Technical Report

Elution of Plant Nutrition Elements from Steel Slag Fertilizers in a Paddy Field

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Abstract

Three fertilizer specimens, made from granulated blast furnace slag, dephosphorization slag or decarburization slag, were prepared to expose their cross section plane to paddy water. These fertilizer specimens were set in paddy soil for 75 days. The distribution and amounts of plant nutrition elements in the cross section plane before and after setting in paddy soil were analyzed by EPMA. Granulated blast furnace slag was composed of non-crystalline matter containing Ca, Si, Mg, and Al homogeneously. There were many microstructures in the dephosphorization slag and decarburization slag which are categorized as steelmaking slag. Ca, Si, and P-coexisting microstructures are important for P elution as well as Ca and Si elution from dephosphorization slag and decarburization slag. Candidate matter composed of Ca, Si, and P-coexisting microstructures is $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ solid solution.

1. Introduction

There are two types of steel slag generated in the steelmaking process using blast furnaces: blast furnace slag and steelmaking slag.

Blast furnace slag is obtained as a by-product when molten pig iron is made from coke and sintered ore in a blast furnace. There are two types of blast furnace slag: granulated blast furnace slag, which is obtained by rapid cooling with water, and slowly-cooled blast furnace slag, which is obtained by slow cooling under air. Dephosphorization slag is obtained as a by-product when lime and other substances are added to molten pig iron to remove phosphorus and silicon. Decarburization slag is obtained as a by-product when the pretreated hot metal is decarburized by adding oxygen and lime in a converter to produce steel. Dephosphorization slag and decarburization slag are also called steelmaking slag. There are two types of steelmaking slag: slowly-cooled slag in the atmosphere, and water cooled slag. According to the annual report of iron and steel slag statistics in fiscal year 2019[1)], Japan's annual crude steel production is 98.43 million tons, while granulated blast furnace slag is 19.11 million tons, slowly-cooled blast furnace slag is 3.64 million tons, and steelmaking slag is 13.42 million tons. Calculations show that for every ton of crude steel production, 231 kg of blast furnace slag and 136 kg of steelmaking slag, that is, totally 367 kg of steel slag are generated.

Blast furnace slag and steelmaking slag are used as raw materials for special fertilizers and ordinary fertilizers, as specified in the Fertilizer Control Law. According to the annual report of iron and steel slag statistics in fiscal year 2019[1)], 140000 tons of blast furnace slag and 120000 tons of steelmaking slag are used for fertilizers and soil conditioners annually, which are only 0.9% and 0.6% of the amount of blast furnace slag and steelmaking slag, respectively. Blast furnace slag contains Ca, Si, Mg, etc., while steelmaking slag contains Ca, Si, P, Mg, Fe, Mn, B, and other elements that nourish plants. Compared with blast furnace slag, steelmaking slag contains more elements that are effective for many types of plants, and this study was conducted to determine whether steelmaking slag could be used for fertilizer applications. In this paper, we use the term "slag fertilizer" to refer to the fertilizer made from blast furnace slag and steelmaking slag.

The content of plant nutrient elements in fertilizers is mostly analyzed by the elution test specified in the Fertilizer Analysis Method (1992)[2)]. **Table 1** shows the particle size and eluent of the specimens used in the elution test analysis of slag fertilizer.

In the elution test, a fine sample of slag fertilizer that has been ground and passed through a 210 μm sieve is used. The large specific surface area of fine particles provides easier elution. For the elution solution, highly leachable solutions such as 0.5 N hydrochloric acid or 2% citric acid (pH 2.1) are used, and the elution is often

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Table 1 Particle size and eluent for elution test described in methods of fertilizer analysis (1992)[2)]

Analysis item	Particle size of sample	Eluent
Soluble silicate Soluble lime Soluble magnesia	Passing through 210 μm sieve	0.5N HCl
Citric acid soluble phosphate Citric acid soluble magnesia Citric acid soluble manganese Citric acid soluble boron		2% citric acid

conducted for about one hour under the condition of shaking and mixing, which is an accelerated test. Since in actual paddy fields, the fertilizer is kept in a static state and the pH of the paddy water is usually near neutral, it is considered that plant nutrient elements are gradually eluted from the slag fertilizer over a long period of time under mild conditions that are different from the elution test used in the analysis. Therefore, we decided to investigate the leaching of plant nutrient elements from slag fertilizer in an actual paddy field. The results of this study are reported in Ref. 3). In Ref. 3), EPMA images of 3 mm × 3 mm fertilizer cross sections were used to illustrate the leaching of the elements. In this paper, the leaching of plant nutrient elements from slag microstructures is described in detail using 350 μm × 350 μm EPMA images.

