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Economical synthesis of complex silicon fertilizer by unique technology using loess

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Abstract–Loess processed material (LPM) was produced as a substitute for silicon, clay and minerals, and applied to tomato and cucumber cultivation. LPM was produced by using a NaOH addition ratio of 30%, a reaction temperature of 1,200 °C, a reaction time of 1 h, and an alumina ball diameter of 10 mm. Treatment with a 200-fold diluted LPM solution resulted in respective increase of 7.8% and 8.3% in the weight and quantity of the tomato fruit, and a 31.7% increase in the quantity of cucumber fruit produced, when compared to the control. On the other hand, commercial silicon fertilizer (CSF), with a price that is estimated to be four times that of LPM, did not significantly increase the yield of tomato or cucumber in terms of weight or quantity. Thus, it is suggested that LPM may be used as a potential complex silicon fertilizer.

Keywords: Economical Synthesis, Loess, Loess Processed Material, Production Conditions, Silicon Fertilizer

INTRODUCTION

Silicon is a major component of soil that is also present in all kinds of plants. Silicon reportedly affects the reproductive growth of the tomato plant [1], whereas the growth response to silicon deficiency in the cucumber plant is characterized by abnormalities in newly developed leaves at the flowering stage and a reduction in pollen fertility [2]. The rice plant is a representative silicon-absorbing plant. It is known that resistance to lodging, disease, pests, and insects increases with an increase in the photosynthetic performance of rice plants. This improved performance is a consequence of improved light reception resulting from adequate silicon absorption [3]. In cases of silicon depletion in rice, necrosis, wilting and decreases in crop yields have been observed [4]. Furthermore, the use of silicon-containing fertilizer is known to increase the soil pH, improve the decomposition of organic materials, increase the nutrient-supplying power of soil, and decrease nitrogen leaching by increasing the efficiency of nitrogen use [5,6]. Many studies have suggested that silicon exerts positive effects on plant growth, including an increase in dry mass and yield, enhanced pollination, and most commonly, an increase in disease resistance [7-11]. Loess refers to soil altered by the weathering of stone, and comprises SiO_2 (40%-60%), Al_2O_3 (10%-30%), and Fe_2O_3 (5%-8%) as the main components, and CaO, MgO, K_2O, Na_2O, TiO_2, and P_2O_5 (all of which are trace elements) as accessory components. Loess covers about 10% of the earth's surface, and is broadly distributed in semi-arid areas within temperate and dry zones. Mainstream loess in Korea refers to soil that has been altered by the weathering of stone such as granite, diorite, quartz porphyry, porphyry, and alum stone [12]. Clay minerals such as vermiculite, chlorite, illite, kaolin, and ferrihydrite in agricultural fields interact with cells, viruses, enzymes, and organic and inorganic nutrients in the soil. Clay also has various physicochemical properties such as the ability to adsorb materials, to act as an elution medium, and to fix various components of soil, in addition to pH buffering and air/water permeability that give rise to a variety of functions. These functions include resistance of organics to microbial attack, interaction with toxic substances, and effects on the activity, ecology, and population dynamics of microorganisms in soil [13-19]. Soluble silicates such as sodium silicate and potassium silicate (Na_2SiO_3 and K_2SiO_3, respectively), are a major class of chemicals, with a wide range of applications in a number of different industrial sectors. Generally, soluble silicates are classified as safe low-risk chemicals that also have regulatory approval for many applications. The largest quantities of soluble silicates are used in the production of detergents, soaps, and cleaners, followed by pulp and paper applications, water treatment, soil stabilization, and coatings [20,21]. Recently, Na_2SiO_3 has found widespread application as a silicon source in agricultural fields. However, because it is prepared using pure silica sand, application of Na_2SiO_3 in agriculture is hampered by the requirement for addition of other minerals. In this study, LPM was produced as a substitute for silicon, as well as clay and minerals. The objectives of this study were to (1) determine the production conditions and cost of LPM derived from loess, and (2) investigate the effect of its appli-

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Table 1. Chemical compositions of loess and LPM

Component	Loess (%)	LPM (%)
SiO_2	37.1	30.1
Al_2O_3	32.1	19.0
Fe_2O_3	13.4	7.47
CaO	0.02	0.95
MgO	0.75	0.73
K_2O	1.95	1.30
Na_2O	0.21	25.6
TiO_2	1.28	0.94
Other	13.19	13.91

cation on tomato and cucumber cultivation.

