## Application of the slag to paddy rice cultivation — Japan's first use of the general waste slag as fertilizer —

#### Kentaroh SUMI

Manager Slag & Metal Recycling Section Engineering & Development Department Environmental Solution Division

### **Toshihiro MIYATANI**

Senior Manager Slag & Metal Recycling Section Engineering & Development Department Environmental Solution Division

## Yuuji SEKI

Manager Slag & Metal Recycling Section Engineering & Development Department Environmental Solution Division

## Hirohisa KAJIYAMA

Section Manager Slag & Metal Recycling Section Engineering & Development Department Environmental Solution Division

## Toshimi NAGATA

Engineering & Development Department director Environmental Solution Division

## Yoshihiro ONO

Senior Manager Strategy Planning Section Engineering & Development Department Environmental Solution Division

#### Abstract

Slag discharge from our company's direct melting system, which is used effectively is the differentiation technology. However the order amount of public works, which occupy 50% of slag market is descending year by year. To utilize total amount of slag efficiently and stably in the future, development of new applications is indispensable. We focused on soluble silicic acid and calcium included in slag, and confirmed that they have an effect on the growth of paddy rice. The general waste slag registered tentatively as siliceous fertilizer for the first time in Japan. We report on results of paddy rice growth effect test, and introduce the expansion of the application for the agriculture field other than paddy rice.

#### 1 Introduction

Approximately 200,000 tons of molten slag are produced from our shaft-furnace type gasification and melting furnaces, which is called the Direct Melting System (DMS), per year (the number of operating facilities was 32 in FY2016), all of which are effectively used. Main applications are aggregate for asphalt mixtures, fine aggregate for secondary concrete products and backfill materials, and 60% to 70% of them are used for public works. However, orders for public works have been decreasing year by year, so new applications need to be developed to continue using slag in a stable and effective way. Nippon Steel & Sumikin Engineering Co. has been working on the utilization of molten slag in the agricultural sector—paddy rice sector, in particular—as part of the new application development, with the aim of utilizing slag in places where it is produced. A paddy rice growth evaluation test was started in FY2012 using molten slag from the Nishigaya DMS plant in Shizuoka City under a collaborative scheme involving government, academia, and industry — Shizuoka City, Shizuoka University, and Nippon Steel & Sumikin Engineering. In addition, Nippon Steel & Sumikin Engineering discussed registration of the fertilizer with the Japanese Ministry of Agriculture, Forestry and Fisheries at the same time. The effect and safety of our slag fertilizer was recognized and in March 2017, Japan's first slag from Municipal Solid Waste (MSW) was provisionally registered as siliceous fertilizer (registration name: DM Calcium Silicate).

This article reports the results of the paddy rice growth evaluation test using our slag along with other projects for using slag in various agricultural sectors other than paddy rice.



# Fig. 1 Shizuoka city Nishigaya DMS plant and slag

## 2 Characteristics of Molten Slag

Our shaft-furnace type gasification and melting furnace (gasifier) melts ash (Ca, Si, and Al) in MSW and ash in auxiliary materials (coke, limestone, or quartz sand) at high temperatures. The high temperature slag is quenched with water and forms slag that mainly consists of silicic acid (SiO<sub>2</sub>), lime (CaO), and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>). At this point, the silicic acid and lime contained in the slag become soluble. In addition, coke is injected into the gasifier with MSW, which raises the temperature at the bottom of the furnace (1,700)to 1,800°C). At such high temperatures, the ash in the processed material is completely melted and the furnace becomes a high temperature reduction atmosphere. Therefore, lead and other low-boiling heavy metals contained in the general waste volatilize and turn into gas. Therefore, the slag's quality is safe since it contains almost no heavy metals and other harmful substances. In addition, limestone (or quartz sand) is injected with MSW, and the injection ratio is adjusted by periodically measuring the components of the slag. This stabilizes the main components of the slag and adjusts the viscosity and fluidity of the molten material at the time of slag discharging (such that it flows smoothly), which enables stable discharge and allows the slag and metal to easily separate based on the specific gravity. As a result, after water granulation and magnetic separation, the slag contains almost no metals and its quality is safe similarly to that of natural materials. Figure 2 shows the overview of the gasifier. Table 1 shows the contents of harmful substances in the slag and Table 2 shows their leaching amounts along with the JIS criteria (JIS A 5031: Melt-solidified slag aggregate for concrete derived from municipal solid waste and sewage sludge). As shown in Tables 1 and 2, the contents of the harmful substances in the slag and the leaching amounts are significantly lower than that of the JIS criteria. The slag has been widely utilized as engineering work materials such as aggregate for asphalt mixtures and secondary concrete products.

