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Circulating Fluidized Bed Combustion Product Addition to Acid Soil: Alfalfa (*Medicago sativa* L.) Composition and Environmental Quality

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To reduce S emissions, petroleum coke with a high concentration of S was combusted with limestone in a circulating fluidized bed (CFB) boiler. The combustion process creates a bed product that has potential for agricultural uses. This CFB product is often alkaline and enriched in S and other essential plant nutrients, but also contains high concentrations of Ni and V. Agricultural land application of CFB product is encouraged, but little information is available related to plant responses and environmental impacts. CFB product and agricultural lime (ag-lime) were applied at rates of 0, 0.5, 1.0, and 2.0 times the soil's lime requirement (LR) to an acidic soil (Wooster silt loam). The 2.0× LR application rate of CFB product was equivalent to 67.2 Mg ha^{-1}. Alfalfa yield was increased 4.6 times by CFB product and 3.8 times by ag-lime compared to untreated control. Application of CFB product increased the concentration of V in soil and alfalfa tissue, but not in soil water, and increased the concentration of Ni in soil and soil water, but not in alfalfa tissue. However, these concentrations did not reach levels that might cause environmental problems.

KEYWORDS: Alfalfa; crop nutrient; trace elements; flue gas desulfurization; petroleum coke; environmental quality; nickel; vanadium

INTRODUCTION

In the United States, use of petroleum coke with high S content for energy production requires the SO_2 produced during burning be removed via some type of scrubbing technology to meet clean air regulations. The scrubbing reaction creates clean coal combustion products (CCB) that are often landfilled, even though the U.S. Environmental Protection Agency has affirmed that such products do not qualify as hazardous waste (*1*). Increasing production of CCBs, due to Phase II of the Clean Air Act Amendments, has led to decreasing availability of landfill space and rising costs for disposal. As a result, there is increased interest in developing beneficial uses for these materials.

At the Bay Shore plant (FirstEnergy Corp.) in Ohio, limestone is added to a circulating fluidized bed (CFB) boiler for removal of SO_2. The CFB process creates both bed ash and fly ash materials during scrubbing that are composed of (1) $CaSO_4$—the SO_2 scrubbing reaction product, (2) excess of limestone, lime, and portlandite, and (3) ash, which contains high concentrations of Ni and V. The CFB product is highly alkaline and has significant acid neutralization potential. Several studies have shown that this property enables these types of CCB products to be used as alkaline amendments for acid agricultural soils (*2*−*4*). Also, the ash component in the CFB product contains many essential plant nutrients that can provide additional benefits for crop growth.

Crude oils typically have high concentrations of Ni and V. Petroleum coke is the heavy residual material left after lighter gases and oils have been extracted from the crude oils. Burning of petroleum coke leads to concentrations of Ni and V in the ash (*5*) that are high enough that some people may question the use of CFB product for land application where agricultural crops are grown. Little information is available, however, on whether these elements are taken up by the crop and pose a health threat when petroleum coke ash is applied to soil. Information is needed to demonstrate both plant responses and other impacts concerning the use of CFB product in agriculture.

MATERIALS AND METHODS

Field studies were conducted on an acidic agricultural soil (Wooster silt loam, fine-loamy, mixed, active, mesic Oxyaquic Fragiudalf) located near Wooster, OH. Prior to treatment, surface (0−20 cm) soil samples were collected, air-dried, and analyzed to determine fertility status, pH, and lime requirements (**Table 1**). Before the beginning of the experiment, 170 kg ha^{-1} P and 580 kg ha^{-1} K were applied to the field on the basis of soil test results and the Ohio Cooperative Extension Service (*6*) recommendations.

