



## Oxidation of FGD-CaSO<sub>3</sub> and effect on soil chemical properties when applied to the soil surface

Liming Chen<sup>a,\*</sup>, Cliff Ramsier<sup>b</sup>, Jerry Bigham<sup>c</sup>, Brian Slater<sup>c</sup>, David Kost<sup>a</sup>, Yong Bok Lee<sup>c</sup>, Warren A. Dick<sup>a</sup>

<sup>a</sup>School of Environment and Natural Resources, The Ohio State University, The Ohio Agricultural Research and Development Center, Wooster, OH, USA

<sup>b</sup>Ag Spectrum Company, Dewitt, IA, USA

<sup>c</sup>School of Environment and Natural Resources, The Ohio State University, Columbus, OH, USA

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### ABSTRACT

Use of high-sulfur coal for power generation in the United States requires the removal of sulfur dioxide (SO<sub>2</sub>) produced during burning in order to meet clean air regulations. If SO<sub>2</sub> is removed from the flue gas using a wet scrubber without forced air oxidation, much of the S product created will be sulfite (SO<sub>3</sub><sup>2-</sup>). Plants take up S in the form of sulfate (SO<sub>4</sub><sup>2-</sup>). Sulfite may cause damage to plant roots, especially in acid soils. For agricultural uses, it is thought that SO<sub>3</sub><sup>2-</sup> in flue gas desulfurization (FGD) products must first oxidize to SO<sub>4</sub><sup>2-</sup> in soils before crops are planted. However, there is little information about the oxidation of SO<sub>3</sub><sup>2-</sup> in FGD product to SO<sub>4</sub><sup>2-</sup> under field conditions. An FGD-CaSO<sub>3</sub> was applied at rates of 0, 1.12, and 3.36 Mg ha<sup>-1</sup> to the surface of an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf). The SO<sub>4</sub><sup>2-</sup> in the surface soil (0–10 cm) was analyzed on days 3, 7, 17, 45, and 61. The distribution of SO<sub>4</sub><sup>2-</sup> and Ca in the 0–90 cm soil layer was also determined on day 61. Results indicated that SO<sub>3</sub><sup>2-</sup> in the FGD-CaSO<sub>3</sub> rapidly oxidized to SO<sub>4</sub><sup>2-</sup> on the field surface during the first week and much of the SO<sub>4</sub><sup>2-</sup> and Ca moved downward into the 0–50 cm soil layer during the experimental period of two months. It is safe to grow plants in soil treated with FGD-CaSO<sub>3</sub> if the application is made at least three days to several weeks before planting.

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### 1. Introduction

The use of high-sulfur coal for electric power generation in the United States requires the removal of SO<sub>2</sub> produced during burning via some type of flue gas scrubbing technology in order to meet clean air regulations. Many FGD (flue gas desulfurization) technologies including wet limestone, Mg-enhanced lime, and lime spray drying are currently used in the power industry, and the wet limestone processes have predominated in the US [1]. Magnesium-enhanced lime FGD and lime spray FGD technologies often produce SO<sub>3</sub><sup>2-</sup>-containing FGD products [2]. If SO<sub>2</sub> is removed from the flue gas using a wet scrubber without forced air oxidation, the FGD product created will contain as much as 30–87% of S as SO<sub>3</sub><sup>2-</sup> [3]. In the United States, the wet limestone without forced air process is still used, and a large amount of FGD-CaSO<sub>3</sub> is produced.

Plants take up S mostly in the form of SO<sub>4</sub><sup>2-</sup> [4]. At low soil pH, SO<sub>3</sub><sup>2-</sup> may cause damage to plant roots [5,6]. However, CaSO<sub>3</sub> can rapidly oxidize to CaSO<sub>4</sub> in oxygenated environments [7]. The reaction rate is strongly affected by concentrations of O<sub>2</sub> and dissolved SO<sub>3</sub><sup>2-</sup>, pH, temperature, and catalysts such as Co<sup>2+</sup>, Cu<sup>2+</sup>, and Mn<sup>2+</sup>

[8–11]. Ritchey et al. [6] reported that CaSO<sub>3</sub> was completely oxidized to CaSO<sub>4</sub> in aqueous solutions in 5 weeks, and approximately one-third of CaSO<sub>3</sub> was oxidized in a soil slurry in 8 days. Lee et al. [11] found that CaSO<sub>3</sub> was completely oxidized in soil–FGD mixtures in 21 days. Wendell and Ritchey [12] reported that when FGD-CaSO<sub>3</sub> product was applied to the soil surface, movement of Al, Ca, and SO<sub>4</sub><sup>2-</sup> in columns of an acid soil was significantly increased.

Gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) is a quality source of both Ca and S for plant nutrition. Gypsum amendments can improve the physical and chemical properties of soils by promoting soil aggregation, increasing water infiltration rates and movement through the soil profile, and mitigating subsoil acidity and Al toxicity [13]. When used as a soil amendment, gypsum is often applied to the surface of fields without mixing. This is especially so when applied to no-tillage fields. FGD-CaSO<sub>3</sub> could function similarly to gypsum when surface-applied if the CaSO<sub>3</sub> is oxidized rapidly to CaSO<sub>4</sub>. However, there is little information on the oxidation of FGD-CaSO<sub>3</sub> to CaSO<sub>4</sub> and movement in cultivated soils under field conditions. The objectives of this study were to determine the oxidation rate of FGD-CaSO<sub>3</sub> applied onto the soil surface of an agricultural field and to evaluate the impact of FGD-CaSO<sub>3</sub> application and oxidation on the movement of plant nutrients and toxic elements in the soil.

\* Corresponding author. Tel.: +1 330 263 3655; fax: +1 330 263 3788.  
E-mail address: [chen.280@osu.edu](mailto:chen.280@osu.edu) (L. Chen).

## 2. Materials and methods

Field studies were conducted on an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf) located near Wooster, OH. Organic matter, pH, and concentrations of selected elements extracted by Mehlich-III extractant [14] from experimental field soil (0–20 cm) are presented in Table 1. The Wooster field had been in continuous corn for three years from 2003 to 2006 under a conventional tillage management system. FGD-CaSO<sub>3</sub> was obtained from American Electric Power Company, Conesville, OH, and FGD-gypsum was obtained from Cinergy Corporation, Cincinnati, OH (Table 2). In these FGD materials, SO<sub>4</sub>-S was measured by ion chromatography (IC), and SO<sub>3</sub>-S was determined by subtraction of SO<sub>4</sub>-S from total S that was determined by dry combustion method. All other elements were analyzed by inductively coupled plasma (ICP) emission spectrometry. The chemical composition of any FGD product is influenced by the type of coal, desulfurization process, and sorbent used. It is also influenced by the location where fly ash is removed from the flue gas stream. The difference in the concentrations of elements including Mg and B between the two study materials is due to the coal sources used. FGD-CaSO<sub>3</sub> was applied at rates of 0, 1.12, and 3.36 Mg ha<sup>-1</sup> to the soil surface, and FGD-gypsum was applied at only a single rate of 1.12 Mg ha<sup>-1</sup> as a positive comparison. Rates used were normal field recommended rates required to improve soil physical and chemical properties such as water and air infiltration and subsoil acidity. These treatments were applied to 1 × 1 m plots arranged in a randomized block with four replicates.

The field experiment was carried out from May 19 to July 19, 2006. Weekly precipitation and average temperature at the exper-

**Table 1**  
Organic matter, pH, and concentrations of selected elements extracted by Mehlich-III extractant from experimental field soil (0–20 cm) at initiation of experiment

pH	Organic matter (%)	Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
		mg kg <sup>-1</sup>										
7.1	3.1	775	0.43	1440	1.5	195	111	311	94	50	51	6.7

**Table 2**  
Characteristics of the FGD-CaSO<sub>3</sub> and FGD-gypsum

Parameter	FGD-CaSO <sub>3</sub>	FGD-gypsum
<i>Sulfur component (%)</i>		
SO <sub>3</sub> -S	22.7	0
SO <sub>4</sub> -S	2.0	18.7
<i>Major elements (g kg<sup>-1</sup>)</i>		
Ca	304	213
S	247	187
<i>Other elements (mg kg<sup>-1</sup>)</i>		
Al	577	228
As	<1.3	<11
B	165	5.8
Ba	20.7	5.5
Cd	<0.05	<1.0
Cr	<0.19	<1.0
Cu	1.69	<3.0
Fe	654	222
K	206	284
Mg	3660	112
Mn	20.5	1.3
Mo	<0.225	<3.0
Ni	3.66	<3.0
Pb	<0.77	<5.0
Se	<2.3	<25.0
Zn	7.1	4.8

