

Dissolution Behavior of Nutrient Elements from Fertilizer Made of Steelmaking Slag, in an Irrigated Paddy Field Environment

Xu Gao¹ · Nobuhiro Maruoka¹ · Sun-joong Kim¹ · Shigeru Ueda¹ · Shin-ya Kitamura¹

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Abstract To produce fertilizer made of steelmaking slag, the combination of mineralogical phases is necessary to be appropriate not only for refining at high temperature, but also for supplementing nutrient elements in paddy fields. In this research, first, the variations in the chemical composition and mineralogical structure of various brands of fertilizer made of steelmaking slag were investigated. The basicity (CaO/SiO_2), free-CaO content, total Fe content, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of fertilizer were found to vary widely depending on the brand. In addition, regarding the mineralogical phases, solid solution consisting of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$, $\text{MgO}\text{--}\text{FeO}$, $\text{CaO}\text{--}\text{Fe}_2\text{O}_3$, free CaO, metallic Fe, and the other phase which included liquid phases at refining temperature were observed. The mass fraction of each phase also varied depending on the brand. Second, the dissolution behavior of each mineralogical phase in the fertilizers into water that simulated the early stage of flooding condition was studied. Regarding the dissolution of Ca, free CaO dissolved in a short time, and the solid solution of $2\text{CaO}\cdot\text{SiO}_2$ and

$3\text{CaO}\cdot\text{P}_2\text{O}_5$ dissolved slowly. Fe barely dissolved from any mineralogical phase except the other phase which consisted of $\text{CaO}\text{--}\text{SiO}_2\text{--}\text{FeO}$. A clear relationship was observed between the dissolution of Fe and the mass fraction of other phase as well as the ratio of Fe^{2+} to Fe^{3+} in Fe oxides in fertilizer made of steelmaking slag.

Keywords Fertilizer · Steelmaking slag · Paddy · Dissolution

Introduction

In Japan, fertilizer made of steelmaking slag is sold under various brand names. To register the category of by-product calcium fertilizer, in addition to the alkali content (35 mass% or more), the maximum size (100 % is smaller than 1.7 mm and 85 % is smaller than 600 μm) is the only other requirement [1]. Therefore, the manufactures of fertilizer production should mainly be crashing and classifying. However, the composition and mineralogical structure of steelmaking slag varied with the steelmaking and slag treatment processes [2, 3]. Therefore, the dissolution behaviors of nutrient elements may be different for each brand.

The dissolution behaviors of various elements from steelmaking slag have been reported under sea water conditions [4] or the standard condition (to investigate the leaching behavior which determined by the environmental regulation) [5]. For agricultural utilization, fertilizer made of steelmaking slag can provide many necessary elements, such as Ca, Si, Fe, Mg, P, and Mn [6], and the positive role of steelmaking slag in agriculture has been expected. In paddy field, the improvement in paddy growth and yield after the application of fertilizer made of steelmaking slag has been confirmed [7]. Therefore, to investigate the effectiveness of fertilizers made

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✉ Xu Gao
xgao@tagen.tohoku.ac.jp
Nobuhiro Maruoka
maruoka@tagen.tohoku.ac.jp
Sun-joong Kim
ksjoong@tagen.tohoku.ac.jp
Shigeru Ueda
tie@tagen.tohoku.ac.jp
Shin-ya Kitamura
kitamura@tagen.tohoku.ac.jp

¹ Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

of steelmaking slag in paddy fields, current authors have measured the dissolution behaviors into pore water among paddy soils [9, 10]. In this experimental system involving soil, it is difficult to clarify the dissolution behavior of the fertilizer itself, as both the pH and oxidation potential widely change during experiments, and also the capacity of soil to absorb the dissolved elements is extremely large. In addition, the role of each mineralogical phase in the dissolution of each element is not clear. To produce fertilizer made of steelmaking slag, the combination of mineralogical phases should be appropriate not only for refining at high temperature but also for supplementing nutrient elements in paddy fields.

With this background, in this research, first, the variations in the chemical composition and mineralogical structure of several brands of fertilizer made of steelmaking slag were investigated. Second, the dissolution behavior of each mineralogical phase appearing in fertilizer made of steelmaking slag into water, that simulated the early stage of flooding conditions, was investigated. Next, by comparing these results with the dissolution behavior of fertilizer made of steelmaking slag, the role of each phase in the dissolution of each element was discussed.

Composition and Structure of Fertilizer Made of Steelmaking Slag

Analysis Method

Steelmaking slags from 11 of the 16 integrated steelmaking mills in Japan are utilized as fertilizer. In most cases, steelmaking slag is sold to a subcontracting company that has a license to produce fertilizer. These companies deal in fertilizer made of steelmaking slag using different brand names. Eleven samples of fertilizer made of steelmaking slag were collected to investigate the differences in composition and mineralogical structure.

Chemical analysis of the samples was conducted by Nittetu-Techno Research Corporation. The total Fe, CaO, SiO₂, Al₂O₃, MgO, MnO, and P₂O₅ contents were analyzed by X-ray fluorescent spectroscopy (XRF). The sample was dried and ground into fine powder, and then pressed into briquettes before analysis [11]. Metallic Fe and FeO were analyzed by titration [12]. Free CaO and free MgO were analyzed by ICP-AES after dissolution by ethylene glycol [13] and ammonium nitrate [14], respectively. The mineralogical structure was measured by electron probe micro-analyzer (EPMA) and X-ray diffraction (XRD).

Results and Discussion

Typical chemical compositions are shown in Table 1. Because several brands of fertilizer made of steelmaking

slag showed similar results, only the results of 8 brands (A to H) are shown in this paper. Every sample contained CaO, SiO₂, and Fe oxide as the main components, with several percents of Al₂O₃, MgO, MnO, and P₂O₅. The ratio of Fe₂O₃ to FeO was higher than that of steelmaking slag sampled just after refining, because of oxidation during slag processing.

The variations in the free CaO content with basicity (mass ratio of CaO to SiO₂) and in the Fe²⁺/Fe³⁺ ratio with total Fe content are shown in Figs. 1 and 2, respectively. A relationship between the basicity and free CaO content was found. The basicity varied from 1.4 to 4.1, and the free CaO content ranged from 1.6 to 8.5 mass% depending on the brand. The variations in the total Fe content and Fe²⁺/Fe³⁺ ratio are 10.2–23.5 mass% and 0.8–3.2, respectively.

