Research article

Evaluating Ion Exchange Capacity of Molten Slag for Hydroponic System

ANTONIO PEREZ FUENTES
Graduate School of Agro-Environmental Science, Tokyo University of Agriculture, Tokyo, Japan

SARVESH MASKEY
Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan

HIROMU OKAZAWA*
Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan
Email: h1okazaw@nodai.ac.jp

YURI YAMAZAKI
Faculty of Agriculture, Tottori University, Tottori, Japan

TOMONORI FUJIKAWA
Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan

TOSHIMITSU ASAI
Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan

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Abstract Hydroponic farming promotes high-efficiency water, fertilizers, and high productivity under a controlled environment. However, the use of this system needs consistent application of fertilizers, increasing the cost of operations. Molten Slag (MS), a waste from the Municipal Solid Waste Incineration has essential nutrients that can be used as fertilizer. The objective of this study was to clarify the releasing process of nutrients by molten slag to be applied as a substrate in hydroponic system. For this, anion and cation contents of three varieties of Molten Slag (MS1, MS2, MS3) were determined in the laboratory by a shaking method. The nutrient content, P_2O_5, K_2O, MgO and CaO were in MS1, MS3 and MS2. The quantification ion released was performed at 1, 6, 12 and 24 hours. It was observed that MS3 had performed the best condition in the releasing process of K^+, Mg^+, SO_4^{2-} and Cl^-. Although MS1 had higher nutrient content, MS3 released higher contents of those minerals among the samples. According to the result of this study, it was confirmed that MS3 has a high potential for hydroponic farming.

Keywords molten slag, hydroponic system, ion exchange capacity, releasing nutrients

INTRODUCTION

Around 200 billion tons of fertilizers are produced annually for agricultural purposes (FAOSTAT, 2021). The use of these fertilizers and water supply tends to increase to provide food safety for 9 million people toward 2050. The benefit of fertilizers in agricultural production is remarkable since it improves yields and keeps fertile soil. On the other hand, the constant use of fertilizers not only increase the costs but hazard the ecological balance with releasing of greenhouse gases and eutrophication to water bodies (Sedlacek et al., 2020).

Molten Slag (MS) is a by-product of the Municipal Solid Waste Incineration -MSWI- process (Fig. 1). The process to generate molten slag starts with the addition of wastes inside a furnace, this waste can be paper, plastic, glass, steel, aluminum, food waste/raw garbage, waste oil, among others. After burning most of the organic wastes, the residues are separated as ferrous materials (aluminum, steel, incombustibles), vitreous material and molten slag. The gas generated in those furnaces goes through a chamber for purification and generation of energy, and the fly ash is also collected for future processing. The composition of molten slag varies according to the diverse wastes in every municipality and the type of furnace in which they are processed (Czop and Łaz´niewska-Piekarczyk, 2020). Molten slag shares similarities to the slag generated by the iron and steelmaking process, and they have been tested for correct use as a cement aggregate, road building and for soil correction (Dubey et al., 2019; Zeng et al., 2020; Devnita et al., 2021). Altland, et al. (2015) described the possibility of up taking micro-nutrients from these types of slag and the spontaneous vegetation in landfills where molten slag is storage (Gomes et al., 2016) opens to discussion if the contents of Ca, K, Mg, and Na, from molten slag can be a good source of nutrients for plants. Molten slag collected from MSWI has not been used in agriculture and recent studies (Kobayashi et al., 2004; Sekito et al., 2014) found that there was not leaching of heavy metals in several samples analyzed. As the generation of wastes increases around the world, this study reveals the possibility to release beneficial ions to assess the growth of crops with this material.