2. Experimental Methods and Results

2.1 Preparation for the static test of slag fertilizer in a paddy field

2.1.1 Preparation of specimens for paddy field placement

Three types of slag fertilizers (granulated blast furnace slag, dephosphorization slag, and decarburization slag) were prepared for the static test in a paddy field. In each case, the slag was pulverized into fine particles and then granulated into spheres about 3 mm in diameter using a pelletizer. By using the granulated slag fertilizer after grinding to fine grains for the test, it was expected that the various microstructures constituting each slag could be included in the pelletized fertilizers and that the leaching of elements from various microstructures could be efficiently investigated by EPMA by increasing the specific surface area.

Ten grains of each slag fertilizer were embedded in a cylindrical resin (epoxy) at approximately the same distance from the bottom. The cylindrical resin in which these slag fertilizers were embedded was ground from the top surface to expose a circular fertilizer cross-section. The surface of the exposed fertilizer cross-section was polished with diamond paste on a glass plate to produce a resin-embedded specimen of slag fertilizer with a smooth fertilizer cross-section. The cross-section exposed fertilizer surface of the resin-embedded specimen was coated with a gold vapor deposition film using a coater. Concerning selected fertilizer grains without cracks, etc., the EPMA images were acquired, with the use of JXA-8621MX (JEOL), of element distribution for Ca, Si, P, Fe, Mn, Mg, Al, and O, in the areas of 3 mm × 3 mm containing the entire exposed cross-section of the fertilizer (circular shape), and 350 μm × 350 μm for observing the microstructure. After the EPMA images were acquired, the gold deposition film was removed using tissue paper and diamond paste. The resin-embedded specimen of slag fertilizer with the gold vapor deposition film removed was used for the static paddy field test.

2.1.2 Placing and collecting the slag fertilizer in the paddy field

The resin-embedded specimen of slag fertilizer (before placement in the paddy field) is shown in **Fig. 1**.

Fig. 1 Steel slag fertilizers – embedded resin specimen before setting in paddy soil

Fig. 2 Steel slag fertilizers – embedded resin specimen after setting in paddy soil

The resin-embedded specimens were placed in the flooded paddy soil so that the exposed surface of the fertilizer was at the same level as the soil surface, and the leaching test of the slag fertilizer was commenced (**Fig. 2**).

The resin-embedded specimens of each slag fertilizer were collected after 75 days in the paddy field. The resin-embedded specimens were rinsed with distilled water to remove mud, etc., and if there were any adherences to the exposed cross-section of the fertilizer, they were carefully removed using tweezers, Kim wipes moistened with distilled water, or absorbent cotton balls. The top surface of the resin-embedded specimen of each slag fertilizer was again coated with a gold vapor deposition film using a coater, and EPMA images of each element were acquired after the paddy field test in a 3 mm × 3 mm area and in a 350 μm × 350 μm area at the same location on the same fertilizer grain cross section as analyzed before the paddy field test. In this paper, the results of EPMA analysis of the 350 μm × 350 μm area are presented.

2.2 EPMA analysis results

By comparing the EPMA images before and after the paddy field static test, we investigated from which microstructure of the slag fertilizer the plant nutrient elements were leached. In the EPMA image, the elements are colored in descending order of abundance: white, pink, red, orange, yellow, yellowish green, turquoise blue, light blue, blue, dark blue, and black (“black” means “not detected”). The color of each element was chosen to facilitate comparison before and after the test, and it should be noted that the elemental amounts cannot be compared between different elements. EPMA images of each slag fertilizer before and after the paddy field test are shown below. Ca, Si, Mg, Al, and O for granulated blast furnace slag fertilizer, and Ca, Si, P, Fe, Mn, Mg, Al, and O for steelmaking slag fertilizer are the elements to be analyzed. The amount of each element was compared before and after the paddy field test at the same location, and if the amount of an element after the test was less than the amount before the test, it was assumed that this element had been leached.

