Technical Report

Steelmaking Slag for Fertilizer Usage

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Abstract

Both blast furnace slag and steelmaking slag have been utilized as raw materials for fertilizer. Fertilizers made of blast furnace slag or steelmaking slag are categorized in slag silicate fertilizer, byproduced lime fertilizer, slag phosphate fertilizer or iron matter of special fertilizer. Effective elements in blast furnace slag are Ca, Si and Mg. Steelmaking slag contains Ca, Si, Mg, P, Mn and Fe. Steelmaking slag also contains plant available Si. Therefore, fertilizers made of steelmaking slag is more useful. Four research examples were introduced. : (1) Formation of silica body cells by application of silicate fertilizer. (2) Registration as phosphate fertilizer. (3) Restoration of paddy fields damaged by Tsunami. (4) Composting of cow manure using steelmaking slag.

1. Introduction

According to Nippon Slag Association's statistics on the use of slag in 2012,¹⁾ the consumption of blast furnace slag was 1 390 000 tons for civil engineering, 18220000 tons for cement production, and 3340000 tons for sub-base course material. The consumption of steelmaking slag was 3470000 tons for civil engineering, 530000 tons for cement production, and 260000 tons for sub-base course material. On the contrary, the use of slag as a raw material for fertilizer or soil amendment still remains relatively small-160000 tons for blast furnace slag and 100000 tons for steelmaking slag. However, fertilizers and soil amendments represent an ecofriendly application wherein the advantageous chemical properties of steelmaking slag can be utilized to promote the growth of plants and increase the yield of agricultural products. Steelmaking slag is officially specified by the Fertilizer Control Law in Japan. When registered as an ordinary fertilizer or notified as a special fertilizer, steelmaking slag can be commercialized as such.

In this study, the author first describes the history of fertilizers using steelmaking slag as a raw material and the specifications of fertilizers given by the Fertilizer Control Law. Next, the author compares blast furnace slag and steelmaking slag as raw materials for fertilizer and explain the effective elements contained in them. Then, a few examples of the R&D that has been conducted since 2009 to expand the use of steelmaking slag for fertilizer is presented. Note that in this study, the term "steelmaking slag" refers to the slags from the steel making process using basic oxygen furnace.

2. Main Subject

2.1 History of fertilizer using steelmaking slag as a raw material and the fertilizer control law

The use of steelmaking slag as a raw material for fertilizer began to spread mainly in Europe. In 1878, the Thomas converter process was invented in England. Since then, the process had been developed in Germany. In 1882, Wagner, a German, reported that slag produced in the Thomas converter process could be made into phosphate fertilizer.²⁾ "Thomas phosphate fertilizer" manufactured from ground converter steelmaking slag soon became widespread as it proved to be a valuable source of phosphoric acid for plant life. In the 1960s, annual production of Thomas phosphate fertilizer in Germany reached as much as 2500000 tons. In Japan, the Thomas converter process was introduced to the Kawasaki plant of the former Nippon Kokan K.K. in 1918, and Thomas phosphate fertilizer was manufactured for some time. However, the Thomas converter process did not spread widely in Japan. In Germany, the production of Thomas phosphate fertilizer had decreased sharply since the mid-1970s as the NPK chemical fertilizer capable of simultaneously supplying nitrogen (N), phosphorus (P), and potassium (K) that are indispensable for the growth of plants came to be used. Today, Thomas phosphate fertilizer is not produced anymore.

In Japan, for some time after the World War II, a great variety of substances, including those which apparently had no fertilizer effects, had been used as "fertilizers." Under this situation, the Fertilizer Control Law was put into effect in 1950. Of the substances that had been used as fertilizers until the enactment of the Fertilizer Control Law, those which the farmers can recognize by their five senses

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as having some fertilizer effect are approved as special fertilizers by the law. Special fertilizers include, for example, fish lees, rice bran, and compost. Looking at fertilizers using steelmaking slag as a raw material, those which contain iron are approved as special fertilizers. Special fertilizers (containing iron) are specified as those which contain limonite (includes bog iron ore), slag (only slag intended to supply mainly iron and containing 10% or more iron), or iron powder and weathered rock containing 10% or more iron.

In addition to the special fertilizers, ordinary fertilizers were newly included in the Fertilizer Control Law. Although ordinary fertilizers are those whose official specifications had been stated clearly, they are defined as any fertilizers other than special fertilizers, probably because of the circumstances that led to the enactment of the Fertilizer Control Law. Ordinary fertilizers include nitrogenous fertilizer, phosphate fertilizer, potash fertilizer, lime fertilizer, magnesia fertilizer, silicate fertilizer, and manganese fertilizer. At present, as ordinary fertilizers using steelmaking slag as a raw material, slag silicate fertilizer, byproduct lime fertilizer, and slag phosphate fertilizer are specified (**Tables 1–3**³).