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)



Fig. 2 Overview of the gasifier

Item	Unit	Content	Target	
Cadmium	mg/kg	< 10	≤ 150	
Lead	mg/kg	< 15	≤ 150	
Hexavalent chromium	mg/kg	< 10	≤ 250	
Arsenic	mg/kg	< 10	≤ 150	
Total mercury	mg/kg	< 1	≤ 15	
Selenium	mg/kg	< 10	≤ 150	
Fluorine	mg/kg	< 400	≤ 4000	
Boron	mg/kg	< 400	≤ 4000	

Table 2 Harmful substance leaching amount of slag

T.	<b>TT</b> •	T 1:	The second se	
Item	Unit	Leaching amount	Target	
Cadmium	mg/L	< 0.001	≤ 0.01	
Lead	mg/L	< 0.005	≤ 0.01	
Hexavalent chromium	mg/L	< 0.02	≤ 0.05	
Arsenic	mg/L	< 0.005	≤ 0.01	
Total mercury	mg/L	< 0.0005	≤ 0.0005	
Selenium	mg/L	< 0.002	≤ 0.01	
Fluorine	mg/L	< 0.08	$\leq 0.8$	
Boron	mg/kg	< 0.1	≤ 1.0	

## 3 Fertilizer Components of DM Calcium Silicate

One type of slag fertilizer for growing paddy rice is slag siliceous fertilizer (registration name: Calcium Silicate) made from iron and steel slag. The components of our slag (hereinafter referred to as DM Calcium Silicate. DM Calcium Silicate is the registration name when the fertilizer was provisionally registered and it has been registered as a trademark) are similar to those of Calcium Silicate. Therefore, DM Calcium Silicate was expected to work well in the growth of paddy rice as siliceous fertilizer as is the case with Calcium Silicate. Table 3 shows the main components of DM Calcium Silicate and Table 4 compares the components of the siliceous fertilizer between DM Calcium Silicate and Calcium Silicate.

## Table 3 Main component of slag

Item	Silicon dioxide	Calcium oxide	Aluminum oxide	
	(SiO <sub>2</sub> )	(CaO)	(Al <sub>2</sub> O <sub>3</sub> )	
Analysis value	35.4	37.6	19.4	

 Table 4
 Component comparison of siliceous fertilizer

Item	Soluble silicic acid	Alkalinity	Citric acid-soluble magnesium
DM Calcium Silicate	M Calcium Silicate 31.8		1.53
Calcium Silicate	31.6	48.0	5.99

The characteristics of each component of the siliceous fertilizer are described below.

• Soluble silicic acid:

Accelerates the growth of leaves, stems, and roots. Improves the light receiving conditions, which enhances the photosynthesis capacity and improves the ripening of brown rice. It strengthens (hardens) the surface of leaves and stalks, which enhances the resistance to insects and disease and reduces wind damage due to typhoons. • Alkalinity:

Mainly calcium. Improves the acidification of soil to bring it into line with neutral pH.

• Citric acid-soluble magnesium:

Magnesium. Supplies nutrients for plants.

## 4 Paddy Rice Growth Evaluation Test Using DM Calcium Silicate

A paddy rice growth evaluation test was conducted using DM Calcium Silicate. A pot test was conducted at the Japan Fertilizer and Feed

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)

Inspection Association and a cultivated land (paddy field) test was conducted at Shizuoka University. For the pot test, a/5000 Wagner pots (plant pots with a cross section of 200 cm<sup>2</sup>) were used. Table 5 lists the properties of the soil put in the pots.