Typical cross sections of fertilizer particles observed by EPMA are shown in Fig. 3, where C is the abbreviation of CaO, S is SiO₂, M is MgO, F is FeO, A is Al₂O₃, and P is P₂O₅. In every sample, 2CaO·SiO₂ (C2S), MgO·FeO_x (MF), and CaO·FeO_x (CF) phases were commonly observed. In addition to these phases which could be easily observed within all fertilizer samples, phases that could be considered as liquid phases at the refining temperature were also observed, and these phases are defined as the ‘other phase’ in this study.

By quantitative analysis of each phase using EPMA and the chemical compositions of the samples, the mass fraction of each phase was estimated. In this calculation, 2CaO·SiO₂, which forms the solid solution with 3CaO·P₂O₅ (C2S–C3P), and the MF, CF, free CaO, metallic Fe, and other phase were considered as mineralogical phases. The other phase was separated into three categories according to the main compounds, which were CaO–SiO₂–FeO_x (C–S–F), CaO–SiO₂–Al₂O₃ (C–S–A), and the remaining phase. The average composition of each phase was calculated as the average values of several positions on the phases of the same category.

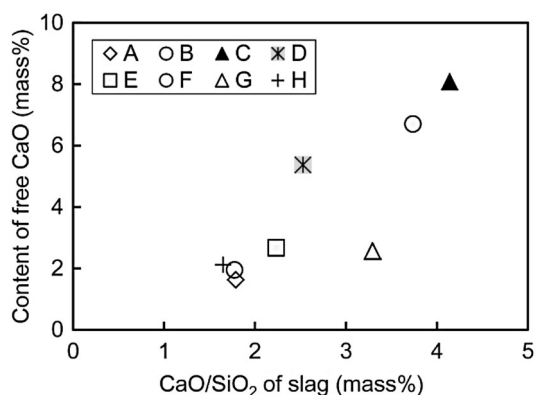
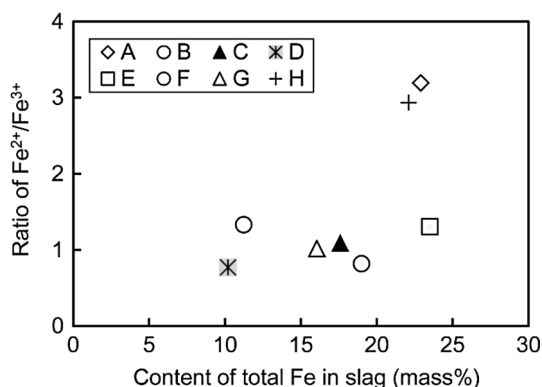
In the following calculation, the mass fractions of each mineralogical phase except for free CaO and metallic Fe were considered. The mass balance of an oxide NO_n is written in Eq. (1). The concentration of NO_n in slag measured by chemical analysis is NO_n^T mass%, and the concentrations of NO_n in the C2S–C3P, CF, MF, C–S–F, C–S–A, and the remaining phase measured by EPMA are NO_n^{C2S} mass%, NO_n^{CF} mass%, NO_n^{MF} mass%, NO_n^{C–S–F} mass%, NO_n^{C–S–A} mass%, and NO_n^{rem} mass%, respectively. The mass fractions of the C2S–C3P, CF, MF, C–S–F, C–S–A, and remaining phase are, V^{C2S}, V^{CF}, V^{MF}, V^{C–S–F}, V^{C–S–A}, and V^{rem}, respectively.

$$\begin{aligned}
 \text{NO}_n^T = & V^{C2S} \times \text{NO}_n^{C2S} + V^{CF} \times \text{NO}_n^{CF} + V^{MF} \times \text{NO}_n^{MF} \\
 & + V^{CSF} \times \text{NO}_n^{CSF} + V^{CSA} \times \text{NO}_n^{CSA} + V^{rem} \times \text{NO}_n^{rem}
 \end{aligned}
 \tag{1}$$

Table 1 Composition of fertilizers made of steelmaking slag (mass%)

Brands	CaO	SiO ₂	T-Fe	FeO	Fe ₂ O ₃	M-Fe	Al ₂ O ₃	MnO	MgO	P ₂ O ₅	f-CaO ^a	f-MgO ^a
A	31.3	17.5	22.9	20.7	7.2	1.8	3.5	5.9	5.9	2.8	1.6	0.018
B	42.6	11.4	19.0	10.3	14.0	1.2	1.5	4.0	8.9	2.2	6.9	0.014
C	47.6	11.5	17.6	10.9	11.1	1.4	3.0	1.6	5.6	2.6	8.5	0.010
D	46.2	18.3	10.2	5.2	7.5	0.9	6.1	3.4	4.4	1.4	5.3	0.006
E	33.7	15.1	23.5	12.7	10.8	6.1	3.4	2.5	7.3	3.3	2.6	0.017
F	39.6	22.3	11.2	6.46	5.4	2.5	6.0	2.4	4.8	1.3	1.8	0.011
G	38.6	11.7	16.1	9.77	10.7	1.0	4.3	4.8	4.7	1.7	2.3	0.004
H	31.3	19.0	22.1	19.2	7.3	2.1	3.4	5.4	6.3	3.2	2.1	0.004

^a f-CaO, f-MgO stand for free-CaO and free-MgO, respectively

**Fig. 1** Relationship between basicity (CaO/SiO₂) and free-CaO content of various brands of fertilizers made of steelmaking slag**Fig. 2** Relationship between total Fe content and the Fe²⁺/Fe³⁺ ratio of various brands of fertilizers made of steelmaking slag

The mass fraction of each phase can be calculated, when this equation is written for CaO, SiO₂, FeO, MgO, P₂O₅, MnO, and Al₂O₃ and these simultaneous equations are solved. Although each slag contained FeO and Fe₂O₃, to calculate Eq. (1) for FeO, FeO^T was calculated by conversion from the analyzed total Fe value.

The mass fractions of typical mineralogical phases are summarized in Table 2. In every brand, the C2S–C3P

phase was the major phase, with a mass fraction of 22.5 to nearly 47.2 depending on the basicity. The mass fractions of the CF, MF, and other phase varied in each brand. The compositions of the other phase are summarized in Fig. 4 by projection in the phase diagram of the CaO–SiO₂–FeO system (a) and the CaO–SiO₂–Al₂O₃ system (b). Depending on the cooling conditions of the slag, in some cases, the other phase was not uniform, and many small phases were precipitated thus the composition was widely scattered. In some samples, the Al₂O₃ content was so high that this brand would be considered a mixture of steelmaking slag with blast furnace slag. In other samples, the other phase was glassy, and its composition was located in the region of liquid composition at the refining temperature.

