Evaluation of Candidate Silicon Fertilizers

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ABSTRACT

Silicon (Si) fertilization for rice (*Oryza sativa* L.) and sugarcane (*Saccharum officinarum* L.) production on organic and sandy soils in south Florida has become routine. It has given rise to an interest among growers in finding suitable Si fertilizers in addition to the currently used sources of calcium silicate ($CaSiO_3$). A laboratory procedure has been developed for identifying candidate Si fertilizers (potential Si sources) based on Si dissolution in tris hydroxymethyl aminomethane (TRIS) buffered water (pH = 7) over a 48-h period. It was found that there is good correlation between mineral Si sources with adequate amounts of $CaSiO_3$ and Si uptake in rice straw. Similar Si sources also demonstrate a classic first order leaching reaction. Therefore, the lab procedure can identify suitable Si sources for further testing after the second leaching day due to its first order predictability.

INTRODUCTION

Fertilization with Si is widely used for rice and sugarcane on the organic soils of the Everglades Agricultural Area in south Florida and on adjacent sandy soils. The principal Si source is $CaSiO_3$ from the electric furnace production of P (Tisdale and Nelson, 1975). This material is sparingly soluble, and provides plant-available Si to long-season crops such as sugarcane and to several crops in a rotation over several years (Anderson et al., 1987). Growers are interested in determining the suitability of various sources of this and other mineral Si products as Si fertilizers, and various suppliers have products to offer as Si fertilizers. Field testing of candidate Si fertilizers (potential Si sources) provides the most definitive evaluation of the sources. However, field testing is expensive and time consuming. A relatively quick and inexpensive laboratory test is needed to screen candidate materials to identify the ones with enough promise to warrant field testing.

Various methods have been proposed for evaluating candidate Si fertilizers. In Japan, solubility in water, 0.5 M HCl, or in pH 4.0 acetate buffer have been used (Takahashi, 1981; Kato and Owa, 1997). However, several Japanese researchers have determined that these reagents poorly define the Si-release potential of calcium silicates in soil. Kato and Owa (1997) pointed out that unsatisfactory results occur because the methods do not simulate reactions that occur in the soil. When $CaSiO_3$ is placed in water or acid, an increase in pH and dissolution of Ca occurs. Both repress further dissolution of $CaSiO_3$. In the soil, however, pH change is buff-

ered and Ca is absorbed by the growing plants, both of which favor additional dissolution.

We have developed a quick and simple method for evaluating candidate Si fertilizers which considers the points made by Kato and Owa (1997). Buffered water is passed through a stationary layer of candidate Si fertilizer. By doing so, the material is subjected neither to a gradual increase in pH nor to an environment of increasing Ca concentration. The total quantity of Si dissolved in this manner over a 24-h period is used to identify materials with potential for being Si fertilizers. Silicon dissolution is quantified for a second 24-h to identify materials that are highly soluble, such as $Na_2SiO_3 \cdot 9H_2O$, and which might be exhausted excessively rapidly in the field. The laboratory procedure is not designed to rank similar Si fertilizers, but rather to separate those that are worthy of consideration for field testing from those that are unlikely to be useful Si fertilizers. It was developed for mineral Si sources and may not be suitable for organic sources such as rice hulls.

For purposes of verifying the laboratory procedure, a comparison between the laboratory results of several candidate Si fertilizers submitted to our laboratory and Si uptake by rice in the greenhouse is reported herein.

METHODS AND MATERIALS

Laboratory Procedure

Five slag materials containing Si were used in the comparison study between the laboratory procedure and the greenhouse study. Another group of three Si-containing slag materials was used in the extended 10 d laboratory procedure.

Duplicate 3-g samples of each slag material were mixed with 5 g of medium density polyethylene (Sigma-Aldrich, # 33,211-9, St. Louis, MO) and placed in a 20 mL plastic syringe. Glass wool above and below the mix was used to retain the mixture in the center of the syringe.

A stopper fitted with Tygon tubing was inserted in place of the syringe plunger. A peristaltic pump was used to pass 0.1M TRIS buffer (pH 7) upward through the syringe at the rate of 1 mL min⁻¹. As this process occurs, the candidate fertilizer leaches Si into solution. The buffer solution then passed out the top of the syringe into a collection bottle. The total quantity of water passed through the column during two successive 24-h periods was separately analyzed for Si by the Heteropoly Blue method (Eaton et al., 1995), at a 650-nm wavelength as measured on a Brinkmann, Model 910 colorimeter (Brinkmann Instruments, Westbury, NY).

Silicon results are expressed as mg Si dissolved g⁻¹ of candidate material in each 24-h period. In practice, results are compared to those for a finely-divided very pure $CaSiO_3$ mineral (wollastonite), which serves as a reference.

