Oxidation in Soil of $CaSO_3$ from Flue Gas Desulfurization Product and Effect on Corn Establishment

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ABSTRACT

Application of gypsum ($CaSO_4 \cdot 2H_2O$) to agricultural soils has a long history. Hannebachite ($CaSO_3 \cdot H_2O$) is a product created when coal is burned and sulfur is scrubbed from the flue gases. It is considered inferior to gypsum as an agricultural amendment because it can negatively impact plant growth, especially in acid soils, and has poor handling properties. For agricultural use of FGD-$CaSO_3$, it must first be oxidized to sulfate (SO_4^{2-}) in soils before crops are planted. However, there is little information about the oxidation rate of sulfite (SO_3^{2-}) under field conditions. An FGD-$CaSO_3$ was applied at rates of 0, 1.12 and 3.36 Mg ha^{-1} to the surface of an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf). Oxidation of SO_3^{2-} was determined by measuring SO_4^{2-} in the surface soil (0-10 cm) on 0, 1, 2, 3, 8, and 14 days after application. Corn was planted on the same days as samples were analyzed for SO_4^{2-} and corn emergence and growth were measured. It is safe for plants if FGD-$CaSO_3$ is applied to field surface two weeks before planting.

INTRODUCTION

Plants take up S mostly in the form of SO_4^{2-}. At low soil pH, SO_3^{2-} may be converted to sulfur dioxide (SO_2) which is toxic to plants (Ritchey et al., 1995). However, $CaSO_3$ can rapidly oxidize to $CaSO_4$ in oxygenated environments (Pasiuk-Bronikowska et al., 1992). The reaction rate is strongly affected by concentrations of dissolved SO_3^{2-} and O_2, pH, and temperature (Lancia and Musmarra, 1999; Hao and Dick, 2000; Lee et al., 2007). For agricultural use, FGD products are often applied to the surface of the fields. However, there is no report on the oxidation of FGD-$CaSO_3$ and its effect on the emergence and growth of plants under field conditions. The objectives of this study were to determine the oxidation rate of FGD-$CaSO_3$ at the soil surface of an agricultural field and to evaluate the impact of FGD-$CaSO_3$ on corn emergence and growth.

MATERIALS AND METHODS

A field study was conducted on an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf) located near Wooster, OH. Selected characteristics of the soil are presented in Table 1. FGD-$CaSO_3$ was obtained from American Electric Power Company, Conesville, OH, and FGD-gypsum was obtained from Cinergy Corporation, Cincinnati, OH (Table 2). FGD-$CaSO_3$ was applied at rates of 0, 1.12, and 3.36 Mg ha^{-1} to the soil surface, and FGD-gypsum was applied at only a single rate of 1.12 Mg ha^{-1} as a positive comparison. Rates used were normal field recommended rates required to improve soil physical and chemical properties. These treatments were applied to 1 x 1 m plots arranged in a randomized block with four replicates.

Table 1. pH and concentrations of selected elements extracted from experimental field soil (0-20 cm) by Mehlich-III.

pH	P	K	Ca	Mg	S	B	Cu	Fe	Mn	Mo	Zn	Al
	------ mg kg^{-1} ------											
7.1	50	111	1440	311	51	0.43	1.5	195	94	0.03	6.7	775

Table 2. Characteristics of the FGD-$CaSO_3$ and FGD-gypsum used.

Parameter	FGD-$CaSO_3$	FGD-gypsum
Sulfur component (%)		
SO_3-S	17.0	0
SO_4-S	0.7	18.5
Element (mg kg^{-1})		
P	6.3	<0.80
K	278	75
Ca	247000	222000
Mg	7480	105
S	177000	185000
B	261	4.7
Cu	<0.20	<0.20
Fe	726	122
Mn	23.9	0.06
Mo	0.40	0.32
Zn	17.9	18.5
Al	1660	251

The field experiment was carried out from May 21 to June 25, 2007. On days 0, 1, 2, 3, 8 and 14 after treatments, soil samples (0-10 cm) were collected and SO_4^{2-} was extracted (2:3 soil to water ratio) with double deionized water and analyzed by ion chromatography. Concentrations of various elements in the extracts on day 14 were analyzed by inductively coupled plasma (ICP) emission spectrometry. Thirteen seeds of corn were sown in each plot on the same days as samples were analyzed for SO_4^{2-}. The rates of corn emergence were measured on day 8 after sowing, and dry weight of corn plants was determined on day 21 after sowing. Corn plants sown on day 14 were dried in a 65° C oven and ground to pass a 1-mm sieve. Concentrations of elements were determined by ICP emission spectrometry after $HClO_4$:HNO_3 digestion.