Of the various fertilizers using steelmaking slag as a raw materi-

al, the most typical one is "slag silicate fertilizer." Silicate fertilizer is the world's first fertilizer specification established in 1955 in Japan where rice is primarily grown. In the 1960s, the annual production of slag silicate fertilizer was more than one million tons.⁴⁾ In those days, blast furnace slag was used as a raw material for slag silicate fertilizer. Till date, slag silicate fertilizer using blast furnace slag as a raw material has been used under the brand name "Keikaru." However, as in the case of Thomas phosphate fertilizer of Germany, the production of slag silicate fertilizer made from blast furnace slag began to decrease sharply in the early 1970s. According to Nippon Slag Association's statistics on the use of slag in 2012, the total consumption of blast furnace and steelmaking slags for fertilizer and soil amendment was 260000 tons.

2.2 Fertilizers made from blast furnace slag and steelmaking slag

Iron and steel slag can largely be divided into blast furnace slag and steelmaking slag. **Table 4** shows the representative chemical composition of blast furnace slag and steelmaking slag, respectively.⁵⁾

Approximately 160000 tons of blast furnace slag are consumed annually as a raw material for slag silicate fertilizer "Keikaru." With

Table 1 Stag sincate fer unzer in fer unzer control law	Fable 1	Slag silicate	fertilizer in	fertilizer	control law ³
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Category in Fertilizer control law	Minimum contents of effective constituents (%)	Maximum contents of hazardous constituents (%)	Other regulation
Slag Silicate fertilizer (made of Blast furnace slag or Steelmaking slag)	Case1. In case, Guarantee for soluble SiO2 and alkalinity Soluble SiO2 \ge 10% Alkalinity \ge 35% Case2. In case, Guarantee for Citric acid soluble MgO or Citric acid soluble MgO or Citric acid soluble MgO or Citric acid soluble MgO Soluble SiO2 \ge 10% Alkalinity \ge 20% Citric acid soluble MgO \ge Soluble SiO2 (%)× 1 Citric acid soluble Mn \ge Soluble SiO2 (%)× 1 Citric acid soluble Mn \ge Soluble SiO2 (%)× 1 Citric acid soluble B \ge Soluble SiO2 (%)× 0.05	Case1. In case, soluble SiO2 \ge 20% (1) Ni = Soluble SiO2 (%)× 0.01 Cr = Soluble SiO2 (%)× 0.1 Ti = Soluble SiO2 (%)× 0.04 (2) Ni = 0.4% Cr = 4.0% Ti = 1.5% Case2. Other than case 1 Ni = 0.2% Cr = 2.0% Ti = 1.0%	Case1. In case, soluble SiO2 ≥ 20% All particles must go through 2mm width net sieve. In case, other than granulized blast furnace slag, More than 60% particles must go through 600µm width net sieve. Case2. Other than case 1 Only for slags, All particles must go through 2mm width net sieve. Soluble CaO ≥ 40% Case3. In case, Alkalinity < 30%, Slag silicate fertilizer whose alkalinity is guaranteed higher than 30% must be mixed with hematite.

Table 2	Byproduced	lime	fertilizer	in	fertilizer	control	law ³

Category in Fertilizer control law	Minimum contents of effective constituents (%)	Maximum contents of hazardous constituents (%)	Other regulation
Byproduced Lime fertilizer (From Non-metal mining industry, Food industry, Pulp industry, Chemical industry, Steel industry, non-ferrous metal manufacturing industry)	Case1. Alkalinity≧35% Case2. In case, Citric acid soluble MgO is guaranteed other than alkalinity, Alkalinity≧35% Citric acid soluble MgO≧ 1%	Case1. Ni = Alkalinity (%) \times 0.01 Cr = Alkalinity (%) \times 0.1 Ti = Alkalinity (%) \times 0.04 Case2. Otherthan Case1, Ni = 0.4% Cr = 4.0% Ti = 1.5%	Concerned with fertilizers made of Slag, All particles must go through 1.7mm width net sieve. More than 85% of them must go through 600µm width net sieve.