Although not part of the normal Si dissolution evaluation procedure, Si dissolution from wollastonite and

three other mineral Si sources was measured in 24-h increments over a 10-d period using the previously-described technique for the purpose of quantifying the change in dissolution over time. Calcium and Mg in the TRIS-buffer extracts were determined (Rich, D. unpublished data, 2001) using a Varian, Model 220 FS, atomic absorption spectrometer (Varian, Inc., Palo Alto, CA). Correlation data was provided by the SAS system CORR procedure (SAS, 2003).

Greenhouse Evaluation

The same candidate Si fertilizers used in the laboratory analyses were mixed with a low-Si containing organic soil (Pahokee muck, Euic, hyperthermic Lithic Halosaprists) at 0 to 20 Mg ha^{-1}, based on the surface area of the pots (11.4-cm diam) utilized in the study, replicated five times. Nine rice seeds were planted in each pot, and thinned to three plants per pot after the seedlings became established. The rice was grown in a flooded condition, with appropriate N, P, and K fertilization. At grain maturity (~ 4 mo), straw was harvested and analyzed for Si (Elliott and Snyder, 1991). The Si concentration of the straw was used as a measure of Si released from the fertilizer sources.

The Si leaching data from the laboratory procedure was correlated with the straw Si concentration data from the greenhouse study using the CORR procedure (SAS, 2003).

RESULTS AND DISCUSSION

A considerable range in Si dissolution was observed among the five Si sources (Table 1). Silicon dissolution was lower in the second 24-h period than in the first. A good correlation was obtained between Si dissolution by any of the three measures presented and Si in the rice straw (straw Si vs 24-h, 48-h and total, r = 0.95, 0.92, and 0.95, respectively). Silicon release during the first 24-h was sufficient to characterize the sources. The second 24-h period was used mainly to verify that a source was not so soluble that no residual Si release could be expected. An example of this characteristic would be sodium silicate (very soluble). By contrast, in the case of CaSiO$_3$, a moderately insoluble salt (K$_{sp}$ ≈ 10^{-7}), leaching would continue for many days.

Silicon concentration in the straw grown in Si-source 5 is somewhat greater than might be expected from the very low Si release data obtained in the laboratory (Table 1). This is most likely due to its uptake from low Si content occurring naturally in the soil. Silicon release from the other sources probably was sufficiently high so as to overwhelm the amount of native Si in the soil. The laboratory procedure provides a sufficiently reliable evaluation of Si release from candidate Si fertilizers to identify those that are worthy of further evaluation in the field.

Using the same laboratory methodology, the 48-h Si-leaching procedure was extended to 10 d in order to further investigate the Si release rate of wollastonite and other Si sources. It was found that the Si release rate data was consistent with a classical first order leaching reaction (Fig. 1). This means that for every day of leaching there is a predictable decrease in Si concentration.

For Si leaching from wollastonite, a curvilinear line was obtained over the 10-d period (Fig. 1). However, a straight line was obtained when the log N (Si) leaching rate was plotted against the same 10-d period, which indicates a classic first order reaction. This means that it should have a half-life relationship;

$$t_{(1/2)} = 1 + [\ln 2/k] \qquad \text{Eq. [1]}$$

where, t = days, and k = rate constant, and, satisfy a first order relationship;

$$t = 1 + [(1/k) \ln (C_1/C)] \qquad \text{Eq. [2]}$$

where, C$_1$ = the initial concentration of Si in the leachate (Day 1.), C = the concentration of Si in the leachate at any time, and t = days. All data from the wollastonite 10-d leaching procedure satisfy Eq. [1] and [2].

The half-life was calculated as 3.4 d by Eq. [1], and the rate constant for the leaching reaction was determined to be 0.29 by calculating the slope of the log N function in Fig. 1 (Table 2). The rate constant value and any concentration can then be used in Eq. [2] to calculate various time or concentration measurements. Similarly, in a study of Si dissolution from three additional Si slag sources over a 10-d period, all data obtained were
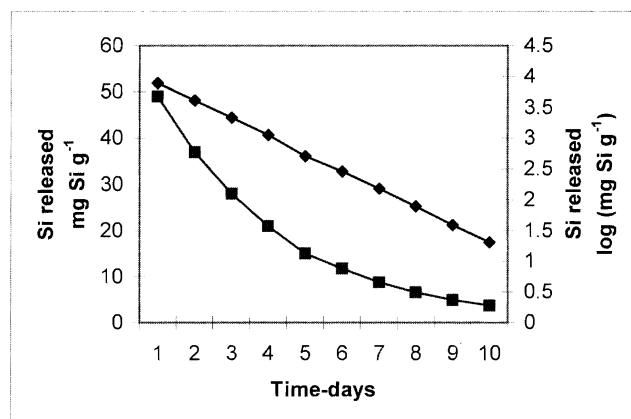
Table 1. Comparison between Si released from five mineral Si sources in the laboratory evaluation and the Si concentration in rice straw from the greenhouse study.