MATERIALS AND METHODS

1. Materials

Loess (particle size <3 mm) was purchased from Boryung Hwangto Company (Hongseong, Korea). The chemical composition of loess, as determined by inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer DV 3300, USA), is presented in Table 1. NaOH was purchased from DAEJUNG CHEMICALS & METALS Co., Ltd., (Korea). All chemicals used were of analytical grade.

2. Reaction Conditions for the Production of LPM Containing Available SiO_2 from Loess

Loess and NaOH were mixed together and placed in a 1 L alumina crucible. The reaction was in an electric furnace (Ajeon Heating Industrial Co., Korea). The optimal conditions for the reaction of loess and NaOH were determined by varying the reaction temperature (600 °C, 800 °C, 1,000 °C, 1,200 °C, and 1,400 °C), reaction time (1 h, 2 h, 3 h, and 4 h), and concentration of NaOH (20%, 30%, and 40%). The reaction product (LPM) was cooled for one day at room temperature and then crushed using a hammer mill (Korea Pulverizing Machinery Co, Ltd., Korea) and a ball mill (Daihan Scientific Co. Ltd., Korea). LPM particles (<75 μm) were recovered using standard mesh (Chunggyesanggongsa Co., Ltd., Korea), and the yield of available SiO_2 was calculated.

3. Wet Ball Milling Conditions for the Extraction of Available SiO_2 from LPM

LPM was crushed to a particle size of <3 mm using a hammer mill, and subsequently used in the wet ball milling experiments. The rotation speed of the zirconia ball mill (18 cm inner diameter and 22 cm in height) was maintained at 300 rpm for ten days after addition of the alumina balls (0.5 kg), crushed LPM (0.5 kg), and water (0.5 kg). The effect of the size of alumina ball on the extraction of available SiO_2 from LPM was determined from the calculated yields obtained with different alumina ball sizes (1 mm, 5 mm, 10 mm, and 20 mm).

4. Plant Materials and Treatments

Field experiments were conducted on an experimental farm at Dongguk University (Siksadong, Ilsan, Gyeonggi-do, Korea) for 60 days (from May to July 2014). The experimental design used was the randomized complete block design, with three replications. Select chemical properties of the soil are summarized in Table 2. The ambient temperature was between 16 and 25 °C and the relative humidity was between 64% and 76%. The treatment applied to the soil used for the production of tomato and cucumber plants involved the use of LPM generated by ball milling at 0.88 kg N/100 m^2 in conjunction with compost (100 kg/100 m^2), and 12 plots, each measuring 1.8×2.4 m (area=4.32 m^2), were used in the tomato and cucumber growth experiment. Each plot was separated by furrows to avoid any fertilizer drift. Six seedlings per plot were transplanted on May 23, 2014. Commercially available hybrids Shin Heuk Su F1 and AsiaUnchun F1 (Asia seed Co. Ltd, Seoul, Korea) were used as tomato and cucumber cultivar. The transplanted tomato and cucumber seedlings were treated with diluted solutions of LPM (×200, ×1000) and CSF (×1000), every two weeks. Seedlings with no treatment were used as the control group. The undiluted LPM comprised 30 wt% solid content and 9 wt% of available SiO_2. CSF contained 22 wt% of available SiO_2, with 12 wt% alkaline content, 0.05 wt% of available boron, and 0.0005 wt% of available molybdenum.

5. Analytical Methods

The chemical compositions of loess and LPM were analyzed using ICP-OES (Perkin Elmer DV 3300, USA) according to the KS L-4007 Method in Korea [22]. The available SiO_2 was analyzed at an absorbance of 700 nm using the 1 N NaOAc (pH 4.0) buffering extraction method [23]. Growth of the tomato and cucumber cultivars was analyzed in accordance with the standard method of agricultural research [24]. The soil properties were analyzed in accordance with the Method of Soil Chemical Analysis in Korea as follows [25]: the pH was measured with a pH meter at a soil-water ratio of 1 : 5. Organic matter was analyzed by the Tyurin method, and available P_2O_5 was analyzed by the Lancaster method. Exchangeable cations such as K, Ca, and Mg were analyzed by ICP-OES after buffer extraction with 1 N NH_4OAc (pH 7.0). The total nitrogen was determined by the Kjeldahl method after sulfuric acid digestion.