Dissolution Behavior of Nutrient Elements

Experimental Method

To clarify the dissolution behavior, oxides with the same compositions as the mineralogical phases identified by EPMA were synthesized. The composition of each synthetic mineralogical phase is shown in Table 3; the values were the average composition of phases with the same category for all tested fertilizers measured by EPMA. Initially, CaCO₃ was sintered at 1273 K to make CaO, and Fe₂O₃ was reduced at 1723 K by metallic Fe to make FeO. For other compounds of the synthesized phases, commercial reagents were used. To make C2S–C3P, after CaO and SiO₂ were sintered for 48 h at 1873 K to make 2CaO·SiO₂, the mixture of 2CaO·SiO₂ and the reagents of 3CaO·P₂O₅, FeO, and Al₂O₃ were sintered for 48 h at 1873 K. To make MF and CF, a mixture of MgO, FeO, MnO and a mixture of CaO, Al₂O₃, and Fe₂O₃ were sintered for 48 h at 1573 and 1473 K, respectively. To make free CaO, a small amount of FeO, MnO, and MgO were mixed with CaO and then sintered at 1273 K for 48 h. To make the C–S–F phase, as brand A showed a higher fraction of the C–S–F phase according to Table 2, the average composition of C–S–F phase in brand A was selected for

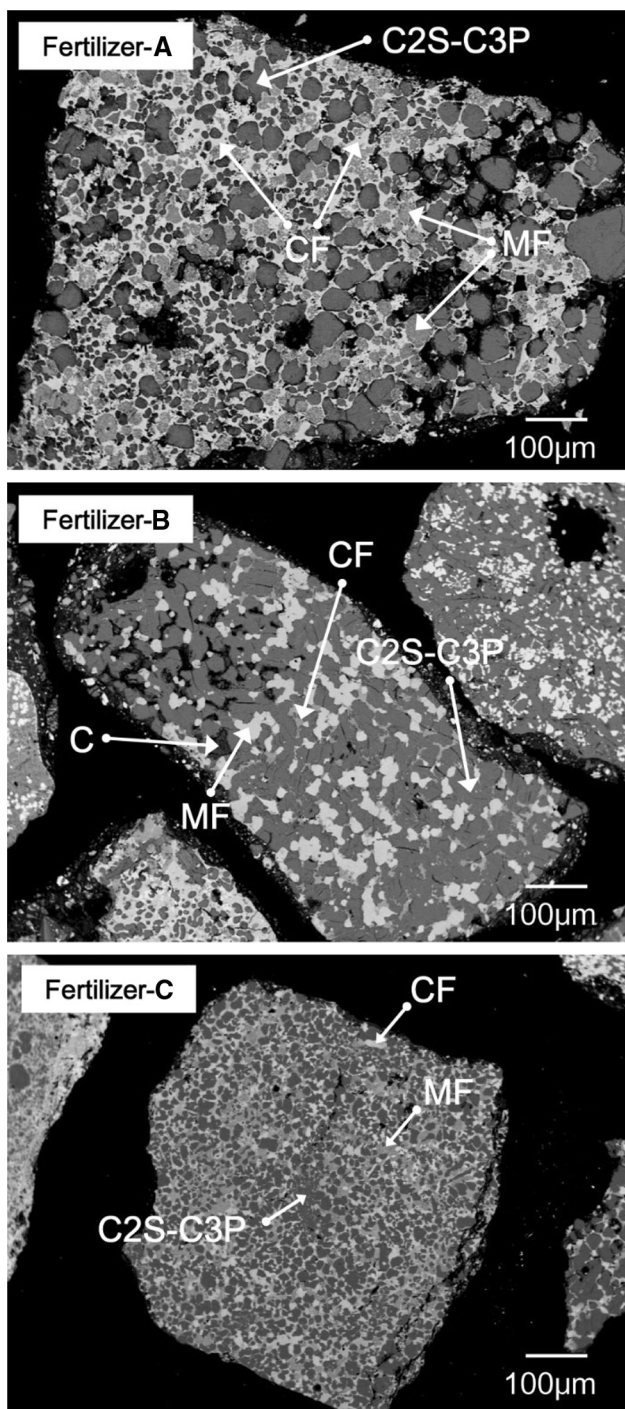


Fig. 3 Typical cross sections of fertilizer particles observed by EPMA

synthesis in this study. The raw materials for synthesizing the C–S–F phase were CaO, SiO₂, 3CaO·P₂O₅, MgO, MnO, Al₂O₃, and Fe oxide. In particular, for Fe oxide, because the Fe²⁺/Fe³⁺ ratio in the C–S–F phase was impossible to evaluate, either FeO or Fe₂O₃ was used during synthesis. Therefore, the C–S–F phase was prepared as C–S–Fe³⁺ or C–S–Fe²⁺, as shown in Table 3. The total Fe contents of both

Table 2 Mass fractions of mineralogical phases in fertilizers made of steelmaking slag (mass%)

Brand	C2S–C3P	CF	MF	Others		
				C–S–A	C–S–F	Remained
A	30.6	7.7	9.5	0.5	29.4	18.8
B	37.4	33.8	13.4	–	2.9	4.5
C	47.2	24.8	7.3	5.0	4.4	–
D	29.8	26.4	4.7	23.4	–	9.5
E	28.7	20.1	22.2	2.6	17.0	1.1
F	22.5	19.5	6.1	33.2	13.9	0.6
G	31.8	32.7	25.1	–	7.1	–
H	25.3	4.5	16.9	15.8	21.2	12.3