## 4-1 Pot test (in 2013)

Soil origin	Soil type (alluvial soil or diluvium)	рН	Electrical conductivity (dS/m)	Cation exchange capacity (meq/100 g of oven-dry soil)	Specific gravity (g/mL)	Maximum water capacity (g/100 g of oven-dry soil)
Tokushima Prefecture	Alluvial soil	5.7	0.11	17.1	1.18	62.0

Table 5Analysis results of soil

Phosphate	Available phosphate	Exchangeable base (mg/100 g of oven-dry soil)		Available silicic acid	T-N	T-P <sub>2</sub> O <sub>5</sub>	T-K <sub>2</sub> O	
coefficient	(mg/100g of oven-dry soil)	CaO	MgO	K <sub>2</sub> O	(mg/100 g of oven-dry soil)	(%)	(%)	(%)
680	11	325	48	13	9.6	0.18	0.17	0.15

In order to ensure that the effect of the silicic acid and alkalinity can be easily seen in the test, the available silicic acid amount (amount representing the silicic acid that soil can supply to plants) and pH of the soil used for the test were both lower than that of general soil.

The soil described above was put in pots. DM Calcium Silicate was applied to some, Calcium Silicate was applied to others as comparative fertilizer, and no slag was put into the other pots. Paddy rice (Koshihikari) seedlings were planted. Their growth was compared under the same conditions until the harvest of rice ears.

The reference amount of DM Calcium Silicate and Calcium Silicate applied was 120 kg/10 a (approximately 2 g/pot). Two groups were provided for each type of fertilizer in the test: One group for which the reference amount was used and the other group for which the amount applied was double the reference amount. The growth of the rice for the four groups was compared to a group for which no slag was applied (control group). During the growing process, nitrogen, phosphoric acid, and potassium were appropriately applied to all the pots as common fertilizer components required for the growth of paddy rice.

In the test, the weight of harvested paddy rice and the content of silicic acid in the paddy rice were measured to calculate the amount of silicic acid that the paddy rice had absorbed. The stem and ear of the paddy rice were studied separately. The amount of silicic acid absorbed was calculated for the stalks and unhulled rice as typical sections of

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)



the stem and ear for comparison. Figure 3 shows

the actual pot test. Figure 4 shows the test results.

Fig. 3 State of pot test



Fig. 4 Absorption rate of silicic acid (The control group as 100)

When DM Calcium Silicate was applied, the amounts of silicic acid that the stalks and unhulled rice of the paddy rice absorbed increased approximately 10 to 25% from that of the control group. In addition, a similar trend was seen in the comparative fertilizer (Calcium Silicate). Doubling the amount applied did not result in the disturbance of growth.

#### 4-2 Cultivated land test (2013 to 2015)

The cultivated land test of paddy rice was conducted in a test paddy field at Shizuoka University's Faculty of Agriculture. Table 6 shows the analyzed properties of the soil of the paddy field used.

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)

Soil origin	Soil type (alluvial soil or diluvium)	рН	Electrical conductivity (dS/m)	Cation exchange capacity (meq/100 g of oven-dry soil)	Specific gravity (g/mL)	Maximum water capacity (g/100 g of oven-dry soil)
Shizuoka City	Alluvial soil	6.1	0.06	14.8	1.08	61.5

Table 6 Soil analysis results of the paddy field

S

Phosphoric acid absorption coefficient	Available phosphoric acid (mg/100 g of oven-dry soil)	Exchangeable base (mg/100 g of oven-dry soil) CaO MgO K <sub>2</sub> O		Available silicic acid (mg/100 g of oven-dry soil)	T-N (%)	T-P <sub>2</sub> O <sub>5</sub> (%)	T-K2O (%)	
910	6.3	264	38	6.7	20.1	0.21	0.16	2.04

The pH and available silicic acid amount shown in Table 6 were standard values, so general soil was used.

"Koshihikari" was used as the paddy rice variety. In the paddy field test, DM Calcium Silicate equivalent to 120 kg/10 a was applied as the reference amount group and the amount of DM Calcium Silicate was doubled for comparison as the double group as is the case with the pot test described above. The comparative fertilizer (Calcium Silicate) equivalent to 120 kg/10 a was applied as another reference amount group and it was doubled as another double group. Two groups to which no slag was applied were provided (control groups). The paddy field was divided as shown in Fig. 5 (1 section =  $6 \times 5$  m) for comparison. Figure 6 shows the actual paddy field test.