Si source	Silica leached in the laboratory			Straw Si
	0-24 h	24-48 h	Total	
	--------------- mg Si g^{-1} ---------------			mg kg^{-1}
1	16.4	12.6	29.0	27
2	14.7	11.3	26.0	28
3	11.4	4.7	16.1	22
4	8.3	3.9	12.2	12
5	1.6	0.8	2.4	18

Fig. 1. Silicon dissolution from wollastonite by the laboratory procedure where ◆ = log (mg Si g^{-1}) and ■ = mg Si g^{-1}.
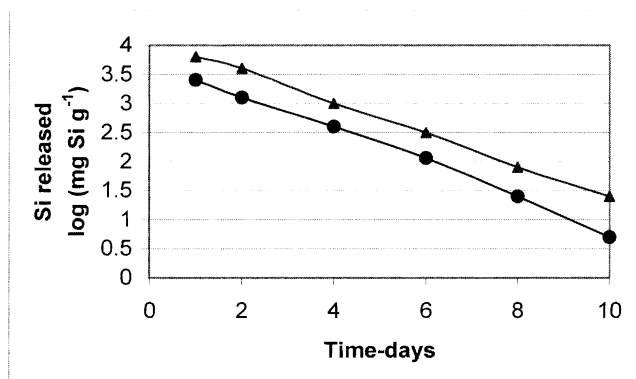
Fig. 2. Comparison between Si dissolution by the laboratory procedure for an average of three mineral Si sources and wollastonite (▲ = wollastonite, ● = average of three slag sources).

consistent with a first order leaching reaction with a half-life of 3.4. When compared to wollastonite, data for the three Si sources are also consistent with a first order plot. The data from the three sources are averaged and presented along with that for wollastonite (Fig. 2).

Among the various sources of Si, $CaSiO_3$ has the unique distinction of not being too insoluble to provide plant-available Si, or so soluble that Si might not be available throughout the growing season of long-term crops such as sugarcane. Although its solubility product is $\sim 10^{-7}$, it can still ionize sufficiently to release Si into the soil: $CaSiO_3 = [Ca^{+2}] + [SiO_3^{-2}]$. By our laboratory procedure, this translates into about 45 to 50 mg Si g^{-1} of slag in the first 24-h period, and 36 to 38 mg in Day 2. By contrast, $MgSiO_3$ is a very insoluble source, $(K_{sp} \sim 10^{-12})$ while $Na_2SiO_3 \cdot 9H_2O$ is very soluble (Table 3).

The second 24-h period identifies highly soluble Si sources i.e., $Na_2SiO_3 \cdot 9H_2O$ which likely are too soluble to provide long-term Si to crops such as sugarcane. We suggest that for an acceptable Si source, the 24 to 48 h leaching values should be $\sim 75\%$ of the 0 to 24 h values. The release rate data could provide a basis for predicting the residence time of a source. For example, once the 24 to 48 h dissolution value is known, a simple calculation using Eq. [2] will predict future dissolution over time.

Table 2. Rate constants and half-life values for three mineral Si sources.

Si source	k	$t_{(1/2)}$ Days
1	0.285	3.43
2	0.283	3.45
3	0.285	3.43

Table 3. Leaching characteristics of selected Si sources.

Source	0-24 h	24-48 h	Solubility
	---------- mg Si g^{-1} ----------		
$CaSiO_3$	45-50	36-38	Moderate
$MgSiO_3$	0.8-1.0	0	Very insoluble
Other Silicates†	10-18	6-10	Moderate
$Na_2SiO_3 \cdot 9H_2O$	100+	0	Very soluble

†Mixed: Calcium/Magnesium Silicates (D. Rich, unpublished, 2001).

CONCLUSIONS

It was shown that there is strong correlation between the data from the lab procedure and the greenhouse rice straw uptake study (r = 0.92-0.95). Data from the lab procedure indicates that the Si-leaching pattern can be predicted after the second day. This is due to the first order rate of the leaching reaction. Candidate Si mineral sources can be identified after the second day as good, medium, or poor using the lab leaching procedure. This is accomplished by calculating the percent (%) of the 48 h leaching output compared to the 24 h leaching output. For example, if the leachate for the 48 h period is about 70 to 80% of the 24 h period then that candidate Si source would be classified as good. Whereas, if the leachate is $\sim$ 45 to 55% of the 24-h period that Si source would be a medium candidate. Finally, if the leachate is only 20 to 35% or less from that of the 24-h period, that Si source would be considered poor.

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