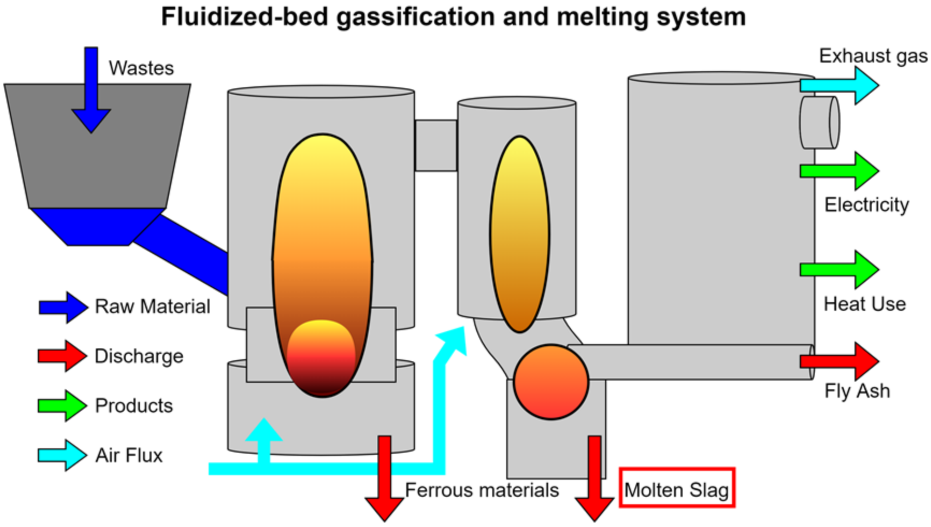

Fig. 1 Municipal solid waste incineration process

OBJECTIVE

The objective of this study was to quantify and record the releasing process of nutrients released and retained by three types of molten slag from the Kanto region in Japan and estimate the availability of those nutrients for crop production under hydroponic conditions.

METHODOLOGY

We collected three types of molten slag from Kofu (MS1), Kamiina (MS2) and Nishi-Akikawa (MS3), the dried content of CaO, MgO, K_2O and P_2O_5 was determined in principle, then the analysis of releasing those minerals was carried out. First, we prepared 10 g of every sample inside a bottle with 50 mL of Ultra-Pure Water and two replicates. The samples were shaken at 180 rpm for 1, 6, 12 and 24 hours. Electrical conductivity (EC), pH and anion/cation contents were measured. Anion and cation contents in the water samples, which were filtered by membrane filter with a diameter of 0.45 μm, were measured by a spectrometric method using Ion analyzer (IA-300, HORIBA). Only seven ions were involved in the discussion, considering plant growth, and the concentration is given in mg/L. ANOVA and T-test were applied to find any significant difference among the samples.

RESULTS AND DISCUSSION

Chemical Properties of Molten Slag

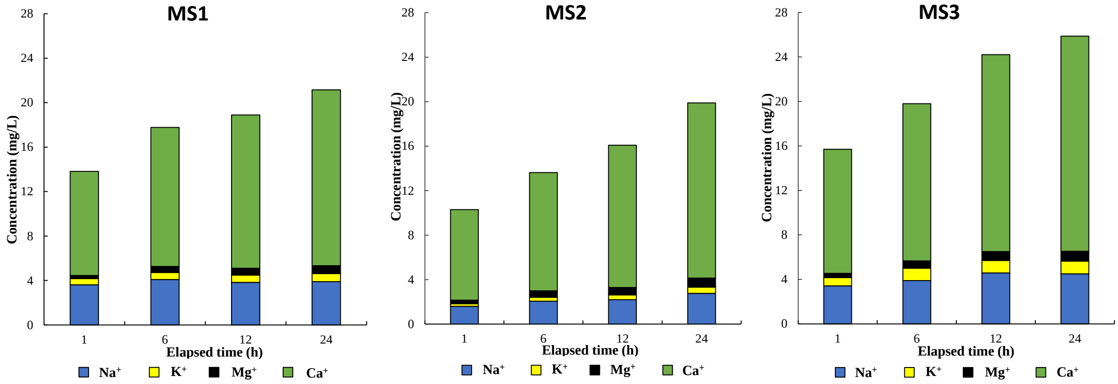

Fig. 2 Amount of cation released by every type of slag along 1, 6, 12 and 24 hours of shaking treatment

Table 1 Chemical properties of three varieties of molten slag

	Per Wind Dried Material				Per Dried Material								
	pH	EC	CEC	Bulk density	NH_4-N	Inorg. N	P_2O_5	K_2O	MgO	CaO	Zn	Cu	Fe
Units		mS/cm	meq/100g	kg/m^3	mg/100g	mg/100g	mg/100g	mg/100g	mg/100g	mg/100g	mg/kg	mg/kg	mg/kg
MS1	7.17	0.04	ND	1.58	0.6	0.6	21	2.6	8.6	142	48	208	34.7
MS2	7.78	0.04	ND	1.59	0.9	0.9	12	1.6	6.2	42	34	106	12.9
MS3	7.84	0.06	0.1	1.51	0.6	0.6	7	2.2	5.3	103	102	182	40.7

Obtained by dry method in Katakura Co Op Agri Labs *ND: Not Detected*

MS1 has higher content of P_2O_5, K_2O, MgO, CaO, and Cu as shown in Table 1. On the other hand, MS2 has the lowest nutrient content in all aspects, except for P_2O_5 and MgO, including the highest density.