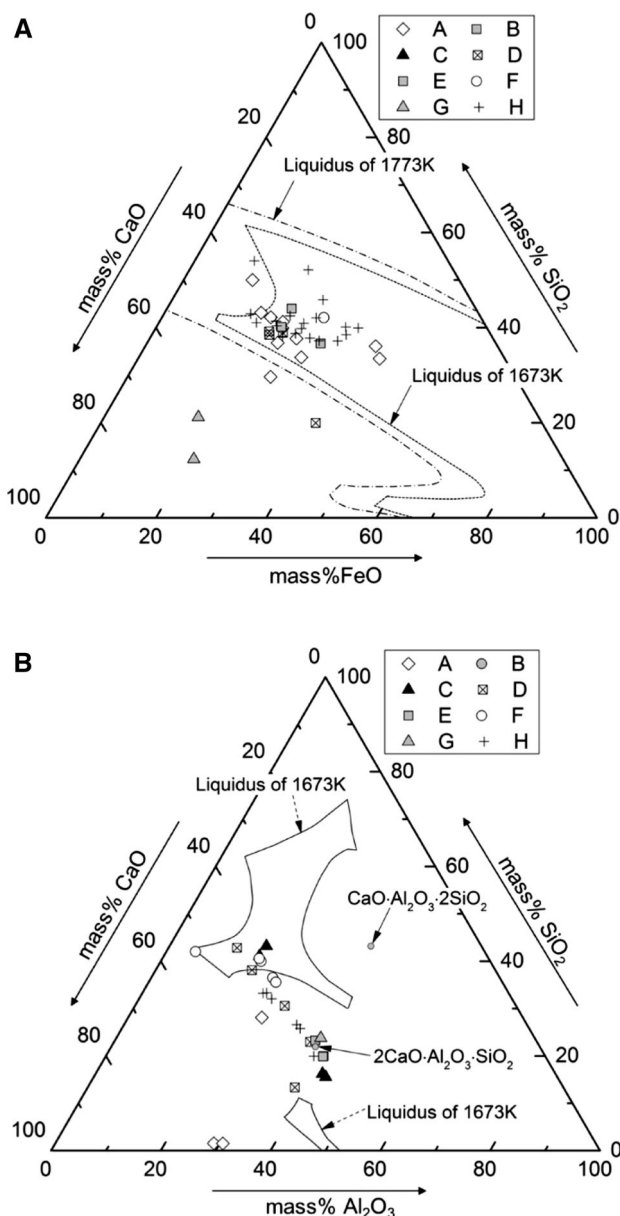
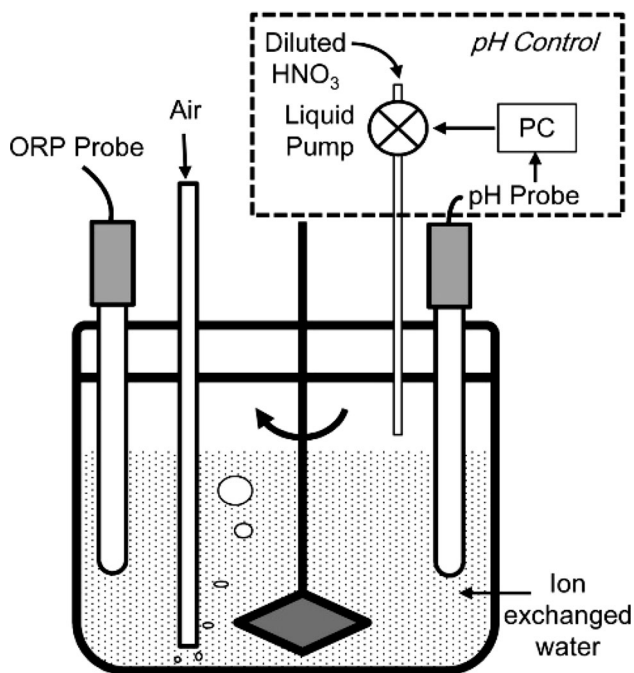


Fig. 4 Projection of the other phase in the phase diagram of the CaO–SiO₂–FeO (a) and the CaO–SiO₂–Al₂O₃ ternary system (b), mass%

Table 3 Composition of synthetic mineralogical phases (mass%)

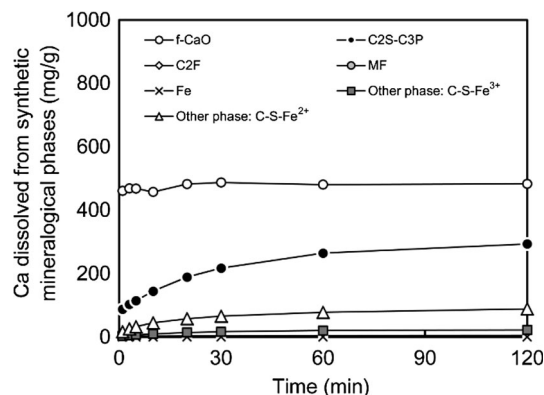
	CaO	SiO ₂	MgO	P ₂ O ₅	MnO	FeO	Fe ₂ O ₃	Al ₂ O ₃
C2S–C3P	64.1	27.7	–	6.2	–	1.4	–	0.5
CF	38.7	–	–	–	–	–	55.8	5.5
f-CaO	82.0	–	1.1	–	6.4	10.5	–	–
MF	3.2	–	26.1	–	9.6	61.1	–	–
C–S–Fe ^{2+a}	28.8	29.3	4.0	3.6	7.0	24.8	–	2.5
C–S–Fe ^{3+a}	28.3	28.5	7.5	3.5	6.8	–	22.7	2.7

^a C-S-Fe²⁺ means C-S-F phase using FeO as iron oxide, while C-S-Fe³⁺ using Fe₂O₃ as iron oxide

**Fig. 5** Experimental setup for leaching test

C–S–Fe³⁺ and C–S–Fe²⁺ were the same. In detail, the oxide mixture for preparing C–S–Fe²⁺ was melted for 3 h at 1673 K within an Fe crucible and then quenched by water. For the C–S–Fe³⁺ phase, oxide mixture containing Fe₂O₃ was melted for 3 h at 1673 K using a MgO crucible and then quenched by He gas spray.

The experimental setup for the leaching test is shown in Fig. 5. The leaching test was conducted using air-saturated water with a controlled pH of 5. The air-saturation and pH were determined to simulate the soil solution of paddy fields in the early period after flooding [8]. Before the leaching experiments, 400 mL of ion-exchanged water was poured into a Teflon container and kept at 298 K using an isothermal water bath. Then air bubbling as well as agitation by a mechanical stirrer began. After air saturation was established by air bubbling for about 30 min, 1 g of solid sample (smaller than 53 μm), which was either the synthetic mineralogical phase or the fertilizer made of

**Fig. 6** Leaching behavior of Ca in aqueous solution from each synthetic mineralogical phase

steelmaking slag, was dropped into the water. At the meantime, the pH control system was launched. Dilute nitric acid solution was used to control the pH. When the pH had decreased to 5, sampling of the solution was started and then repeated at certain intervals. The sampled solution was analyzed by ICP-AES, and the residue after leaching was collected and analyzed by XRD.