6. Statistical Analysis

The plant growth data were subjected to ANOVA split-plot design, and the statistical significance was compared by using Duncan's multiple range test (p=0.05) using the statistical software SPSS (ver. 21, IBM Corp., USA). All data are presented as ±standard errors

Table 2. Chemical properties of the soil before transplanting seedlings

pH	EC (dS/m)	OM (g/kg)	Available P_2O_5 (mg/kg)	T-N (%)	Available SiO_2 (mg/kg)	Exchangeable cation ($cmol^+$/kg)		
						K	Ca	Mg
7.4	1.57	6	257	0.070	260	0.59	8.5	3.3

EC=electric conductivity, OM=organic matter, T-N=total nitrogen of the mean (SEM).

RESULTS AND DISCUSSION

1. Characterization of LPM

LPM was produced by the wet milling process involving the reaction of a mixture of loess and sodium hydroxide (NaOH) heated in an electric furnace. When loess and NaOH react at 1,200 °C, the SiO_2 component in loess is converted to Na_2SiO_3, as illustrated in Eq. (1):

$$SiO_2+2NaOH \rightarrow Na_2SiO_3+H_2O\uparrow \quad (1)$$

Fig. 1 presents a schematic reaction diagram for the production of LPM from loess and NaOH. The LPM is generated as a slurry containing loess-removing SiO_2, Na_2SiO_3, and minerals. The slurry separates into a solid part containing loess-removing SiO_2, and a liquid part containing Na_2SiO_3 and minerals. The residual SiO_2 content in loess-removing SiO_2 is about 10% of the total SiO_2 content, because the maximum extraction yield (EY) was 90.7% (Table 3). Table 1 shows the analytically determined mineral components of loess and LPM. The SiO_2 content was 37% for loess and 30.1% for LPM. The increased level of Na_2O in LPM was attributed to the addition of NaOH to the reaction.

2. Reaction Conditions for the Production of LPM Containing Available SiO_2 from Loess

The two types of production yields [from Eq. (1)], Y_1 and Y_2, were calculated from Eqs. (2) and (3):

$$Y_1\ (\%)=S/S_0\times 100 \quad (2)$$

$$Y_2\ (\%)=S/R_0\times 100 \quad (3)$$

where Y_1 is the available SiO_2 yield for Na_2SiO_3 in LPM, Y_2 is the available SiO_2 yield for added NaOH, S is the SiO_2 content of Na_2SiO_3 in LPM, S_0 is the SiO_2 content in the added loess, and R_0 is the added NaOH content. The effect of the NaOH addition ratio on Y_1 and Y_2 was investigated for NaOH addition ratios ranging from 20% to 40%. As shown in Fig. 2(a), Y_1 increased from 10% to 80% with an increase in the NaOH addition ratio from 20% to 40%. From Eq. (1), the theoretical value of Y_1 was 100%. The difference between the experimental and theoretical yield for Y_1 is attributed to incomplete dissolution of Na_2SiO_3 in the LPM. LPM was pro-

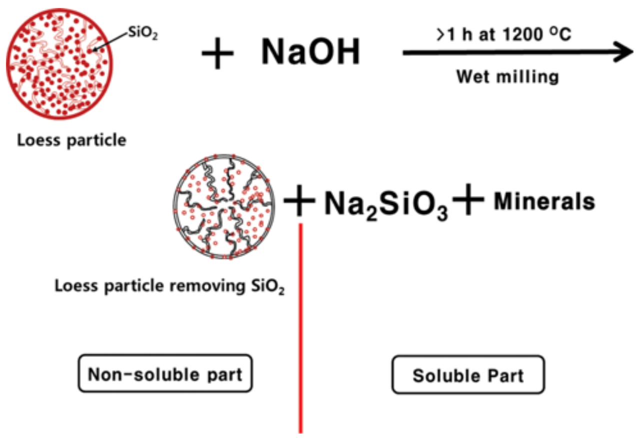

Fig. 1. Schematic of reaction for the production of LPM from loess.