Releasing of Cations by Molten Slag

During the test, pH values did not raise levels higher than nine, but this value is still considered high for crop development. It was expected that MS1 would have the largest EC due to the significant amounts of CaO, MgO and K_2O, however, after 24 hours none of those ions tend to increase in this material. The leachate of calcium explains the peak values observed at 6 hours of shaking into the water, producing carbonation's reaction (Huntzinger et al., 2009).

K^+ plays a significant role in many synthetic, physiological and biochemical processes in plants. This element is present in the soil in low concentrations, from 0.2% to 3.3% of the total soil mass (Barker and Pilbeam 2015). Although a low value of K^+ was found in this releasing process of molten slag, the concentrations in the dried material are acceptable. The range goes from 0.0011 to 0.0028 mg/g in MS2 and from 0.0037 to 0.0057 mg/g in MS3. At least 16%, 21% and 31% were released from the MS1, MS2 and MS3, respectively. MS3 is the most suitable supplying more K^+ into the water.

Even though MS1 has more significant amounts of MgO than MS3, it was observed that the percentage of Mg^+ released by MS1 is lower compared to MS3, producing almost the double amount of Mg^+ released in the same period. In comparison, MS2 has around 0.062 mg/g and released 0.0068 mg/g. It is only about 10% of MgO.

For the efficient process to obtain better gas in the incineration process, calcium oxide is added to clean the impurities (Zheng et al., 2018), this component remains in the slag and becomes the most abundant next to the silicates. MS1 was the material with the highest content in many compounds, having values of Ca^{2+} superior to 1.4 mg/g; moreover, after 24 hours in the shaking process, it was determined that the values of the Ca^{2+} released are still low compared to 26% released from the MS2. Calcium is not an essential nutrient for plants, but it is a requirement. An excessive amount of Ca^{2+} can result in plants toxicity. Plants can allocate around 100 mg/g per dry matter (Römheld, 2012; White and Brown, 2010). When the delivery of Ca^{2+} to the soil exceeds the plant's uptake capacity, there is a risk of accumulation of Ca^{2+} at the surface of the roots and most of the time to the precipitation as $CaCO_3$, $CaSO_4$, or Ca oxalate in rhizocylinders around the roots induced by P deficiency (Newman and Römheld, 1998; Marschner and Rengel, 2012). Ca^{2+} released by MS3 ranges between 7.5 and 13%, meanwhile in MS1 and MS2, it goes from 4.6 to 7.7% and from 13.5 until 26%, respectively.

The primary function of Na^+ seems to be to maintain osmolality in the plant tissues of the halophyte seepweed under NaCl conditions (Mori et al., 2010). However, Na^+ is not considered a nutrient for most plant species. Subbarao et al. (1999) showed that it could be a substitute for potassium in *Beta sp*. to a large extent and, it has been accepted as a micronutrient in some C4 plants that require Na^+ for cotransport. Although Na^+ values were not obtained in the dried content analysis of the samples, it was observed that there was a leaching of sodium along with the shaking test, there was not a variation among the shaking period, but there is a significant difference among the three samples. Assuming that the contents of sodium in MS2 are also lower than the following two samples as occur for the minerals, this is the reason why this sample had the lowest trend, as observed in Fig. 2. High Na/Ca ratios may lead to a deficiency of Ca^{2+} in Sodic or saline soils due to the excess of Na^+ in the soils (White, 2015) that's why it is important to consider that ratios of Na/Ca are also balanced. The ratio of Na/Ca of Molten slag goes from 0.03 to 0.05 in all the samples with contents from 0.020 mg/g in MS1, 0.011 mg/g in MS2 and 0.022 mg/g in MS3.