Category in Fertilizer control law	Minimum contents of effective constituents (%)	Maximum contents of hazardous constituents (%)	Other regulation
Slag Phosphate fertilizer (From Steelmaking slag)	Case1. Citric acid soluble P2O5 \geq 3% Alkalinity \geq 20% Soluble SiO2 \geq 10% Case2. In case, Citric acid soluble MgO or Citric acid soluble Mn is guaranteed other than Alkalinity \geq 20% and Soluble SiO2 \geq 10%. Citric acid soluble MgO \geq 1% Citric acid soluble Mn \geq 1%	Cd = Citric acid soluble P2O5 (%) × 0.00015 Ni = Citric acid soluble P2O5 (%) × 0.01 Cr = Citric acid soluble P2O5 (%) × 0.1	All particles must go through 4mm width net sieve.

(%)

Table 3 Slag phosphate fertilizer in fertilizer control law³⁾

Table 4 Typical compositions of blast furnace slag and steelmaking slag

							(70)
	CaO	SiO ₂	MgO	MnO	Fe	Al ₂ O ₃	P ₂ O ₅
Blast furnace slag	41.7	33.8	7.4	0.3	0.4	13.4	0.1
Steelmaking slag	45.8	11.0	6.5	5.3	17.4	1.9	1.7

respect to steelmaking slag, about 100000 tons are used annually as a raw material for slag silicate fertilizer, byproduct lime fertilizer, slag phosphate fertilizer, and special fertilizers. Steelmaking slag contains less silicic acid than blast furnace slag. However, the silicic acid contained in steelmaking slag is mostly in the form available easily to plants. Therefore, steelmaking slag is expected to supply silicic acid to plants more efficiently than blast furnace slag.⁶

The chemical composition of steelmaking slag shown in Table 4 is that of basic oxygen furnace slag. Steelmaking slag can be further subdivided into hot-metal pretreatment and basic oxygen furnace slags. The former has been known to contain over 20% silicic acid, where it is used as a raw material for silicate fertilizer. As can be seen by comparing the compositions of blast furnace slag and steelmaking slag from Table 4, steelmaking slag contains not only Ca and Si but also Mg, Mn, Fe, P, and other elements having fertilizer effects. Conversely, blast furnace slag contains a considerable proportion of Al. Since Al easily combines with phosphoric acid in soil, it impedes the absorption of phosphoric acid by the plant. Thus, as a raw material for fertilizer, steelmaking slag is considered more desirable than blast furnace slag.

Figures 1 and **2** show the change in annual consumption of blast furnace and steelmaking slags, respectively, for fertilizer and soil amendment, based on Nippon Slag Association's statistics.¹⁾

From Fig. 1, it can be seen that for the past five years, the annual consumption of blast furnace slag for fertilizer/soil amendment has remained constant at about 150000 tons. While, as can be seen from Fig. 2, the annual consumption of steelmaking slag for fertilizer/soil amendment, which was 69000 tons in 2010, has increased in two consecutive years to 103000 tons in 2012. The implication may be that the usefulness of fertilizers made from steelmaking slag is being increasingly recognized.

2.3 Steelmaking slag-contained elements having fertilizer effects

Before explaining the elements having fertilizer effects, the author discusses how to indicate fertilizer compositions.



Fig. 1 Annual usage of blast furnace slag for fertilizers and soil amendments in Japan





Concerning the fertilizer's composition, it is customary to indicate many of the elements having fertilizer elements in their oxide forms. For example, Ca, Si, Mg, and P are indicated as CaO, SiO₂, MgO, and P_2O_5 and read as lime, silicic acid, magnesia, and phosphoric acid, respectively. However, Mn and Fe are indicated directly by their contents. Chemically speaking, this manner of indicating the fertilizer composition is inaccurate. Nonetheless, the reader is requested to bear in mind the peculiarities of the method of indication in reading the following text.

Effects of silicic acid (SiO₂)

Of the constituents of fertilizers made from steelmaking slag, silicic acid has the most important fertilizer effect. For example, a paddy field has been reported to produce a yield of 6 tons/ha, the absorption of N by rice is 100–120 kg/ha, whereas that of silicic acid by rice is 10 times greater, that is, 1000–1200 kg/ha.⁷⁾ Thus, rice plant requires a large amount of silicic acid. The silicic acid absorbed by the rice roots is consumed to form glassy cells called silica body cells (described later) in the surface layers of stalks and leaves of the rice plant. The silica body cells are hard, transparent cells that are formed in several vertical columns in an orderly manner. They help make the stalks and leaves stand upright, promote photosynthesis by increasing the light-receiving capacity, and protect against diseases.⁸⁾

Silicic acid also affects with quality and flavor of rice. As mentioned above, in a paddy field, as much as about one ton of silicic acid is absorbed by rice per ha. Professor Fujii at Yamagata University points out the possibility that the soil of many paddy fields in Japan can become deficient in silicic acid.⁹⁾ As plants that require silicic acid, sugarcane, corn, wheat, barley, and as rice are well known.