Paddy sluice

Fig. 5 Compartment of the test paddy



Fig. 6 Paddy field test

In the paddy field test, nitrogen, phosphoric acid, and potassium were applied to all the test groups as initial and additional manure based on Shizuoka Prefecture's standards. Regarding crop examination, each test group was further divided into five sections (A to E) as shown in Fig. 7 except the perimeters ( $6 \times 12$  plants per section). Ten plants randomly selected from each section were measured. Figure 8 shows actual harvesting.

Figure 9 compares the weight of unhulled rice and brown rice in the test. When DM Calcium Silicate was applied, the crop increased by 20 to 30% from that of the control group without slag and it was almost equal to that using Calcium Silicate, the comparative fertilizer. In addition, doubling the amount applied did not result in the disturbance of growth.



Fig. 7 Sampling subdivision of each of the test section



Fig. 8 Harvest of the paddy field test



Fig. 9 Weight comparison result unhulled rice and brown rice

Figure 10 compares the amount of silicic acid absorbed by the rice hulls and stalks (total amount) in each test group. The amounts of absorbed silicic acid for the DM Calcium Silicate reference amount group and double group increased by 20 to 50% from that of the control group. The amounts were almost equal to those of the comparative fertilizer (Calcium Silicate). These results show that for the test groups to which DM Calcium Silicate was applied, silicic acid was sufficiently absorbed and thereby the weight increased.



Fig. 10 Absorption rate of silicic acid (The control group as 100)

## **4-3** Food evaluation results of the brown rice

Table 7 shows the harmful element analysis results of the brown rice. As shown in Table 7, the contents of the heavy metals in the brown rice for the DM Calcium Silicate reference group were equal to or lower than the target value. The results are almost the same when compared to the control group. From the above finding, it is evident that DM Calcium Silicate is safe.

Measurement item		Control group	DM Calcium Silicate reference group	Target
Cadmium (Cd)	ppm	0.04	0.05	0.4 or lower
Lead (Pb)	ppm	Not detected	Not detected	
Mercury (Hg)	ppm	Not detected	Not detected	_

Table 8 shows the taste analysis results of the brown rice grains. Amylose, protein, and fatty acid

value in the brown rice were measured. When the eating quality value calculated from these

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)

measurement values is 70 or higher, the rice is judged as having good quality. The value of the brown rice is equal to or higher than that of the control group. From the above finding, it is evident that the quality of the brown rice cultivated using the slag improved from the aspect of taste as well.

Measurement item		Control group	DM Calcium Silicate reference group
Eating quality	Saora	74	76
value	Scole	Average	Comparatively good
Amulaca	0/	19.1	18.9
Amylose	%0	Average	Average
Ductain	0/	7.8	7.6
Protein	%0	Average	Average
Fotty agid value	KOHma/100a	15.1	16.4
Fairy actu value	KOrning/100g	Average	Average

Table 8 Taste analysis of brown rice

As a result of the paddy rice growth comparison test using DM Calcium Silicate at the Japan Fertilizer and Feed Inspection Association and Shizuoka University, it was confirmed that the slag (DM Calcium Silicate) produced from the gasifier is safe and its quality is stable. Based on these results, DM Calcium Silicate from the Nishigaya DMS plant in Shizuoka City was provisionally registered as siliceous fertilizer by the Japanese Ministry of Agriculture, Forestry and Fisheries (provisional registration refers to a situation where fertilizer for which no official specifications have been stipulated in the Japanese Fertilizers Regulation Act is to be registered in accordance with provisional official specifications. Usually, new official specifications are established after a provisional registration period of a few years and then the fertilizer is formally registered). NJ Eco Service (dealer of our slag) received the provisional registration certificate on March 27, 2017.