Figure 3 shows the EPMA images of slag fertilizer made from granulated blast furnace slag, **Fig. 4** shows the EPMA images of

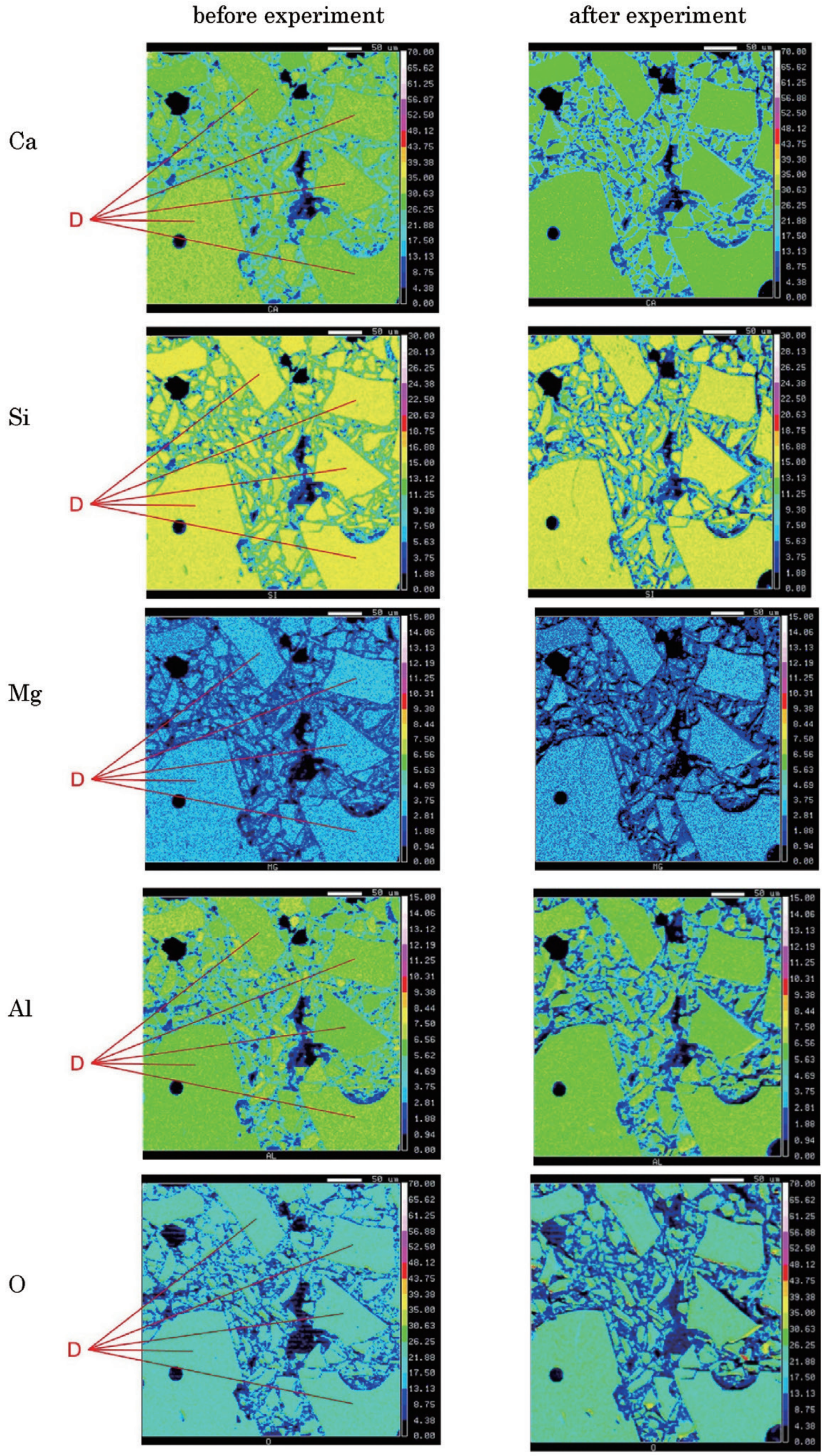

Fig. 3 EPMA mapping (350 μm × 350 μm) of fertilizer made from granulated blast furnace slag

slag fertilizer made from dephosphorization slag, and **Fig. 5** shows the EPMA images of slag fertilizer made from decarburization slag before and after the paddy field test.

From Figs. 3 to 5, the following characteristics were observed in the microstructures of each fertilizer before the paddy field test.

Characteristics of the microstructure of fertilizer made from granulated blast furnace slag

- The microstructure is “Ca, Si, Mg, and Al coexisting”, and homogeneous.

Characteristics of the microstructure of fertilizer made from dephosphorization slag

- Si is detected in the microstructure where Ca is present.
- P is detected in the “Ca and Si coexist” structure.
- Microstructures in which Ca, Si, and P coexist are located in contact with microstructures in which Fe is present.

Characteristics of the microstructure of fertilizer made from decarburization slag

- Si is detected in the microstructure where Ca is present.