Effects of lime (CaO)

Lime (CaO), which is alkaline, is effective to neutralize acid soil. Making the soil alkaline helps protect the plant against soil pathogens. In addition, Ca makes the roots strong and helps promote the absorption of K, which is important to plant life.

Effects of magnesia (MgO)

Magnesia (MgO) is also alkaline and hence, it is effective to neutralize acid soil. In addition, Mg, a constituent element of chlorophyll, promotes photosynthesis.

Effects of phosphoric acid (P,O₅)

Phosphorus (P) is one of the three elements indispensable for plant life. Without P, plants cannot grow. P promotes plant growth, stooling, root extension, blossoming, and fruit bearing.

Effects of manganese (Mn)

Manganese (Mn) is known to impact the production of chlorophyll and promote photosynthesis.

Effects of iron (Fe)

Iron (Fe) transforms hydrogen sulfide in the soil into iron sulfide, thereby making it harmless and reducing damage to the plant roots. In addition, it is known to influence the production of chlorophyll and promote photosynthesis.

2.4 Examples of R&D

(1) Formation of silica body cells and its effect to suppress brown spot disease

In recent years, brown spot disease whereby tiny brown spots appear on the leaves, ears, and stalks of rice plant, causing the plant to wither in worst cases, has become a problem in Niigata and other major rice-producing districts of Japan. Silicate fertilizer is expected to help prevent brown spot disease by forming silica body cells. Therefore, in a joint study with Niigata Agricultural Research Institute and Chiba University, we examined the effect of silicate fertilizer made from steelmaking slag on brown spot disease. As shown in **Fig. 3**, when the slag silicate fertilizer was applied to the soil at a rate of 1 ton/ha, the number of brown spots on the rice plant leaves decreased; the number of silica body cells that formed on the leaf surfaces simultaneously increased. In addition, the leaves were almost free from germs of brown spot disease.

(2) Confirmation of fertilizer effect of phosphoric acid and registration of phosphate fertilizer



Fig. 3 Formation of silica body cells on rice plant leaf by silicate fertilizer and suppression of brown spot disease



Fig. 4 Effect of dephosphorization slag on komatsuna growth

Dephosphorization slag from the hot-metal pretreatment process of Kashima Works contains about 5% phosphoric acid (P_2O_5). With the cooperation of the Resources & Energy Department of Kashima Works, we obtained many samples of dephosphorization slag of the Kashima Works and subjected them to the analyses specified in the Fertilizer Control Law. As a result, it was found that all the samples met the specifications of the slag phosphate fertilizer shown in Table 3. We then examined the effects of dephosphorization slag of the Kashima Works as a slag phosphate fertilizer using komatsuna (Brassica Rapa var. perviridis). Consequently, the fertilizer effect shown in **Fig. 4** could be confirmed.

On the basis of the above results, the dephosphorization slag of Kashima Works is registered as "Phosphate Fertilizer Kashima No. 1" on June 25, 2013. A copy of certificate of the fertilizer registration was shown in **Fig. 5**.

(3) Use of steelmaking slag to improve soil of tsunami-stricken farmland

In the Great East Japan Earthquake, large tracts of farmland were damaged by the tsunami—about 15000 and 5900 ha in the Miyagi and Fukushima prefectures.

Fertilizers made from steelmaking slag contain a large proportion of CaO. When the exchange of sodium ions of seawater adsorbed to the soil particles and calcium ions supplied by the fertilizer takes place, desalting of the soil is expected to be promoted. On the other hand, the deposit of soil brought by a tsunami can become acidic, as sulfuric acid is produced by oxidation of pyrite (FeS₂) contained in the soil. In this case, the alkaline CaO contained in the fertilizer made from steelmaking slag will help improve the soil that



Fig. 5 Fertilizer registration proof of phosphate fertilizer 'Kashima No.1'

has been made acidic by the oxidation of pyrite. In April 2012, a study group led by Professor Goto at Tokyo University of Agriculture applied a fertilizer made from steelmaking slag to the acidified soil of a tsunami-stricken paddy field in Souma City, Fukushima Prefecture to test-cultivate rice. Figure 6 shows the pH value of the paddy field soil before and after the application of the slag fertilizer. After application of the slag fertilizer, the soil that had been acidified to pH 4 was improved to about pH 5.5, which is generally considered suitable for the cultivation of rice. The rice grew favorably and the crop was normal.