**Table 3**

Weekly precipitation and average temperature for the duration of the experiment in 2007 and soil moisture on sampling dates at Wooster

Time interval (date)	Precipitation (cm)	Average temperature (°C)	Sample date	Soil moisture (% by mass)
5/19–25	3.7	12.2	5/19	22.5
5/26–6/1	2.28	22.2	5/22	20.5
6/2–6/8	2.00	17.9	5/26	21.5
6/9–6/15	0	15.6	6/5	19.8
6/16–6/22	6.17	21.8		
6/23–6/29	1.60	20.2		
6/30–7/6	2.38	21.0	7/3	20.1
7/7–7/13	5.56	21.2		
7/14–7/19	1.98	22.2	7/19	18.3
Total	25.7			

imental site and soil moisture on the sampling days are presented in Table 3. On days 3, 7, 17, 45, and 61 after treatments, five soil cores from depth of 0 to 10 cm were collected from each plot and combined to form one sample. Immediately after returning to the lab, a subsample of 20 g soil was put in a test tube, and 30 mL double deionized water was added. After reciprocating shaking for 1 h, the soil suspension was centrifuged, and the supernatant was filtered through a 0.45 μm membrane filter. The pH and electrical conductivity of the extracts were measured using a pH meter and a combination glass electrode. The elements Ca, Mg, K, Al, Fe, Mn, and Zn in the extracts were analyzed by inductively coupled plasma emission spectrometry, and SO<sub>4</sub>-S was determined by ion chromatography. A subsample of 30 g soil was dried in a forced air oven at 65 °C for four days for moisture determination. On day 61 after treatment, two soil cores from each plot were collected to a depth of 90 cm using a hydraulic coring device and sub-sampled at 10-cm intervals. The sub-samples were then mixed to obtain a single sample for each depth increment in each plot, and soils were extracted with water and analyzed as described above.

## 3. Results and discussion

All treatments of FGD-CaSO<sub>3</sub> and FGD-gypsum gradually decreased in the surface (0–10 cm) soil pH during the first 17 days, and then pH gradually recovered after that time (Fig. 1). Wendell and Ritchey [12] and Lee et al. [11] also observed that soil and leachate pH decreased when FGD-CaSO<sub>3</sub> or FGD-gypsum was surface-applied or mixed with soil under laboratory conditions. Lee et al. [11] found that the decrease of pH was approximately 0.5 units when the initial soil pH values were 4.0 and 5.1, and there was little or no divergence in leachate pH with and without FGD-CaSO<sub>3</sub> when the initial soil pH was 7.8. Wendell and Ritchey [12] reported that surface application of FGD-CaSO<sub>3</sub> did not depress leachate pH as much as when incorporated into soil. The electrical conductivity in the soil extracts was significantly increased by FGD-CaSO<sub>3</sub> or FGD-gypsum treatment (Fig. 1). The electrical conductivity trended to decrease over time and was similar for the treatments of 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> or FGD-gypsum. The solubility in water is only 0.054 g L<sup>-1</sup> for CaSO<sub>3</sub> and 2.1 g L<sup>-1</sup> for gypsum [11]. Thus, the similar electrical conductivity for FGD-CaSO<sub>3</sub> or FGD-gypsum treatment suggests that all the FGD-CaSO<sub>3</sub> had been oxidized to SO<sub>4</sub><sup>2-</sup>.

The concentrations of water-soluble SO<sub>4</sub>-S, Ca, Mg, and K in the soil surface layer (0–10 cm) were significantly increased by FGD-CaSO<sub>3</sub> or FGD-gypsum treatment and gradually decreased over time (Fig. 2). The concentrations of SO<sub>4</sub>-S, Ca, Mg, and K by treatment with 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> were similar to those by treatment with FGD-gypsum at all days measured. These results indicated that the SO<sub>3</sub><sup>2-</sup> in the FGD-CaSO<sub>3</sub> was rapidly oxidized in the first three days after surface application. Wendell and Ritchey

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