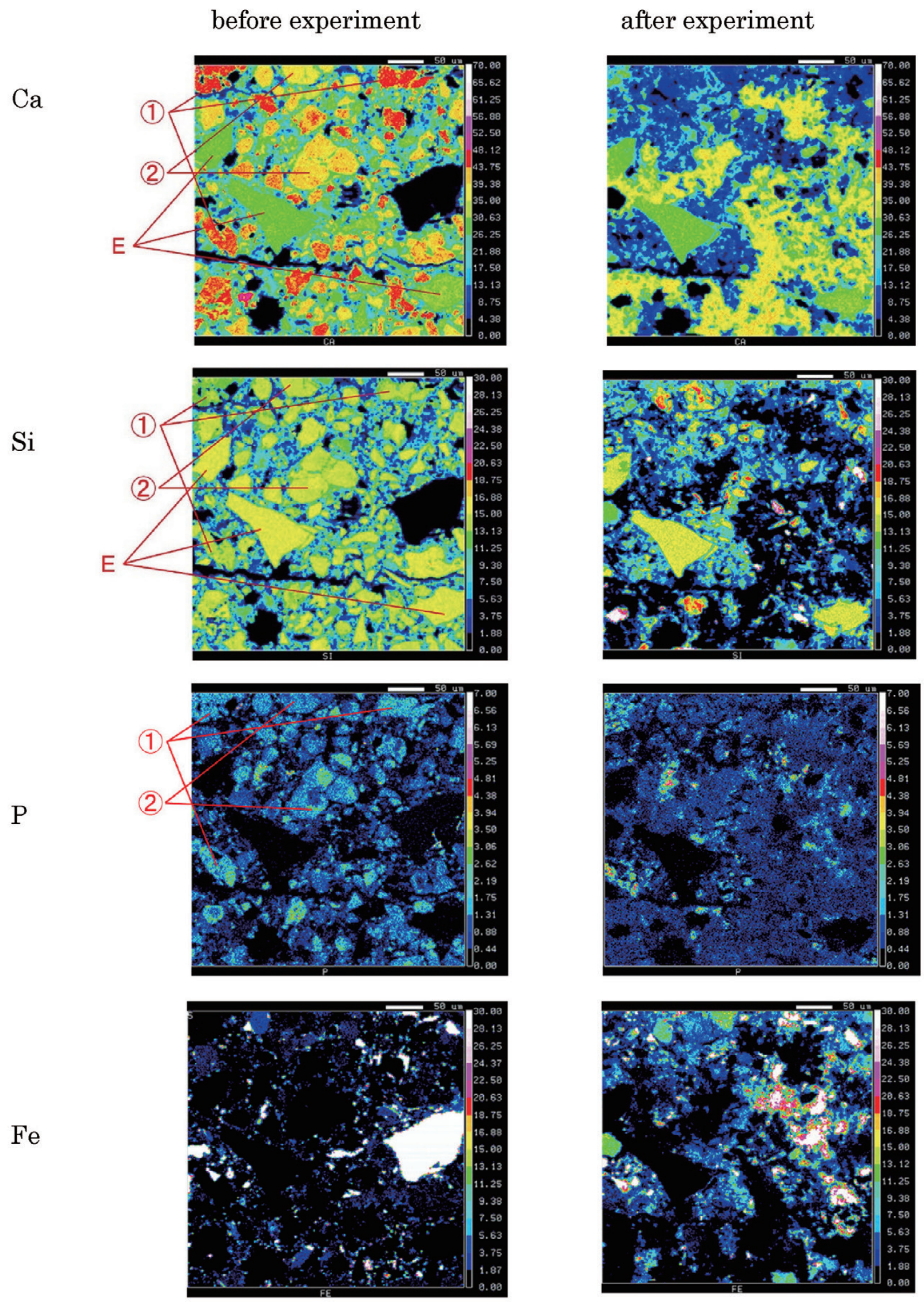

Fig. 4 EPMA mapping (350 μm × 350 μm) of fertilizer made from dephosphorization slag

- P is detected in the microstructure where Ca is present. Especially, most of P is detected in "Ca and Si coexist".
- Mn is detected in the microstructure where Fe is present.
- The "Ca, Si, and P coexisting" microstructures are located in contact with the "Fe-existing" microstructures or the "Fe-and-Mn coexisting" microstructures.

The leaching of the elements from each slag fertilizer is discussed below.

2.3 Discussion

Granulated blast furnace slag is obtained by quenching with water, and therefore consists of homogeneous amorphous material containing Ca, Si, Mg, Al, and O.[3] Figure 3 shows a comparison of the EPMA analysis before and after the test, and the Ca content decreased, suggesting that Ca was leached out by the paddy field test. Although the amount of Si decreased slightly, it is considered that the amount of Si leached by the paddy field test is small.