Results and Discussion

The leaching behavior of Ca when 1 g of each mineralogical phase is added to 400 mL of aqueous solution is shown in Fig. 6. It is clear that free CaO dissolved completely in a short time, and the C2S–C3P phase dissolved slowly for about 1 h. In contrast, Ca did not dissolve from the CF or MF phase. In addition, Ca was also supplied from the C–S–F phase when FeO was used as the Fe oxide (C–S–Fe²⁺), but the dissolution was negligible when Fe₂O₃ was used (C–S–Fe³⁺). By using this result, the dissolution mass of Ca (D'_{Ca}) from 1 g of fertilizer made of steelmaking slag can be estimated using Eq. (2), where, D is the dissolution mass, mg/g; m_F is the amount of fertilizer added to water, g; V is the mass ratio of mineralogical phases as shown in Table 2, mass % (note that $V^{\text{free-Ca}}$ was the mass ratio of free CaO shown in Table 1); and t is the leaching time, min.

$$D'_{Ca} = m_F \times V^{free-Ca} \times D'_{free-Ca} + m_F \times V^{C2S} \times D'_{C2S} + m_F \times V^{CF} \times D'_{CF} + m_F \times V^{MF} \times D'_{MF} + m_F \times V^{C-S-Fe^{2+}} \times D'_{C-S-Fe^{2+}} \text{ (or } m_F \times V^{C-S-Fe^{3+}} \times D'_{C-S-Fe^{3+}} \text{)} \quad (2)$$

The results when t is 120 min are shown in Fig. 7, in comparison with the actual leaching behaviors of fertilizer made of steelmaking slag. In this graph, two columns are shown as the amount of dissolved Ca from either the C–S–Fe²⁺ or C–S–Fe³⁺ phase, because the ratio of Fe²⁺ to Fe³⁺ in the C–S–F phase of the actual fertilizer was unknown. The dissolved mass of Ca calculated by Eq. (2) agreed with that in each brand. The total mass of dissolved Ca was large in the brands that had a high content of free CaO and high basicity, for instance, brands B and C.

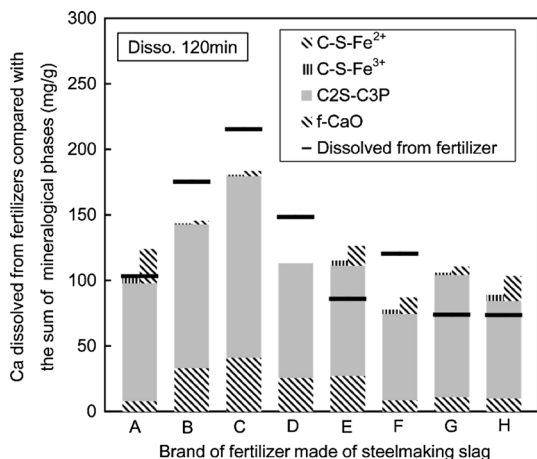


Fig. 7 Mass of Ca dissolved from each fertilizer made of steelmaking slag, comparing with the calculated value

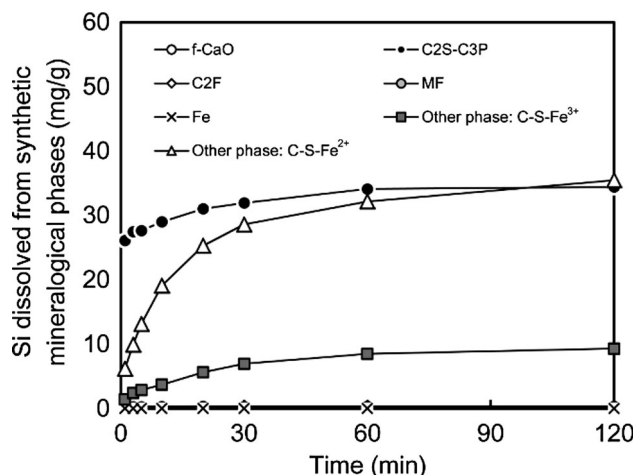


Fig. 8 Leaching behavior of Si in aqueous solution from each mineralogical phase

The leaching behavior of Si when 1 g of each mineralogical phase is added to 400 mL of aqueous solution is shown in Fig. 8. The source of soluble Si was C2S–C3P and the C–S–Fe²⁺ phase. The leaching behavior of Si from fertilizer made of steelmaking slag is shown in Fig. 9 in comparison with the values calculated by the same method as in Eq. (2). The dissolved mass of Si after 120 min for each brand was similar, and the calculated values were smaller than the actual dissolution masses for most brands. The reason is considered to be that the solubility of Si in water should be controlled by a hydro-compound that formed after the dissolution of Si, and a high concentration of Ca²⁺ decreased the content of soluble Si in water. Equations (3) to (5) are introduced to enhance the understanding of this explanation [15, 16], and the calculated

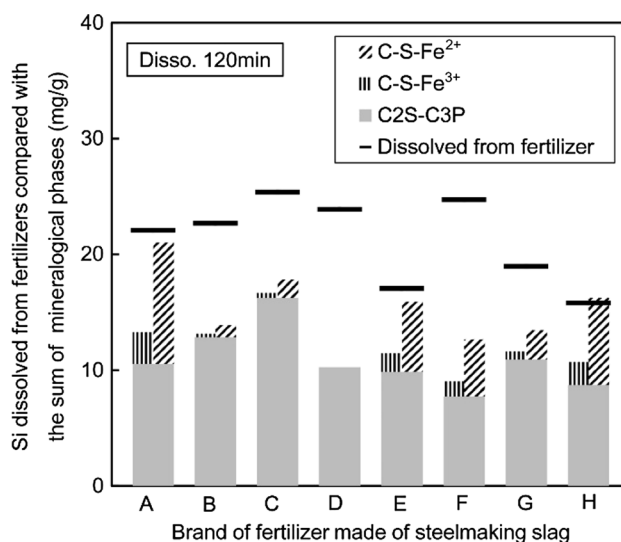


Fig. 9 Mass of Si dissolved from each fertilizer made of steelmaking slag, comparing with the calculated value