## Fig. 11 Fertilizer provisional registration certificate

## 5 Projects for Agricultural Sectors Other Than Paddy Rice and for Lawn Grass

DM Calcium Silicate has been confirmed as effective for growing paddy rice. As other projects for turning slag to fertilizer, Nippon Steel & Sumikin Engineering has been working to apply DM Calcium Silicate to golf courses to cultivate lawn grass by drawing on the characteristics of its components (large amounts of soluble silicic acid and alkalinity are contained) and has been working to expand the use to agricultural sectors (the grass family) other than paddy rice. Such projects are described below.

## 5-1 Cultivating golf course lawn grass

Japanese lawn grass belongs to the grass family. Soluble silicic acid is effective for cultivating lawn grass in golf courses (fairways, in particular), so Nippon Steel & Sumikin Engineering has been promoting the use of DM Calcium Silicate as joint soil for lawn grass and the combined use of soil and DM Calcium Silicate as base materials. Nippon Steel & Sumikin Engineering started these projects in 2011. In FY2016, approximately 5,700 tons of DM Calcium Silicate was used in total at 14 golf courses in Japan.



Fig. 12 Golf course turf soil

## 5-2 Cultivating Makomodake

Zizania latifolia or water bamboo (Makomodake) (see Fig. 13) is a perennial of the grass family. A growth comparison test of Makomodake (variety: Aogara) was conducted in the test paddy field at Shizuoka University's Faculty of Agriculture as conducted with the paddy rice.



Fig. 13 The harvested products of Makomodake

Figure 14 shows the test field for comparing the growth of Makomodake. (DM Calcium Silicate was applied to the zones enclosed with red squares.)



Fig. 14 Growth comparison test situation of Makomodake

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)

## **5-3** Cultivating sugar cane

Sugar cane is a plant in the grass family that belongs to the Saccharum genus. A growth comparison test was conducted in Amami Oshima, Kagoshima Prefecture under the supervision of Shizuoka University's Faculty of Agriculture. Figure 15 shows grown sugar cane approximately one year after the planting. The height of the sugar cane in a section to which DM Calcium Silicate was applied is approximately 2.3 m while that in an ordinary section is approximately 2.0 m. The figure shows that there is a difference in the growth.



Fig. 15 Growth comparison test situation of sugar cane

## 6 Conclusion

Through the growth evaluation test of the paddy rice, it was confirmed that our slag (DM Calcium Silicate) works well as fertilizer to cultivate paddy rice. DM Calcium Silicate has been provisionally registered as siliceous fertilizer, which was the first as MSW slag in Japan. Nippon Steel & Sumikin Engineering aims to obtain formal registration of the slag produced from the Nishigaya incineration plant in Shizuoka City in the future and will cooperate with various other local governments to turn our slag into fertilizer in other areas.

The use of slag as fertilizer is expected to contribute to society in new ways such as by improving Japan's food self-sufficiency rate (contribution to food safety) and by increasing  $CO_2$  absorption through the increased growth rate of rice (contribution to the prevention of global warming), in addition to the conventional social contribution of minimizing final landfill sites.

Nippon Steel & Sumikin Engineering will continue working to contribute to the circular economy through technologies of shaft-furnace type gasification and melting furnaces and the development of slag applications.

Finally, we would like to express our deep gratitude to Professor Morita of Shizuoka University's Faculty of Agriculture and Mr. Ikka, an associate processer at the same faculty, for their enormous help in the various growth evaluation tests.

## References

- Japan Fertilizer and Feed Inspection Association: Test of Effects of Slag on Paddy Rice as Fertilizer (2013)
- Akio Morita and Takashi Ikka: Agricultural Research Center, Graduate School, Shizuoka University, Effects of Slag on the Growth of Rice "Koshihikari" (2014)

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)

- Akio Morita and Takashi Ikka: Shizuoka University, Application of Slag for Growing Paddy Rice, Industrial Machinery, 2017.6, No. 801, pp.14-16
- The Japan Society of Industrial Machinery Manufacturers (JSIM): Eco Slag Usage Promotion Committee, Current Situations of Effective Utilization of Eco Slag and Data, FY2016 version, pp.97-99

Nipponsteel & Sumikin Engineering Technical Report Vol. 9 (2018)