RESULTS AND DISCUSSION

Concentrations of water-soluble SO_4-S in the soil surface layer (0-10 cm) were increased by FGD-$CaSO_3$ or FGD-gypsum treatment (Fig. 1). Concentrations of SO_4-S in soil treated with 1.12 Mg ha^{-1} FGD-$CaSO_3$ were similar to those treated with FGD-gypsum at all days measured. This indicates the SO_3^{2-} in the FGD-$CaSO_3$ was rapidly oxidized after surface application.

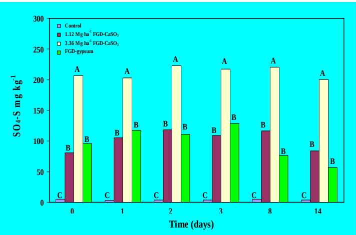

Fig. 1. Changes in water-soluble SO_4-S in the surface 10 cm soil layer over time after surface application of FGD-$CaSO_3$ or FGD-gypsum.

Ca and S concentrations in the soil, were significantly increased by FGD-$CaSO_3$ or FGD-gypsum treatment, as were also water-soluble K and Mg (Table 3). The Ca ions have greater affinity for exchange sites on soil particles than K and Mg ions and the Ca in the FGD-$CaSO_3$ and FGD-gypsum displaced and mobilized K and Mg. As expected, there were higher concentrations of Mg, B, and Mn in soil treated with FGD-$CaSO_3$ than with FGD-gypsum due to their higher concentrations in FGD-$CaSO_3$ (Table 2). Application of FGD-$CaSO_3$ or FGD-gypsum significantly decreased the concentrations of water-soluble P, Fe, Mo, Zn and Al. These decreases were attributed to leaching losses caused by Ca replacement and precipitation reactions. Aluminum is a major factor limiting crop yield in many areas of the world. Surface application of gypsum has become a recommended procedure for Al amelioration. Our results indicate that FGD-$CaSO_3$, like gypsum, is a good product for Al amelioration.

Table 3. Concentrations of selected water-soluble plant nutrients and Al in the surface 10 cm soil layer on day 14 after surface application of FGD-$CaSO_3$ or FGD-gypsum.

Element	Treatment				
	Control	FGD-$CaSO_3$ 1.12 Mg ha^{-1}	FGD-$CaSO_3$ 3.36 Mg ha^{-1}	FGD-gypsum 1.12 Mg ha^{-1}	$LSD_{0.05}$
	------ mg kg^{-1} ------				
P	0.202 a	0.016 c	0.097 b	0.067 bc	0.079
K	5.8 c	11.3 bc	25.0 a	16.1 b	6.2
Ca	7.7 d	78.7 b	202 a	49.6 c	28.2
Mg	3.1 d	20.4 b	40.7 a	14.5 c	5.3
S	3.7 c	85.2 b	209 a	58.7 b	31.0
B	0.02 c	0.05 b	0.14 a	0.01 c	0.02
Cu	<0.001	<0.001	<0.001	<0.001	
Fe	2.547 a	0.170 bc	0.003 c	0.382 b	0.262
Mn	0.067 b	0.088 b	0.431 a	0.005 b	0.122
Mo	0.011 a	0.004 b	0.006 ab	0.001 b	0.006
Zn	0.048 a	0.022 b	0.018 b	0.021 b	0.010
Al	2.74 a	0.05 b	0.03 b	0.19 b	0.19

Means in a row followed by different letters are significantly different at $P<0.05$.