Table 3. Effect of alumina ball diameter on the extraction of available SiO_2 from LPM in wet ball milling

Item	Ball diameter (mm)			
	1	5	10	20
Input of LPM (g)	500	500	500	500
SiO_2 content of input (%)	30.10	30.10	30.10	30.10
Input amount of SiO_2 (g)	150.5	150.5	150.5	150.5
Output of product (g)	122.3	389.5	532.2	532.7
SiO_2 content of output (%)	30.54	29.84	25.47	22.04
Output amount of SiO_2 (g)	37.35	116.23	135.55	117.41
EY (%)	24.82	77.23	90.07	78.01

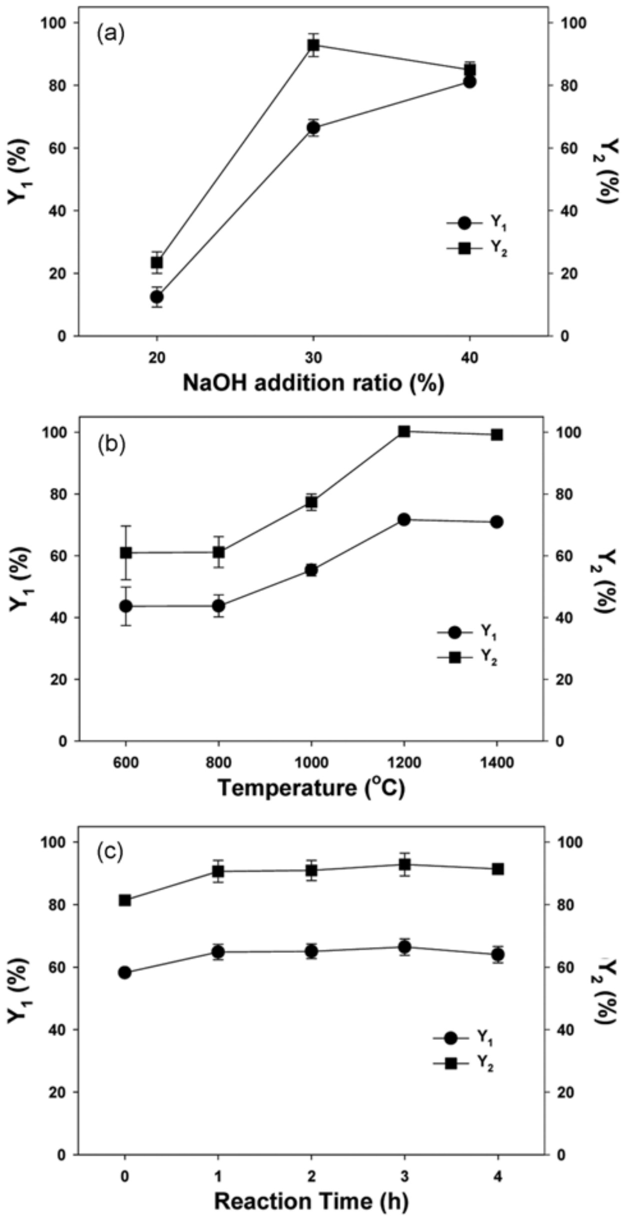

Fig. 2. Effect of reaction conditions on yields: (a) NaOH addition ratio, (b) reaction temperature, and (c) reaction time.

duced from the extraction experiment using a <75 μm mesh to control the particle size. Y_2 increased from 21% to 90% with an increase in the NaOH addition ratio from 20% to 30%, but subsequently decreased to 83% with a further increase in the NaOH addition ratio to 40%. This result is consistent with the theoretical NaOH addition ratio of 33.0% determined using Eq. (1) given that 1 mol of SiO_2 reacts with 2 mol of NaOH, and the SiO_2 content of the loess used in the study was 37%. The theoretical yield for Y_2 was calculated to be 75% [from Eq. (1)]. The difference between the experimental and theoretical yield for Y_2 is derived from the reaction of various other minerals in loess (such as Ca, Mg, and K) with NaOH. The effect of temperature on Y_1 and Y_2 was investigated in the range of 600 to 1,400 °C. As shown in Fig. 2(b), Y_1 increased from 67% to 100% and Y_2 increased from 39% to 72%, with increasing temperature. However, there was no further increase in Y_1 and Y_2 when the temperature exceeded 1,200 °C. This result indicates that the optimal reaction temperature for the conversion of SiO_2 to Na_2SiO_3 is 1,200 °C. The effect of the reaction time on Y_1 and Y_2 was investigated at times ranging from 0 to 4 h at 1,200 °C. As shown in Fig. 2(c), Y_1 and Y_2 increased from 58% to 65% and 80% to 92%, respectively, with increasing reaction time. However, Y_1 and Y_2 did not increase any further when the reaction time exceeded 1 h. This result indicates that a reaction time of 1 h is sufficient for the conversion of SiO_2 to Na_2SiO_3 at 1,200 °C when the NaOH addition ratio is 30%.

