CaO·P2O5, and 2CaO·SiO2–3CaO·P2O5 solid solution into seawater were 16.6 mg/L, 2.17 mg/L, and 2.13 mg/L, respectively. Calcium dissolved from 2CaO·SiO2–3CaO·P2O5 solid solution and 4CaO·P2O5, while no dissolution was observed from 3CaO·P2O5. Silicon dissolved from 2CaO·SiO2–3CaO·P2O5 solid solution and 4CaO·P2O5, while no dissolution was observed from 3CaO·P2O5. Silicon dissolved from 2CaO·SiO2–3CaO·P2O5 solid solution and the final silicon content was 21.0 mg/L. From these results, 4CaO·P2O5 and 2CaO·SiO2–3CaO·P2O5 phase were found to be unstable in seawater, while 3CaO·P2O5 phase was stable in seawater.

Relation between phosphorus contents in steelmaking slags and pure substances and final phosphorus contents...
into artificial seawater after dissolution experiment is shown in Fig. 10. The phosphorus contents in pure substances did not correspond with final phosphorus contents in seawater. The phosphorus content in 2CaO·SiO₂–3CaO·P₂O₅ solid solution was the least among the pure substances treated in the present work, but phosphorus dissolved relatively into seawater. In general terms, there seemed to be no correlation between phosphorus contents in steelmaking slags and final phosphorus contents in artificial seawater. This phenomenon is due to the difference of stability of precipitated phase in steelmaking slag and the kind of phosphorus ion in seawater and it will be discussed later.

Fig. 7. Dissolution behavior of elements in hot metal pretreatment slags into artificial seawater.

Fig. 8. Dissolution behavior of elements in converter slags into artificial seawater.
3.3 Stability Diagram of Elements in Seawater

Solidified steelmaking slag contains various minerals, which provides nutrition for propagation of phytoplankton. It is important to understand the dissolving behavior of minerals into seawater to estimate the best conditions for slag addition to seawater. Stability diagram of silicon, phosphorus, and iron have been determined for these purpose in the present work.

Calculation of stability diagram was carried out at 298 K, because most of the standard free energies of species dissolution are unknown for other temperatures. The content of objective element in seawater and pH were the variables, while concentration of all the other elements such as Ca, Mg, Cl and so on were fixed like as those in natural seawater. Bold lines in the stability diagrams are the solubility limits of each elements and thin lines represent equilibrium concentration of each various dissolved species. Substances in square bracket are the stable solid species that precipitate on the condition. Dissolved substances in seawater are represented in parenthesis. Solid circles show the concentration of dissolved elements in natural seawater.

Fig. 11. Stability diagram of silicon in seawater at 298 K.16)
are several hydration products corresponded to SiO₂, such as H₄SiO₄, H₆SiO₇, H₈Si₃O₁₀ and H₁₀Si₄O₁₃. Due to lack of precise data, we have considered only metamonosilicic acid H₂SiO₃. Silicon in seawater is in equilibrium with vitreous SiO₂, which is reasonable because major constituent of sea sand is SiO₂. On the condition where pH is lower than 9.7, between 9.7 and 11.3, and higher than 11.3, the predominant silicon containing species are H₂SiO₃, H₄SiO₄, and SiO₂⁻², respectively.

Silicon does not dissolve from CaO·SiO₂ or 3CaO·2SiO₂ phase in steelmaking slag because, silicon content in natural seawater is exceeding the Si solubility equilibrated with these calcium silicates. On the other hand, Si can dissolve from 3CaO·SiO₂, 2CaO·SiO₂, CaO·Al₂O₃·SiO₂, and 3CaO·Al₂O₃ into seawater. Therefore, slag basicity should be high enough to precipitate 3CaO·SiO₂ or 2CaO·SiO₂ phase during solidification of steelmaking slags for effective Si dissolution into seawater.

Stability diagram of phosphorus in seawater at 298 K is shown in Fig. 12. In the present work, hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), fluorapatite (Ca₁₀(PO₄)₆F₂), 2CaO·P₂O₅, 3CaO·P₂O₅, and 4CaO·P₂O₅ were considered as possible solid substances that can equilibrate with seawater. Also, H₃PO₄, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻, was taken into account for dissolved species.

Phosphorus is known to be present as hydroxyapatite or fluorapatite deposit in natural, hence seawater is expected to be in equilibrium with these solid substances. However, phosphorus content of seawater is higher than the phosphorus solubility limited by hydroxyapatite or fluorapatite phase. This discrepancy is probably due to inaccuracy of referred Gibbs free energy of formation of these solid complex substances.