The CFB bed product used in this experiment, without any addition of fly ash, had a pH of 11.3 and a total neutralizing power of 48.7% as compared to $CaCO_3$. The agricultural lime (ag-lime) contained dolomite $CaMg(CO_3)_2$ and had a total neutralizing power of 97.0% (**Table 2**). The rates of CFB product or ag-lime applied were based on the soil's lime requirement (i.e., the amount of ag-lime needed to raise

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Table 1. Selected Characteristics of the Wooster Soil (0–20 cm) before Application of Fertilizers and Liming Materials

			exchangeable cations				base saturation		
pH	LR[a] (Mg ha^{-1})	available P (mg kg^{-1})	K	Ca (mg kg^{-1})	Mg	CEC[b] (cmol$_c$ kg^{-1})	Ca (%)	Mg	K
5.0	16.8	5.0	115	323	79	12.2	13.3	5.4	2.4

[a] LR, lime requirement is based on soil lime test index values and is the amount of $CaCO_3$ needed to raise the soil pH to 7.0. [b] Cation exchange capacity.

Table 2. Concentrations of Elements in the Circulating Fluidized Bed (CFB) Product and Agricultural Lime (ag-lime) Used

	CFB product (mg kg^{-1})	ag-lime (mg kg^{-1})		CFB product (mg kg^{-1})	ag-lime (mg kg^{-1})
essential for higher plants			nonessential for higher plants		
B	6.01	<2.0	Al	2020	765
Ca	226000	196000	As	<4.5	<9.0
Cu	1.91	<2.0	Ba	23.6	81.3
Fe	1800	1330	Cd	<0.20	<0.40
K	341	2850	Co	2.76	<2.0
Mg	9820	117000	Cr	3.84	6.3
Mn	100	54	Na	36.8	910
Mo	32.8	3.0	Pb	5.38	61.8
Ni	358	5.0	Se	18.5	<20.0
P	51.7	69.0	Si	466	29.8
S	105000	9460	Sr	86.2	960
Zn	10.3	18.5	V	1220	12.5

Table 3. Dry Weight of Alfalfa in Each Harvest Affected by Application of the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

	Mg ha^{-1}				
	2004		2005		
treatment	1st harvest	2nd harvest	1st harvest	2nd harvest	3rd harvest
control	0.58 d[a]	0.16 c	0.18 b	0.07 b	0.52 c
CFB product					
0.5× LR[b]	1.55 ab	1.37 a	1.59 a	1.43 a	2.33 ab
1.0× LR	1.64 a	1.46 a	1.88 a	1.39 a	2.13 b
2.0× LR	1.10 c	1.34 ab	1.81 a	1.52 a	2.76 a
ag-lime					
0.5× LR	1.12 c	0.94 b	1.57 a	1.16 a	2.28 ab
1.0× LR	1.25 bc	1.12 ab	1.28 a	1.39 a	2.26 ab
2.0× LR	1.39 abc	1.12 ab	1.25 a	1.30 a	2.04 b
LSD$_{0.05}$	0.36	0.40	0.83	0.36	0.60

[a] Different letters in the same column represent a significant difference at $P \leq 0.05$. [b] Lime requirement defined as the equivalent amount of $CaCO_3$ required to neutralize soil acidity and raise the soil pH to 7. Compared to $CaCO_3$, the neutralization equivalency of the CFB product was 48.7% and that of ag-lime was 97.0%.

the soil pH to 7.0) measured using the procedure of Watson and Brown (*7*). The amount of CFB product or ag-lime applied was equivalent to 0.5, 1, and 2 times the lime requirement rate or 16.8, 33.6, and 67.2 Mg ha^{-1} of CFB product and 8.4, 16.8, and 33.6 Mg ha^{-1} of ag-lime, respectively. An untreated control where no CFB product or ag-lime was added to the soil was also included in the experimental design. These seven treatments were applied on June 1, 2004, to plots (3 m × 3 m) arranged in a randomized block with four replicates. Materials were incorporated to a depth of 20 cm with a rototiller. Preinoculated alfalfa seeds were planted at a rate of 13.4 kg ha^{-1} on June 4, 2004. Abundant rain in June and July 2004 in Wooster, OH, helped the alfalfa establish successfully.