3. Wet Ball Milling Conditions for the Extraction of Available SiO_2 from LPM

The effect of the size of alumina ball on the extraction of available SiO_2 from LPM was investigated in the wet ball milling process. Available SiO_2 was extracted from LPM by using a wet ball mill equipped with different alumina balls.

The extraction yield was calculated using Eq. (4):

$$EY\ (\%) = OS/IS \times 100 \tag{4}$$

where EY is the extraction yield of available SiO_2 from LPM, and OS and IS are the output and input of SiO_2, respectively. As shown in Table 3, EY increased with an increase in the diameter of the alumina ball up to 10 mm. However, the use of balls with a diameter of 20 mm caused a decline in EY to 78.01%. These results demonstrate that the EY is affected by the surface area and the collision force of the ball. An increase in the weight of the ball causes EY to increase as a result of an increase in the collision force on the LPM particles. However, with a ball diameter of 20 mm, the effect derived from the increased surface area of the ball exceeds that derived from the increased collision force, resulting in a decrease in EY. Therefore, a ball diameter of 10 mm was optimal for maximizing EY in the wet ball milling process.

4. Effect of LPM Application on the Cultivation of Tomato and Cucumber

The effect of LPM application on the cultivation of tomato and cucumber was investigated by evaluating the length and width of the leaves, in addition to the length, diameter, weight, and quantity of fruit. The efficacy of tomato and cucumber growth was analyzed by comparing the control group (not treated LPM), to

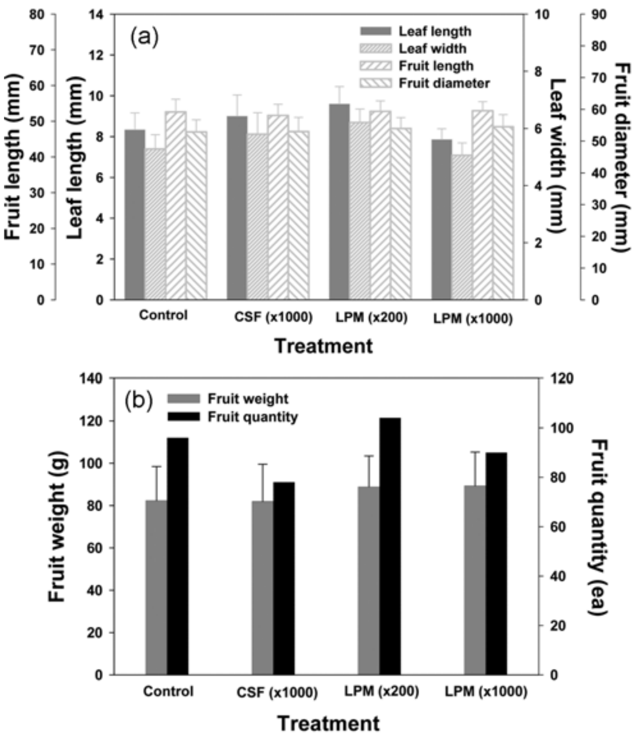

Fig. 3. Effect of LPM and CSF treatments on the growth of tomato: (a) Leaf length, leaf width, fruit width, and fruit diameter; (b) fruit weight and quantity.