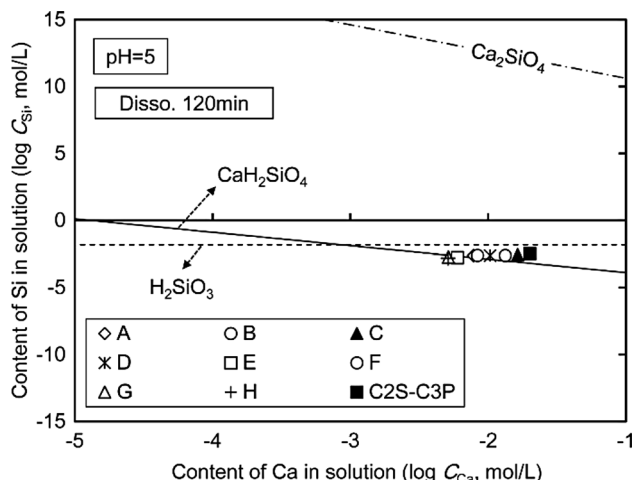
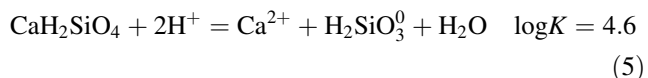
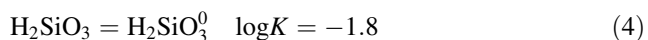
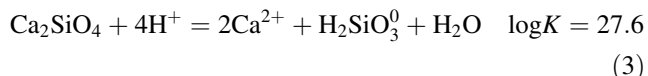


Fig. 10 Effect of dissolved Ca on the solubility of Si in aqueous solution, comparing with experimental results at 120 min

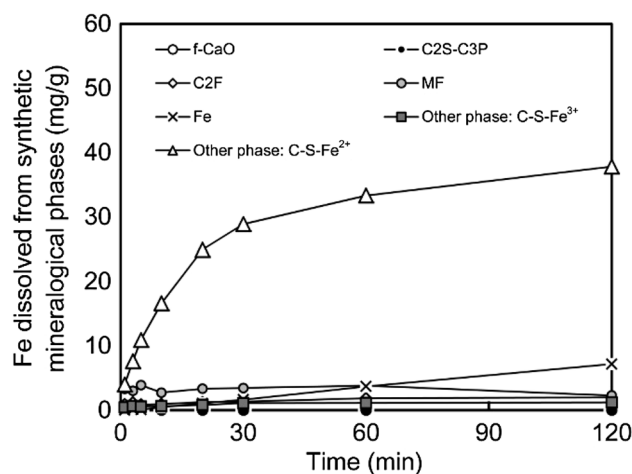
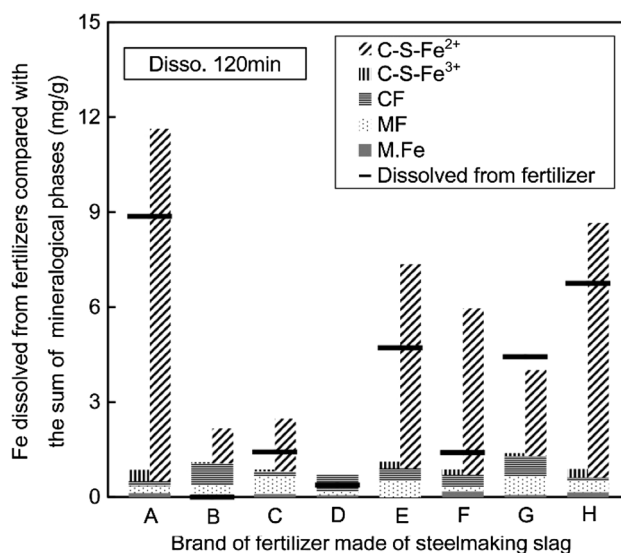
Table 4 Estimated activity coefficient of ions

Species	Activity coefficient
H_2SiO_3^0	1
Ca^{2+}	0.3
H_2PO_4^-	0.8
Fe^{2+}	0.3
Fe^{3+}	0.1

solubility of Si in solution at a pH of 5 as a function of the Ca content of water is shown in Fig. 10. In this calculation, the activity coefficient of ions was determined using Debye Hückel theory [17, 18], and the calculated activity coefficients for Si and the other elements used in this study are summarized in Table 4. According to Fig. 10, the solubility of Si in water could be governed by CaH_2SiO_4 despite of any solid that has been leached, and a higher concentration of Ca^{2+} dissolved from 1 g of C2S–C3P led to a lower content of soluble Si compared to that of 1 g of fertilizers. Therefore, the soluble Si that dissolved from the C2S–C3P in 1 g of fertilizer could be higher than that from 1 g of C2S–C3P alone, and this is the reason why the dissolved masses of Si from fertilizers are higher than those calculated values as shown in Fig. 9. In addition, because both the fertilizers and the C2S–C3P showed similar results, the effect of quickly dissolved Ca from free CaO on the soluble Si was not significant.



The leaching behavior of Fe is shown in Fig. 11. Fe was not dissolved from any mineralogical phase including metallic Fe, except for the C–S– Fe^{2+} phase. The leaching behavior of Fe from fertilizer made of steelmaking slag is shown in Fig. 12 in comparison with the values calculated by the same method as in Eq. (2). The dissolved mass of Fe calculated by Eq. (2) after 120 min agreed well with that of each brand when the Fe oxide was assumed to be FeO. Although the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in Fe oxide in the C–S–F phase of fertilizer made of steelmaking slag was unknown, a clear relationship was observed between the dissolution of Fe and the mass fraction of the C–S–F phase, as shown in Fig. 13. In addition, a clear relation was also found between the dissolution of Fe and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in Fe oxide in fertilizer made of steelmaking slag as shown in Fig. 14. Therefore, the source of Fe dissolved into aqueous solution would be the C–S–F phase, and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the other phase is an important factor.

**Fig. 11** Leaching behavior of Fe in aqueous solution from each mineralogical phase**Fig. 12** Mass of Fe dissolved from each fertilizer made of steelmaking slag, comparing with the calculated value

The leaching behavior of P from mineralogical phase is shown in Fig. 15. It could be considered that P was dissolved from the C2S–C3P phase. The leaching behavior of P from the fertilizer made of steelmaking slag is shown in Fig. 16 in comparison with the values calculated by the same method as Eq. (2). The calculated values were larger than the actual values for every brand. The reason is thought to be that excess Ca dissolved from free CaO reacted with dissolved P to form a hydro-compound with low solubility of P in water. The relationship between soluble P and Ca in water was calculated on the basis of Eqs. (6) and (7) [15, 16, 19]. The result is shown in Fig. 17 in comparison with experimental data for the fertilizers, C2S–C3P, and C–S– Fe^{2+} after leaching for 120 min.