Corn emergence rates were not affected by FGD-$CaSO_3$ or FGD-gypsum treatment compared with the untreated control at all days measured (Table 4). Sown immediately after treatments (0 day), the corn emergence rate was decreased by the 1.12 Mg ha^{-1} FGD-$CaSO_3$ treatment compared with the 1.12 Mg ha^{-1} FGD-gypsum treatment. However, dry weight of corn plants was not affected by FGD-$CaSO_3$ or FGD-gypsum treatment, compared with the untreated control, when corn seeds were sown on days 0, 1, 2 and 8 after treatments, but it was decreased on days 3 and 14. Why there was not a consistent growth response for all days is not clear but may be due to decreasing availability of plant nutrients such as Mo in the soil (Table 3).

Concentrations in corn plant tissue of S were significantly increased by FGD-$CaSO_3$ or FGD-gypsum. However, concentrations of K, Cu and Mo were decreased. Concentrations of B were increased by 3.36 Mg ha^{-1} FGD-$CaSO_3$ compared with 1.12 Mg ha^{-1} FGD-gypsum. This indicated that B in the FGD-$CaSO_3$ was easily taken up by corn plants.

Table 4. Corn emergence rate and dry weight of corn seedlings over time after surface application of FGD-$CaSO_3$ or FGD-gypsum.

Treatment		Days after treatment					
Material	Rate Mg ha^{-1}	0	1	2	3	8	14
		Emergence rate (%)					
Control	0	86.5 ab	84.6	94.2	92.3	86.5	94.2
FGD-$CaSO_3$	1.12	73.1 b	96.2	96.2	84.6	88.5	92.3
	3.36	86.5 ab	94.2	98.1	88.5	90.4	90.4
FGD-gypsum	1.12	100 a	90.4	92.3	88.5	84.6	90.4
$LSD_{0.05}$		26.4	12.5	11.4	12.6	16.0	12.3
		Growth (g/plot)					
Control	0	7.35	6.75	9.66	10.37 a	10.03	9.22 a
FGD-$CaSO_3$	1.12	5.45	7.71	9.31	8.18 b	8.68	6.50 b
	3.36	5.90	7.33	9.84	9.35 ab	7.73	7.51 ab
FGD-gypsum	1.12	6.33	6.84	9.12	8.39 b	8.24	7.72 ab
$LSD_{0.05}$		2.57	1.98	4.00	1.85	2.80	2.36

Means in a row followed by different letters are significantly different at $P<0.05$.

Table 5. Concentrations in corn plant tissue of selected plant nutrients and Al from 21-day-old seedlings planted on day 14 after surface application of FGD-$CaSO_3$ or FGD-gypsum.

Element	Treatment				
	Control	FGD-$CaSO_3$ 1.12 Mg ha^{-1}	FGD-$CaSO_3$ 3.36 Mg ha^{-1}	FGD-gypsum 1.12 Mg ha^{-1}	$LSD_{0.05}$
	------ mg kg^{-1} ------				
P	4820	4870	4980	5050	1340
K	48200 a	47700 ab	47300 ab	44800 b	3270
Ca	2830	3070	3090	3160	583
Mg	2580	2670	2660	2790	294
S	2070 b	2960 a	3090 a	3150 a	720
B	4.75 ab	4.76 ab	5.11 a	4.39 b	0.62
Cu	2.83 a	2.69 a	2.40 ab	1.64 b	0.91
Fe	224	168	156	154	97
Mn	59.6	59.4	54.5	55.4	13.1
Mo	1.08 a	0.88 ab	0.67 b	0.55 b	0.40
Zn	25.9	31.8	31.8	31.3	10.5
Al	105.6	73.7	68.7	52.1	71.3

Means in a row followed by different letters are significantly different at $P<0.05$.

CONCLUSIONS

Sulfite in FGD-$CaSO_3$ was rapidly oxidized to SO_4^{2-} when applied to the moist surface of a field in the spring. Effects of FGD-$CaSO_3$ on water-soluble K, Al, Fe, Mn, and Zn in soils, on corn emergence and growth, and on concentrations of elements in plant tissue were similar to those of FGD-gypsum when applied at the rate of 1.12 Mg ha^{-1}. FGD-$CaSO_3$ provided more Ca, Mg and B to the soil than FGD-gypsum did. It is safe for plants if FGD-$CaSO_3$ is applied to the field surface.

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