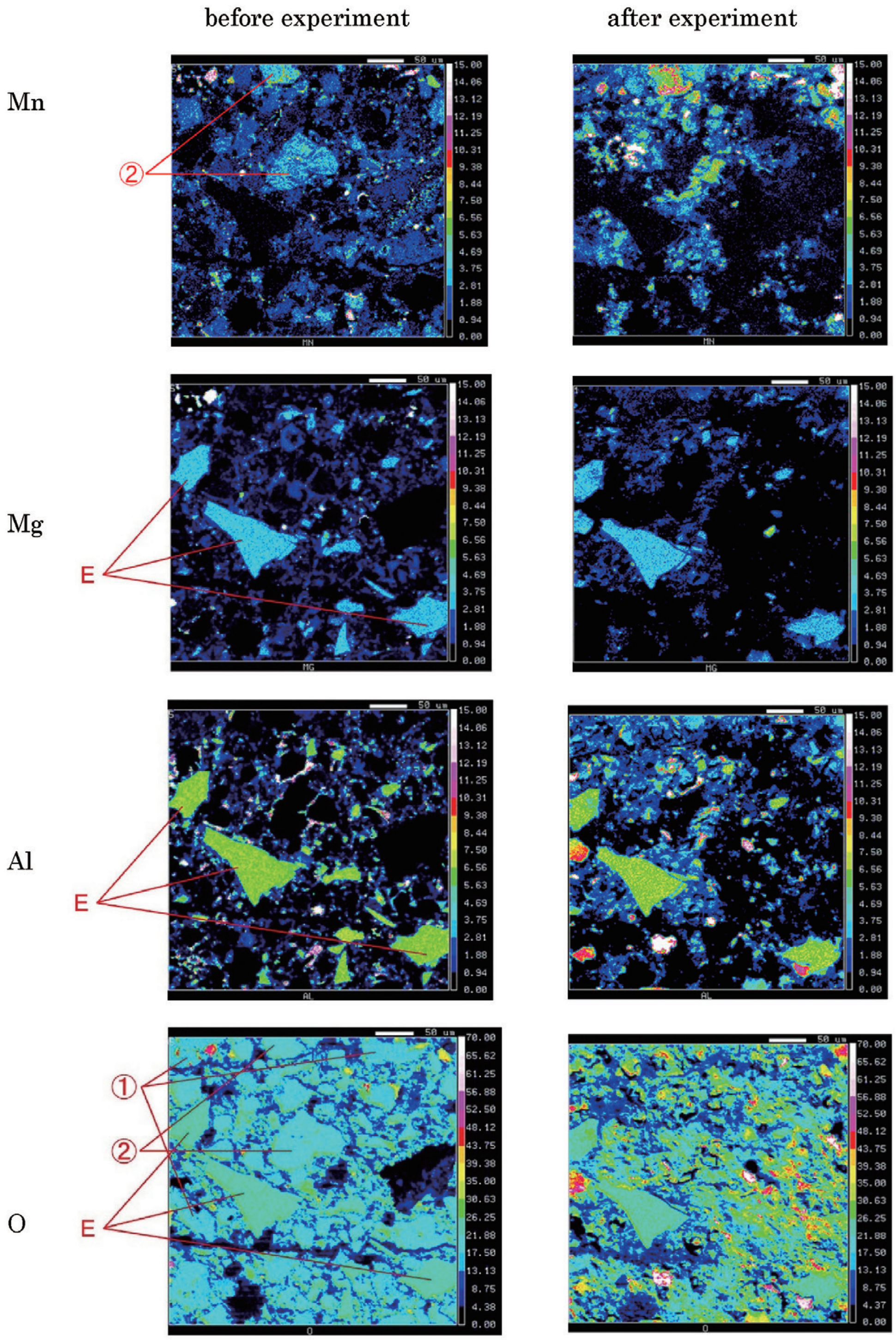

Fig. 4 EPMA mapping (350 μm × 350 μm) of fertilizer made from dephosphorization slag (continued)

As for the fertilizer made from dephosphorization slag and the fertilizer made from decarburization slag, Figs. 4 and 5 show that Ca and Si were leached out mostly from the microstructures coexisting with P. Therefore, the elements observed in the "Ca, Si, and P coexisting" microstructures before the paddy field test, their colors in the EPMA images, and the leachability of Ca, Si, and P (○ leached, × did not leach) are summarized in **Table 2**. The circled numbers in the first column of Table 2 indicate the numbers of each microstructure in the EPMA images (Figs. 3 to 5) of fertilizers made from each slag.