Since the phosphorus content of seawater is higher than the solubility limited by 2CaO·P₂O₅ and 3CaO·P₂O₅ saturation, phosphorus can not dissolve from steelmaking slags consisted of these phases. However, phosphorus concentration equilibrated with 4CaO·P₂O₅ phase is higher than that in natural seawater. Hence, phosphorus can dissolve into seawater if 4CaO·P₂O₅ phase could be present in steelmaking slag.

Phosphorus effectively dissolved from 4CaO·P₂O₅, according to the result of dissolution experiment of phosphorus from pure substances. This is in accordance with the stability diagram of phosphorus in seawater. Phosphorus dissolved also from 3CaO·P₂O₅ phases in the present work. This is probably due to presence of a minute of 4CaO·P₂O₅ phase in 3CaO·P₂O₅ reagent, but there is no evidence here. Even the phosphorus content in 2CaO·SiO₂·3CaO·P₂O₅ solid solution was the least of all pure substances treated in the present work, phosphorus relatively dissolved into seawater. According to the stability diagram, 3CaO·P₂O₅ does not dissolve into seawater, and vice versa for 2CaO·SiO₂.

Hence, the present experimental result suggested the phosphorus was forcibly dissolved with 2CaO·SiO₂ dissolution into seawater.

Stability diagram of iron in seawater at 298 K is shown in Fig. 13. In the present work, Fe(OH)₃, and Fe(OH)₄ were considered as possible solid substances that can equilibrate with seawater. Iron ions equilibrating with Fe(OH)₃, are Fe³⁺ and FeOH₂⁻ and the predominant species change where pH in seawater is 10.5. Iron species coexisting with Fe(OH)₃ are Fe²⁺, FeOH₂⁺, and Fe(OH)₄⁻ and there are predominant where pH of seawater is less than 3.1, between, 3.1 and 4.5, and more than 4.5, respectively. FeO phase is one of the major constituents in steelmaking slag and it can be hydrated and easily form Fe(OH)₂ in seawater. The solubility of Fe²⁺ equilibrating with Fe(OH)₂ is approximately 1 mg/L and it will be enough for multiplication of photo-plankton. However, Fe(OH)₂ is more stable than Fe(OH)₃ in air atmosphere, hence, solubility of the iron ions will drastically decrease when Fe(OH)₂ is oxidized. Therefore, some kinds of ingenuities before oxidation of iron ions are needed to emphasize the iron consumption by photo-planktons.

It is concluded from the above-mentioned discussions that dissolution behavior of elements in steelmaking slag into seawater can be predicted from the stability diagrams. Dissolved phenomena of phases in steelmaking slags are summarized in Table 5 depended on the behavior weather they are soluble or insoluble in seawater.

The stability diagram is a powerful tool for understanding the dissolution behavior of elements in steelmaking slag into seawater. For instance, seeking the conditions for effective nutrition dissolution from steelmaking slag into seawa-
ter is equivalent to adjusting the composition and cooling rate of steelmaking slag where favorable phases for nutrition dissolution are precipitated.

4. Conclusions

The morphology of the precipitated phases in steelmaking slags during cooling period was investigated. It was found from these observations that phases existing in steelmaking slag could be classified into 4 groups. Phase A; the phosphorus concentration was very high (>10 mass%) and containing little iron and silicon, phase B; the main cations were Ca and Si, and some amount of phosphorus (3–6 mass%) was also included while almost no iron was included, phase C; the composition was very close to pure FeO, and phase D; others.

The dissolution behavior of some elements from steelmaking slags and pure substances such as 4CaO·P₂O₅ (8.5 mass% P), 3CaO·P₂O₅ (10.0 mass% P) and 2CaO·SiO₂·3CaO·P₂O₅ (2.8 mass% P) solid solution phases into artificial seawater was studied. The dissolution mechanism of elements from steelmaking slags was discussed by using stability diagram of Si, P and Fe in seawater. The stability diagram is a powerful tool for understanding the dissolution behavior of elements in steelmaking slag into seawater. By using steelmaking slags, which contains 3CaO·SiO₂, 2CaO·SiO₂, 4CaO·P₂O₅ and FeO phases can provide minerals such as Si, P and Fe to seawater. On the other hand, Si and P does not dissolve from 3CaO·SiO₂, CaO·SiO₂ and 3CaO·P₂O₅ phases.

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