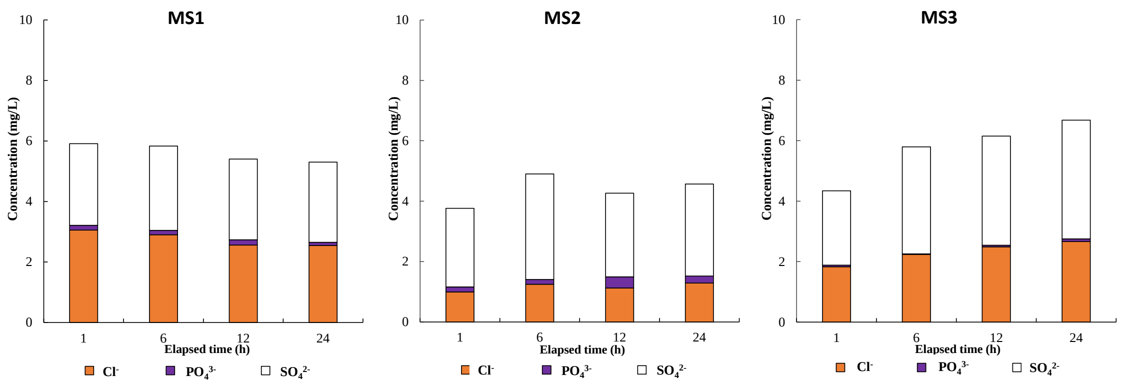

Fig. 3 Anion released by every type of slag along 1, 6, 12 and 24 hours

Anion Concentration

From the three samples analyzed in this study, only MS2 showed a small fraction of PO_4^{2-} released; it is possible to say that 0.3 mg of PO_4^{2-} are available in the water to be taken by the plants from this material. The range of PO_4^{2-} in MS2 goes from 0.0008 mg/g to 0.0018 and finally to 0.0012 mg along the treatment. Only MS2 could perform this condition from the three samples since MS1 and MS3 didn't show great changes during the same period.

SO_4^{2-} is an important nutrient that acts as a major structural component of proteins, also participates in several processes like photosynthesis, N_2 fixation, chlorophyll production, and catalytic activities of many enzymes (Mills and Jones, 1996; Hawkesford, 2010). An unbalanced application of N fertilizers with low or lack of sulfur can indicate the plant's sulfur deficiency. In principle, the samples of molten slag released around 0.013 mg/g of SO_4^{2-} at the first hour, but after 24 hours, it was only MS3 which increased to 0.019 mg/g. Since the molten slag can't provide nitrogen such as NH_4^+ or NO_3^-, the sufficiency of sulfates in agricultural systems will be directly related to the content from an external nitrogen source. Although molten slag can provide few SO_4^{2-} to crops systems, this quantity is not enough to accomplish the plant requirements.

Cl^- concentrations up to 500 mg/L have been supplied in sweet onion and demonstrated that the requirement of chlorides is only exceeded by N, P and K (Randle, 2005). Furthermore, the concentration observed in the releasing process from the three types of molten slag doesn't exceed more than 3 mg/L by 200 g of MS. Therefore, this amount of Cl^- found doesn't represent a hazard for crop growth but enriches the micronutrients uptake by plants in the water content.

It was observed that MS1 is the material with the highest content of nutrients per dried soil. This condition does not guarantee that the releasing amounts of nutrients from molten slag is related to the mineral content in every type. Although MS2 does not have great amounts of nutrients, it was observed that EC increased due to high amounts of Ca^{2+} released.

CONCLUSION

In this study, three varieties of molten slag under releasing treatment of nutrients for crop system proved a remarkable difference among the quantities of nutrients released by every type of slag analyzed. MS3 had performed the highest amounts of nutrients released by g of sample, finding that the percentage of K^+ available for plants is higher in MS3 than MS1 and MS2. Even when the content of Ca^{2+} is lower in MS2, the final concentration in the water was higher than the following two samples, which can increase pH levels due to the chemical reactions of Ca^{2+} when it contacts water. It was indeed MS3 that released more Mg^+ ions into the water and SO_4^{2-} that can make a difference in plant nutrition. Certainly, PO_4^{2-} is one of the major important anions for crop development yet low concentrations were found in this experiment: therefore, deep analysis and a different methodology should be considered to set the availability of this nutrient in crop systems. It is expected that MS3 will perform better plant growth as it promises essential nutrients for plant development. Since the melting furnace is feed by same type of raw material, a comprehensive study will be focused on the differences of every of system combined with analysis switching sampling periods to confirm the releasing process.

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