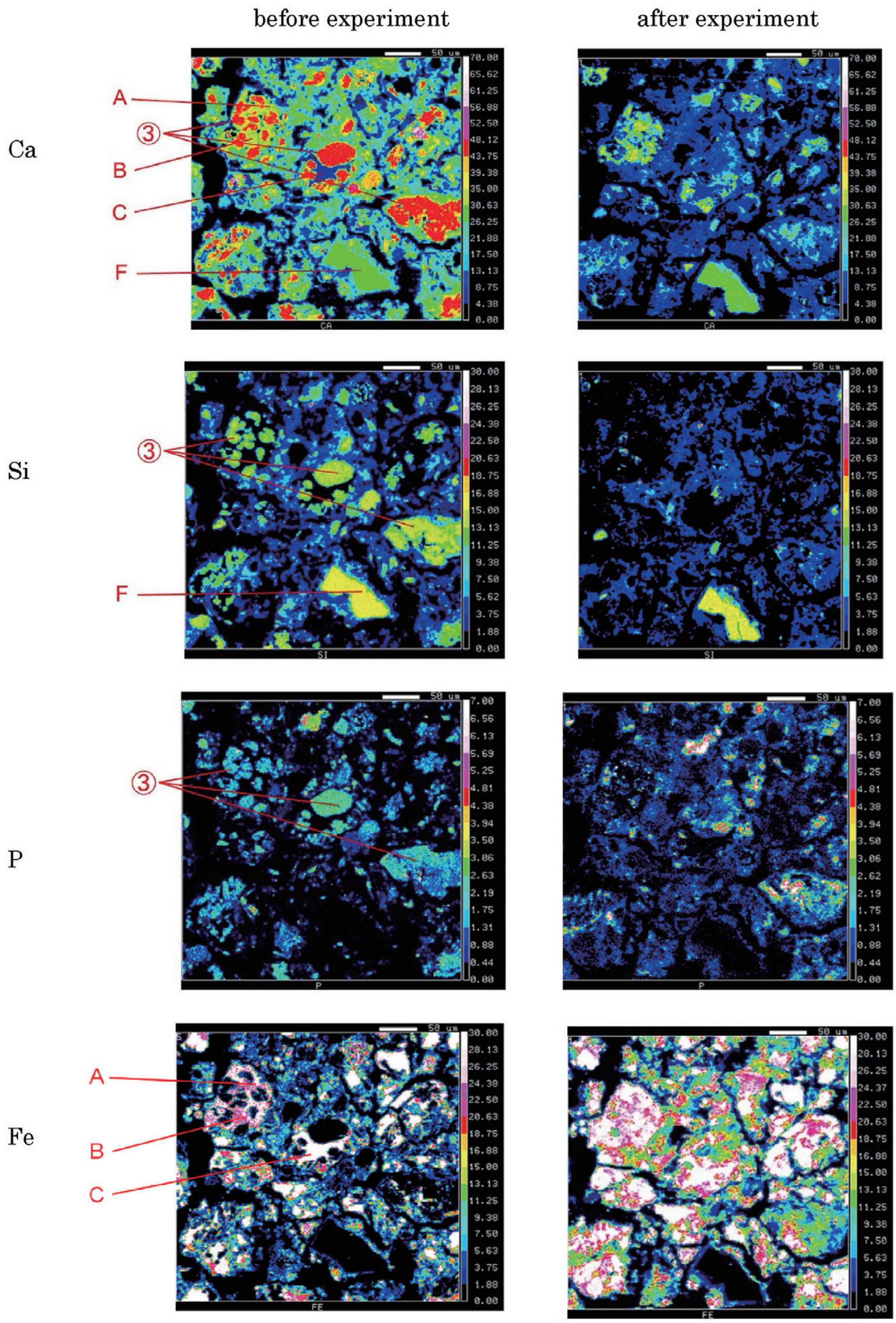

Fig. 5 EPMA mapping (350 μm × 350 μm) of fertilizer made from decarburization slag

Three types of “Ca, Si, and P coexisting” microstructures were observed in the fertilizer made from dephosphorization slag and the fertilizer made from decarburization slag used in this study. Ca, Si, and P were leached from all the “Ca, Si, and P coexisting” structures after 75 days of the paddy field test. Therefore, the “Ca, Si, and P coexisting” structure is considered to play an important role in the leaching of Ca, Si, and P in the fertilizer made from dephosphorization slag and the fertilizer made from decarburization slag.

$2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ solid solution is considered as a candidate constituent of this “Ca, Si, and P coexisting” structure.[4] Silicocarnotite ($5CaO \cdot SiO_2 \cdot P_2O_5$) and Nargelschmittite ($7CaO \cdot 2SiO_2 \cdot P_2O_5$) are recognized as crystalline materials related to the $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ solid solution. However, these crystalline materials were not detected by X-ray diffraction.