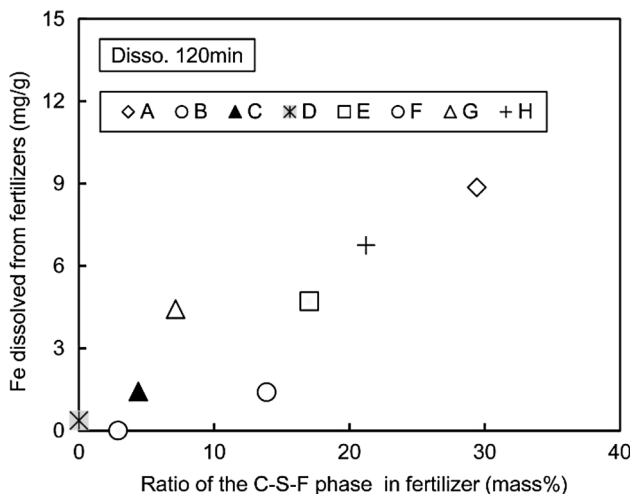


Fig. 13 Relationship between the dissolution of Fe and the mass fraction of the C-S-F phase in fertilizer made of steelmaking slag

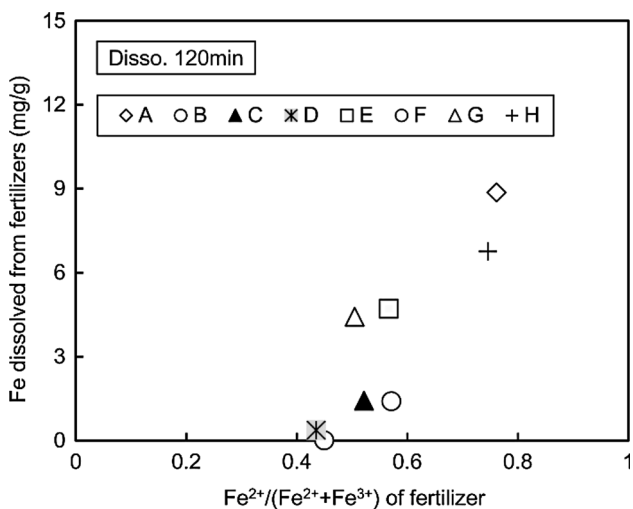


Fig. 14 Relationship between the dissolution of Fe and the Fe^{2+}/Fe^{3+} ratio in Fe oxide in fertilizer made of steelmaking slag

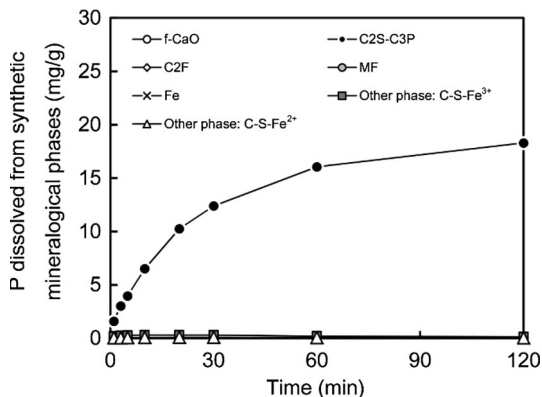


Fig. 15 Leaching behavior of P in aqueous solution from each mineralogical phase

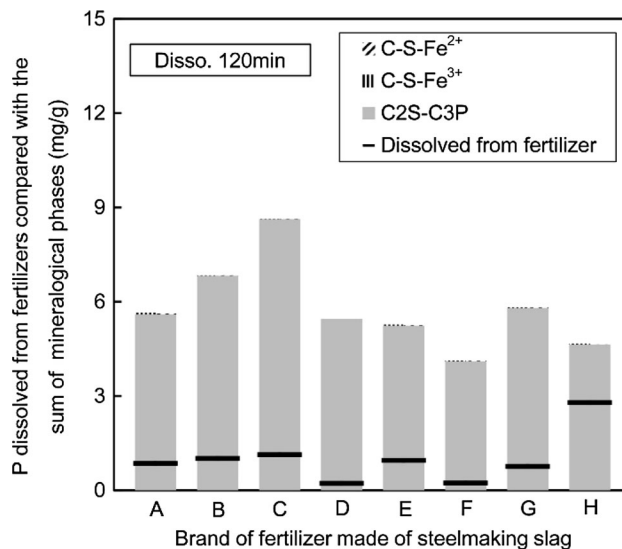


Fig. 16 Mass of P dissolved from each fertilizer made of steelmaking slag, comparing with the calculated value

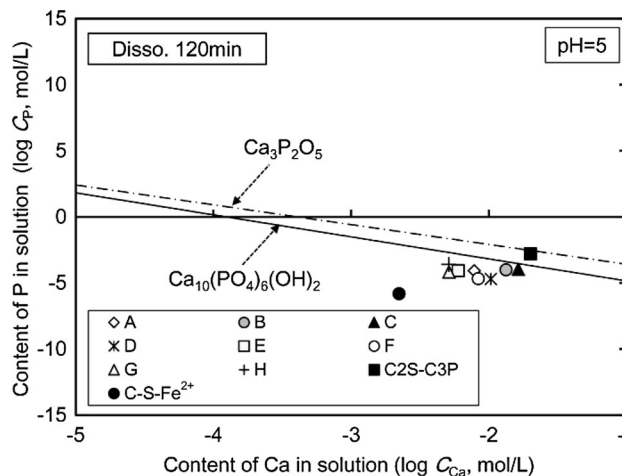
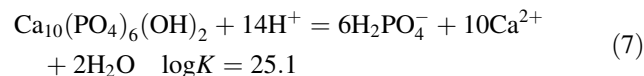
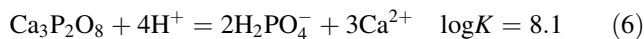


Fig. 17 Effect of dissolved Ca on the solubility of P in aqueous solution, comparing with experimental results at 120 min

Compared to the results for C2S-C3P without free CaO, those for the fertilizers are obviously located below the equilibrium line of $3CaO \cdot P_2O_5$ but close to that of $Ca_{10}(PO_4)_6(OH)_2$. Therefore, when the free CaO dissolved together with C2S-C3P, which is exactly the case in fertilizers, the quickly released Ca^{2+} from free CaO could react with the P that dissolved next from C2S-C3P, decreasing the amount of soluble P.