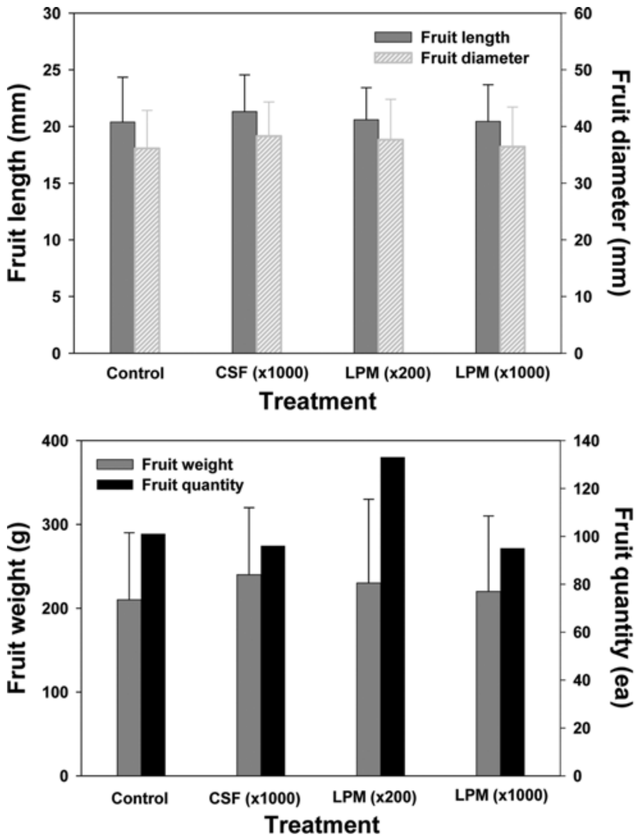

Fig. 4. Effect of LPM and CSF treatments on the growth of cucumber: (a) Fruit length and diameter, (b) fruit weight and quantity.

the plants treated with 200-fold diluted LPM, 1000-fold diluted LPM, and 1000-fold diluted CSF. As shown in Fig. 3(a), treatment with LPM and CSF did not significantly increase the length and width of the tomato leaves and fruit. However, treatment with 200-fold diluted LPM solution increased the weight of the tomato fruit by 7.8% and the quantity by 8.3% as shown in Fig. 3(b). Treatment with LPM and CSF did not significantly increase the length and width of the cucumber fruit as shown in Fig. 4(a). In addition, treatment with LPM did not significantly increase the weight of the cucumber fruit, whereas the quantity noticeably increased by 31.7%, when compared to the control, as shown in Fig. 4(b). CSF did not significantly increase the weight and quantity of the tomato and cucumber fruit as shown in Fig. 3(b) and 4(b), respectively. This is considered to be due to a shortage of various minerals. It was previously reported [1,2] that silicon affects the reproductive growth of the tomato plant and promotes the growth and yield of cucumber plants. Here, we supplemented various minerals with silicon.

The results achieved with the application of LPM compare favorably with previously reported results. The supply of soluble materials such as silicon and minerals in LPM can increase the extent of microorganisms and enzyme activity in cultivated soil, and the loess-particle removing SiO_2 in LPM can also increase the amount of adsorption of microorganisms, soil enzymes, and fertilizer components such as nitrogen, phosphorous, potassium, calcium, and magnesium [26]. Overall, it is suggested that LPM may be used as a potential complex silicon agent in agriculture.

5. Estimated Production Cost of LPM

The estimated production cost of LPM from loess is shown in Table 4. The LPM production capacity was assumed to be 1,000 ton/yr, based on a solid content of 30% in the slurry. The consumption of loess and NaOH is estimated to be 260 and 78 ton/yr, respectively. The respective prices of loess and NaOH are estimated at $50/ton and $0.67/kg. The unit prices will decrease with increases in purchase quantities. Melting and crushing can be carried out continuously with the use of a continuous melting furnace. The cost of a continuous melting furnace with a capacity of 1 ton/d is estimated at $400,000. The energy consumption of the furnace is approximately 4.6 kcal/kg when using natural gas, and can be reduced with an increase in scale. The time required for the production of one batch of ball milled product is about 5 d. The size of the ball mill is about 27.7 m^3, and based on a working volume of 50%, a production of 16.67 ton/batch, a specific gravity of 1.205 for LPM (30% solid content), and a production output of 60 batches/yr, the calculations are as follows:

$$300 \text{ d/yr} \times 1 \text{ batch}/5 \text{ d} = 60 \text{ batches/yr} \tag{5}$$

$$1{,}000 \text{ ton/yr} \times (1 \text{ yr}/60 \text{ batches}) = 16.67 \text{ ton/batch} \tag{6}$$

$$16.67 \text{ ton}/(1.205\times0.5) \fallingdotseq 27.7 \text{ m}^3 \tag{7}$$

The price of a 30 m^3 ball mill is assumed to be $90,000. It may be more cost effective to repair the interior of a used ball mill than to purchase a new one, due to the high cost of external steel plates. The calculated total production cost per kg of LPM is $0.6404, including other costs such as utilities, labor, depreciation, maintenance, building rent, packaging containers, and profit markup of 20% (Table 4). The current price of CSF (commercial silicon fertilizer) is about $13.3333/kg. The price of LPM is 25% that of CSF, although the amount of LPM used is assumed to be five-times more than that of CSF. An increase in production capacity will further reduce the price of LPM.

CONCLUSIONS

LPM as a complex silicon fertilizer was produced from loess and applied to the cultivation of tomato and cucumber. LPM pro-

Table 4. Estimated production cost of LPM (1,000 ton/yr, based on a solid content of 30% in the slurry)

Item		Cost/year ($)	Cost/kg ($)	Remarks (description of cost calculation)
Raw materials	Loess	13,000	0.0130	260 ton x $50/ton
	Sodium hydroxide	52,260	0.0523	78,000 kg x $0.67/kg
Utility	Electricity	3,600	0.0036	240 kw/d x 300 d x $0.05/kw
	Natural gas	103.5	0.0001	4.6 kcal/kg x 300,000 kg x $0.075/1000 kcal
	Water	177.6	0.0002	600 ton x $0.296/ton
Labor	Manager	41,667	0.0417	1 x $41,667
	Operator	100,000	0.1000	3 x $33,333
	Lab technician	25,000	0.0250	1 x $25,000
	Sales	33,333	0.0333	1 x $33,333
Misc.	Maintenance	65,500	0.0300	About 10% (repair+transport+others)
	Building rent	25,000	0.0250	Floor space: 330 m^2
	Packing container	125,000	0.1250	50,000 ea x $2.5
Depreciation	Equipment	49,000	0.0490	$490,000/10 yr - Continuous furnace and crusher: $400,000 - Ball mill (10$m^3$x3): $90,000
Total		533,641	0.5336	
Profit		106,728	0.1067	20%
Factory price		640,369	0.6404	

duced from the reaction of loess and NaOH in a furnace at a temperature of 1,200 °C, contains loess-removing SiO_2, Na_2SiO_3, and minerals. The optimal conditions for LPM were as follows: NaOH addition ratio of 30%, reaction temperature of 1,200 °C, and a reaction time of 1 h. The extraction yield of available SiO_2 from LPM, using the wet ball milling process with a 10 mm (diameter) alumina ball, was 90.07%. The effect of LPM treatment on tomato and cucumber fruit was excellent, resulting in a percentage increase in quantity of 8.3% for tomato and 31.7% for cucumber. In contrast, CSF did not significantly increase the quantity of either type of fruit. The estimated cost for the production of LPM was 25% that of CSF, although the amount of LPM required is assumed to be five-times more than that of CSF. An increase in production capacity will further reduce the price of LPM. Therefore, LPM may be practically applied as a complex silicon fertilizer. However, further work is required to evaluate the efficacy of LPM in the production of crops and to investigate the production cost in greater detail.

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NOMENCLATURE

Y_1	: available SiO_2 yield for Na_2SiO_3 in LPM [%]
Y_2	: available SiO_2 yield for added NaOH content [%]
S	: SiO_2 content of Na_2SiO_3 in LPM
S_0	: SiO_2 content in the added loess
R_0	: added NaOH content
EY	: extraction yield of available SiO_2 from LPM [%]
OS	: output amount of SiO_2
IS	: input amount of SiO_2

Abbreviation

LPM	: loess processed material
CSF	: commercial silicate fertilizer
×200	: 200-fold diluted solution
×1000	: 1000-fold diluted solution
EC	: electric conductivity
OM	: organic matter
T-N	: total nitrogen

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