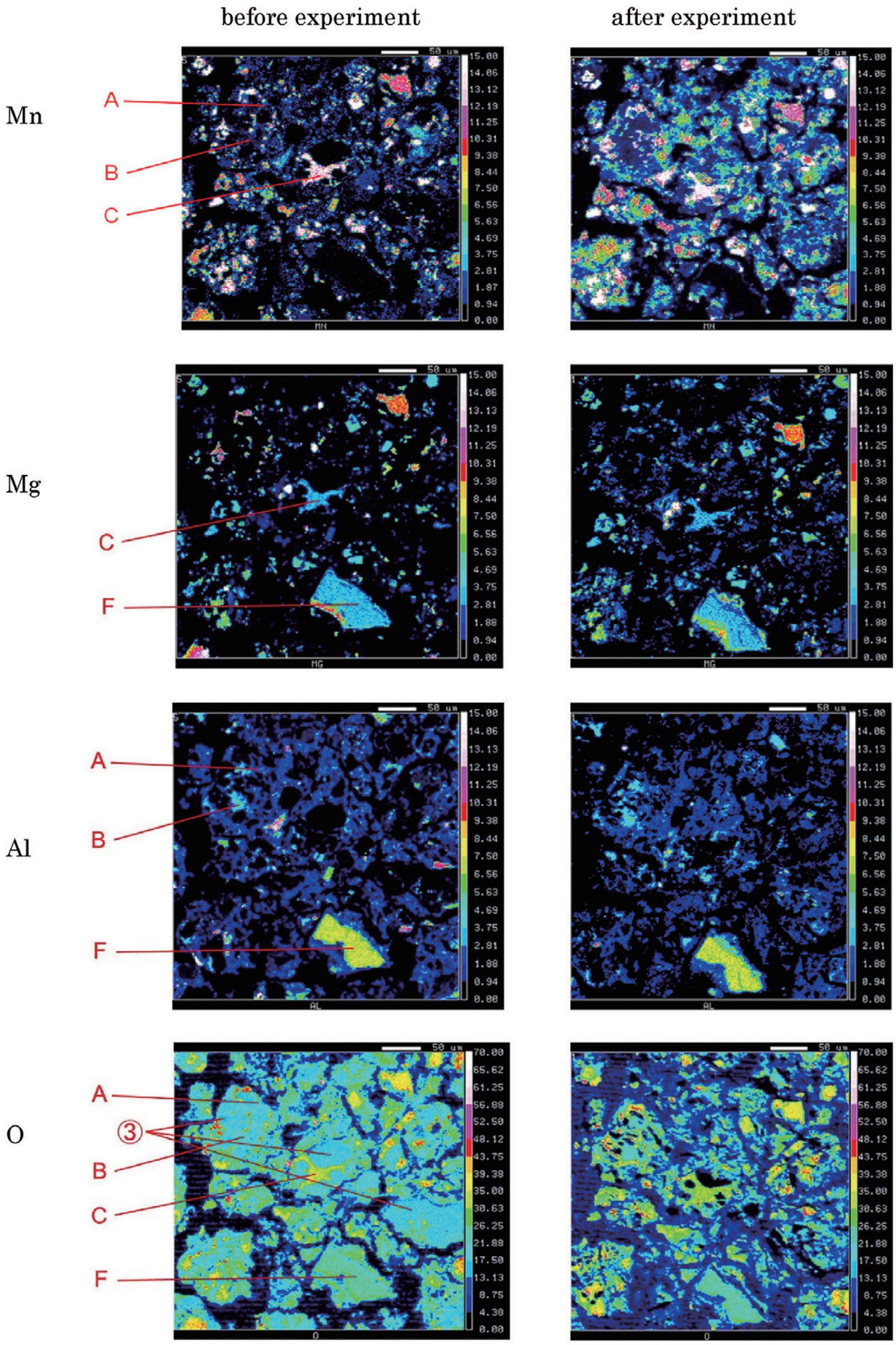

Fig. 5 EPMA mapping (350 μm × 350 μm) of fertilizer made from decarburization slag (continued)

The fertilizer made from decarburization slag had a “Ca, Fe, Mn, and Al coexisting” structure, and “Ca, Si, and P coexisting” structures were scattered in an island-like pattern within this structure. After 75 days in the paddy field, the “Ca, Si, and P coexisting” structure dissolved and disappeared, but the “Ca, Fe, Mn, and Al coexisting” structure remained without dissolution.