In comparison, the dissolved Si was not significantly affected by free CaO as mentioned, this can be explained by comparing the equilibrium Ca^{2+} concentration on the

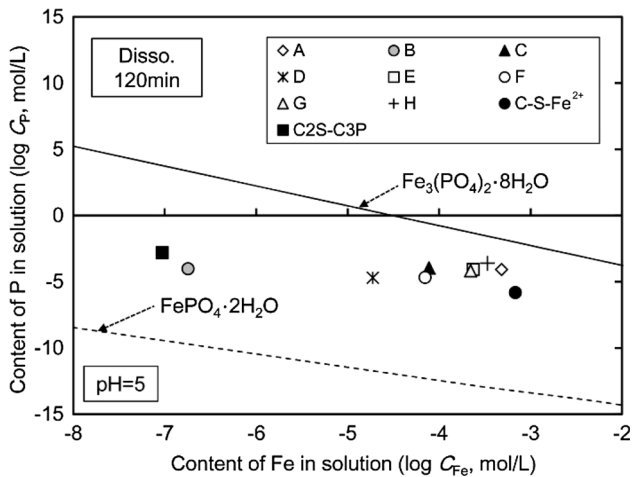


Fig. 18 Effect of dissolved Fe on the solubility of P in aqueous solution, comparing with experimental results at 120 min

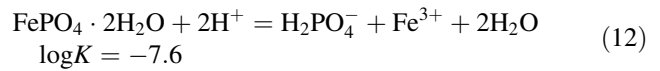
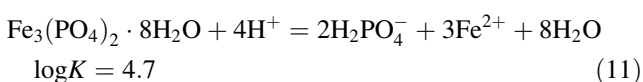
basis of Eqs. (5) and (7). When assuming the activities of dissolved P and Si are 1, the $\log K$ for Eqs. (5) and (7) can be expressed as the relation between the activity of Ca^{2+} and pH, as shown in Eqs. (8) and (9). Here, the a means activity. At same pH, the relation between the equilibrium Ca^{2+} concentration according to Eqs. (5) and (7) can be obtained as shown in Eq. (10). Here, the C means concentration, mol/L. Therefore, the $C_{\text{Ca}^{2+}}^{(5)}$ is 10 times higher than $C_{\text{Ca}^{2+}}^{(7)}$, and then the dissolved P is more sensitive to the excess Ca dissolved from free-CaO than that of Si.

$$\log K_{(5)} = \log a_{\text{Ca}^{2+}}^{(5)} + 2\text{pH} = 4.6 \quad (8)$$

$$\log K_{(7)} = 10 \times \log a_{\text{Ca}^{2+}}^{(7)} + 14\text{pH} = 25.1 \quad (9)$$

$$C_{\text{Ca}^{2+}}^{(5)} = 10 \times \left[C_{\text{Ca}^{2+}}^{(7)} \right]^{1.4} \quad (10)$$

In addition, the easily dissolvable C–S– Fe^{2+} phase, which contributed to the dissolution of Ca, Si, and Fe, showed a content of soluble P even lower than that of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. This is because, in addition to Ca, the existence of Fe cations in aqueous solution could also decrease the solubility of P [20, 21]. The relation between dissolved P and Fe in water was calculated using Eqs. (11) and (12) [15, 16, 19], and the result is shown in Fig. 18. The results for fertilizers were similar and independent of the amount of dissolved Fe, indicating that the effect of dissolved Ca on soluble P was stronger than that of Fe for fertilizers that contained free CaO. For the C–S– Fe^{2+} phase, the amount of dissolved Fe was the highest but that of dissolved Ca was the lowest; therefore, there is a high possibility that the dissolved P formed hydro-compounds with Fe cations during the dissolution of the C–S– Fe^{2+} phase.



Conclusions

To produce fertilizer made of steelmaking slag, the combination of mineralogical phases should be appropriate not only for refining at high temperature but also for supplementing nutrient elements in paddy fields. In this research, first, the variations in the chemical composition and mineralogical structure of various brands of fertilizer made of steelmaking slag were investigated. Second, the dissolution behavior of each mineralogical phase in fertilizer made of steelmaking slag into water that simulates the early stage of flooding conditions was examined. The following results were obtained.

1. The basicity of the fertilizer made of steelmaking slag varied from 1.4 to 4.1 and the free CaO content ranged from 1.6 to 8.5 mass% depending on the brand. The ranges of total Fe content and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio are 10.2–23.5 mass% and 0.8–3.2, respectively.
2. In every brand, $2\text{CaO} \cdot \text{SiO}_2$ which formed a solid solution with $3\text{CaO} \cdot \text{P}_2\text{O}_5$ (C2S–C3P); the MF, CF, free CaO, metallic Fe, and the other phase which included liquid phases at the refining temperature were observed. The major phase was the C2S–C3P phase, and its fraction was 22.5–47.2 mass% depending on the basicity.
3. It was found that free CaO dissolved completely in a short time and C2S–C3P phase dissolved slowly for about 1 h. In addition, Ca was also supplied from the C–S– Fe^{2+} phase, but dissolution of the C–S– Fe^{3+} phase was negligible. The dissolved mass of Ca estimated by the dissolution of each phase agreed well with that for each brand of fertilizer made of steelmaking slag.
4. Fe was not dissolved from any mineralogical phase including metallic Fe except for the C–S– Fe^{2+} phase. Although, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in Fe oxides in the C–S–F phase of the fertilizer made of steelmaking slag was not known, a clear relationship was observed between the dissolution of Fe and the mass fraction of the other phase as well as the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in Fe oxide in fertilizer made of steelmaking slag.
5. Both Si and P were dissolved mainly from C2S–C3P solid solution. The dissolved mass of P estimated as the sum of the mineralogical phases was higher than that of the fertilizers, but in contrast, that of Si was lower. This could be explained as follows: first, for fertilizers, excess Ca^{2+} dissolved from free CaO increased the share of Ca in the dissolved Ca:Si:P ratio compared to that in C2S–C3P alone, and this

excess Ca^{2+} reacted with P precedence over Si to form $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which showed lower P solubility than $3\text{CaO}\cdot\text{P}_2\text{O}_5$ in water. Second, for C2S–C3P, the amount of dissolved Ca was larger than that dissolved from fertilizers with the same amount, therefore, the amount of soluble Si in water which obeyed the equilibrium of CaH_2SiO_4 was decreased. This high Ca^{2+} content did not decrease the amount of soluble P, as the ratio of dissolved Ca:Si:P still followed the dissolution of C2S–C3P, and there was no excess Ca^{2+} .

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