On the basis of the results of the above soil improvement and rice test cultivation carried out in 2012, Tokyo University of Agriculture, Souma City, and JA Souma have since 2013 jointly carried on the restoration of the tsunami-stricken farmland in Fukushima as the Souma project (Fig. 7). During 2013, fertilizer made from steelmaking slag was applied at an average rate of 5 tons/ha to 40 ha of tsunami-stricken farmland, and the rice crop was almost the same as





Fig. 7 Souma Project

Start of the Souma project

in the years before the farmland was attacked by the tsunami. The Souma project has been continued. They plan the restoration of about 200 ha of farmland for 2014.

Apart from the Souma project, as part of the industrial development project of the Iron and Steel Institute of Japan, research on the restoration of tsunami-stricken farmland utilizing steelmaking slag has been conducted in the Miyagi Prefecture till the end of 2014 under the leadership of Professor Kitamura at the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University and Associate Professor Ito at the Field Environmental Research Center, Tohoku University.

(4) Use of steelmaking slag as compost

Composted animal wastes can be utilized as fertilizer containing N and P. By mixing steelmaking slag in animal wastes, it is possible to make compost that contains not only N and P but also Ca, Si, Mg, Mn, Fe, and others. Figure 8 shows a scene of a composting test using cow manure added to 15mass% steelmaking slag and cow manure without steelmaking slag. Figure 9 shows the time-serial change in temperature of compost measured at a depth of 20 cm from the surface. When steelmaking slag was added to the cow manure, the temperature of the compost rose to about 70°C. On the contrast, without steelmaking slag, the compost temperature only rose to about 58°C. When the compost was stirred up every 10 days, its temperature first dropped, and then rose again. Since the temperature of the compost added to steelmaking slag remained at 65°C-70°C, it was considered that the composting had progressed in a short period of time. Figure 10 shows the results of a decay ripeness test of the compost using komatsuna.

The compost made by adding steelmaking slag to cow manure gave a germination rate of 80% or more and hence, it was judged that the compost could be used to cultivate crops.

Figure 11 shows the results of a cabbage cultivation test performed assuming three different cases: use of compost made by adding steelmaking slag to cow manure, use of compost without steelmaking slag, and use of no compost. The yield was highest when the compost made by adding steelmaking slag was used.

As described above, it was found possible to mix steelmaking slag in animal wastes to make compost.

2.5 Problems involved in using steelmaking slag as fertilizer

The fertilizer made from steelmaking slag contains very small proportions of N and K, which are indispensable for plant life. Besides, it does not contain much P. Therefore, it needs to be used together with a chemical fertilizer that contains substantial amounts of N, P, and K. It may be said that the fertilizer made from steelmaking slag is given low priority when the farmer considers the cost of fertilizer and the burden of fertilizer application. In order to spread the use of the fertilizer made from steelmaking slag, it is necessary to compensate for its weak points.

For example, the rice plant requires a large amount of silicon (Si). Reportedly, the Si content of the paddy soil in Japan has been decreasing. Under such a condition, it is hoped that the fertilizer using steelmaking slag that is capable of effectively supplying silicic



Fig. 8 Composting of cow manure



Fig. 9 Temperature of compost at 20 cm depth from the surface



Fig. 10 Compost maturation test for komatsuna



Fig. 11 Fertilizer effect of compost with steelmaking slag on cabbage yield

acid to plants will become widespread. In addition, if new benefits of Mn, Fe, Mg, and, so on, other than the Si and Ca also contained in steelmaking slag are found, there is a possibility that new uses thereof will be developed.

The most important point in using steelmaking slag as fertilizer is checking for harmful heavy metals. The term "slag" is used in the specifications of slag silicate fertilizer and slag phosphate fertilizer in the Fertilizer Control Law. There is a fear that the term should suggest that those fertilizers contain harmful heavy metals. In order to secure the reliability of steelmaking slag as fertilizer, it is absolutely necessary to conform to the regulations on harmful heavy metals provided by the Fertilizer Control Law and the soil environmental standards provided by the Basic Law for Environmental Pollution Control.

3. Conclusion

Steelmaking slag contains Si, Ca, P, Mg, Mn, Fe, and various other elements required in fertilizers. In addition to the conventional silicate and lime fertilizers, slag phosphate fertilizers have come to be registered. Since paddy rice consumes a large amount of Si, the slag silicate fertilizer has become widespread, although it is effective in improving acid soil. While steelmaking slag may directly be used as fertilizer, it can be mixed with animal wastes, and such, to make compost. By so doing, it becomes possible to utilize animal wastes effectively and supply plants with many different nutrients at the same time.

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