Table 3 shows the leachability (○ leached, × did not leach) of the elements contained in the “Fe-containing” structure that contained the “Ca, Si, and P-containing” structure. In Table 3, the alphabetic symbols in the first column are those of the microstructures shown in Fig. 5.

Fertilizer made from decarburization slag has a “Ca, Fe, Mn, and Mg coexisting” structure. Adjacent to this structure, a “Ca, Si, and P coexisting” structure was observed. After 75 days in the paddy field, the “Ca, Si, and P coexisting” structure dissolved and disappeared, but the “Ca, Fe, Mn, and Mg coexisting” structure remained without dissolution.

Table 4 shows the “Fe-containing” microstructure which contacts with the “Ca, Si, P-coexisting” microstructure, and the leachability (○ leached, × did not leach) of the elements contained in these microstructures. In Table 4, the alphabetic symbols in the first column are those of the microstructures shown in Fig. 5.

Next, **Table 5** shows the leachability of Ca and Si (○ leached, × did not leach) in the “Ca and Si but not P” structures observed before the test in fertilizers made from each slag. In Table 5, the alphabetic symbols in the first column are those for each microstructure in each EPMA image (Figs. 3 to 5) of fertilizer made from slag.

Dicalcium silicate $2CaO\cdot SiO_2$ is a recognized cause of leaching of Ca and Si from slag. In Ref. 3), it was reported that a crystalline material, Ca_2SiO_4, was detected by X-ray diffraction. However, as can be seen in Table 5, “only Ca, Si, and O coexist” microstructure was not observed in the slag fertilizer analyzed by EPMA. Although dicalcium silicate $2CaO\cdot SiO_2$ is well known as a constituent material of slag, the EPMA results suggest that there is no microstructure consisting only of dicalcium silicate $2CaO\cdot SiO_2$ in the dephosphorization slag and the decarburization slag analyzed in this study.

A comparison of Table 2 and Table 5 shows that the microstructures “containing Ca and Si but not P” in Table 5 all contained Al, and Ca and Si were not leached out. It is possible that the presence of Al instead of P suppresses the leaching of Ca and Si.

A comparison of Table 3 and Table 5 suggests that the first con-

Table 2 Ca, Si, P – coexisting microstructure

	Ca	Si	P	Fe	Mn	Mg	Al	O	solubility
dephosphorization slag (2 types)									
①	Ca	Si	P					O	○
②	Ca	Si	P		Mn			O	○
decarburization slag (1 type)									
③	Ca	Si	P					O	○

Table 3 Fe – containing microstructure in which Ca, Si, P – coexisting microstructure exists

	Ca	Si	P	Fe	Mn	Mg	Al	O	solubility
decarburization slag (2 types)									
A	Ca			Fe	Mn		Al	O	×
B	Ca			Fe	Mn		Al	O	×

Table 4 Fe – containing microstructure which contacts with Ca, Si, P – coexisting microstructure

	Ca	Si	P	Fe	Mn	Mg	Al	O	solubility
decarburization slag (1 type)									
C	Ca			Fe	Mn	Mg		O	×

Table 5 Ca, Si – containing microstructure which does not contain P

	Ca	Si	P	Fe	Mn	Mg	Al	O	solubility
granulated blast furnace slag (1 type)									
D	Ca	Si				Mg	Al	O	×
dephosphorization slag (1 type)									
E	Ca	Si				Mg	Al	O	×
decarburization slag (1 type)									
F	Ca	Si				Mg	Al	O	×

dition for leaching of Ca and Si from "Ca and Si coexisting" microstructure is "P coexistence". It can be concluded that the "Ca, Si, and P coexisting" structure plays an important role in the leaching of not only Ca and Si, but also P in fertilizers made from steelmaking slag.

3. Conclusion

Three types of granular fertilizers made from granulated blast furnace slag, dephosphorization slag, and decarburization slag were prepared for use in rice paddies with their cross sections exposed. The distribution and amount of plant nutritional elements in the fertilizer cross section before and after 75 days of the paddy field test were analyzed by EPMA. The fertilizer made from granulated blast furnace slag was considered to be composed of amorphous material with Ca, Si, Mg, and Al. In the case of fertilizer made from steelmaking slag, such as dephosphorization slag and decarburization slag, a variety of microstructures were observed. The "Ca, Si, P coexisting" structure was found to play an important role in the leaching of P as well as Ca and Si. The constituent material of this "Ca, Si, P coexisting" microstructure is considered to be $2CaO \cdot SiO_2$-$3CaO \cdot P_2O_5$ solid solution.

References

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