The alfalfa plants were harvested two times in 2004 and three times in 2005. Alfalfa tissue was sampled by clipping a randomly selected 1-m^2 area from each plot. Alfalfa samples were air-dried in the greenhouse for 14 days, weighed, and ground to pass a 1-mm sieve. Total N in the alfalfa was determined by combustion method (*8*). Concentrations of other elements, including Ni and V, were determined by inductively coupled plasma (ICP) emission spectrometry after $HClO_4$:HNO_3 digestion (*9*).

On Aug 20, 2004, and Sept 1, 2005, five soil cores were collected from the 0 to 20-cm soil layer of each plot. Soil samples were air-dried, crushed, and passed through a 2-mm sieve. Subsamples were then either extracted with Mehlich III solution (*10*) or completely digested with acid using a microwave procedure (*11*). The concentrations of elements in the Mehlich III extracts and microwave digests were determined by ICP emission spectrometry.

Suction lysimeters were installed 60 cm below the soil surface in the control plots and in the plots receiving CFB product or ag-lime at the 2× lime requirement rate on Aug 24, 2004. Soil water was collected on March 21, 2005. NO_3-N and SO_4-S were determined by ion chromatography (*12*). Concentrations of other elements were determined by ICP emission spectrometry.

The results obtained for each of the dependent variables in this study were analyzed statistically using a model that included treatment and replication as independent variables. Data were subjected to analysis of variance (ANOVA) using the PROC GLM statement of the SAS statistics program (*13*). When the analysis generated a significant *F* value ($P \leq 0.05$) for treatments, the means were compared by the least significant difference (LSD) test using the appropriate error term to calculate the LSD value.

RESULTS AND DISCUSSION

Effects of CFB Product as a Lime Substitute on Alfalfa Growth. Mean dry weight yields of alfalfa from the two harvests in 2004 and three harvests in 2005 were all significantly ($P \leq 0.05$) increased by CFB product or ag-lime treatments (**Table 3**). Mean dry weight yields of alfalfa from the first harvest in 2004 were increased from 89 to 181% by CFB product or ag-lime. The highest yield was the treatment with CFB product at the 1× lime requirement (LR) rate. At the application rates of 0.5× LR and 1× LR, the yield of alfalfa was significantly greater when soil was treated with CFB product compared to ag-lime. The yields of alfalfa increased with an increase of ag-lime application rate. However, in the first harvest of 2004, the yield of alfalfa decreased when it was treated with CFB product at the 2× LR compared with the treatments at the 0.5× and 1× LR rate. This was probably because CFB product contained a large amount of dissolved salts that inhibited the germination and growth of alfalfa at the higher rate (*14*, *15*).

CFB product or ag-lime increased the yield of alfalfa 5−9 times compared with the untreated control in the second harvest in 2004 (**Table 3**). The growth of alfalfa treated with CFB product at the 2× LR rate was obviously improved compared to the first harvest. There were no significant differences in the yields between the three rates of CFB product. At the application rate of 0.5× LR, the yield of alfalfa was significantly higher when treated with CFB product than when treated with ag-lime. There were no significant differences in the dry weight of alfalfa between CFB product and ag-lime treatments or between the three application rates in the first and second harvests in 2005. At the application rate of 2× LR, the yield of alfalfa in the third harvest in 2005 was significantly higher when treated with CFB product than when treated with ag-lime (**Table 3**).

Cumulative yields of alfalfa from 2004 to 2005 are presented in **Figure 1**. CFB product or ag-lime increased the yields of alfalfa 3.8−4.6 times compared with the untreated control. The cumulative mean yields of alfalfa treated with CFB product were significantly ($P \leq 0.05$) higher than those of alfalfa treated with ag-lime, which were 8.44 Mg ha^{-1} by CFB product treatments

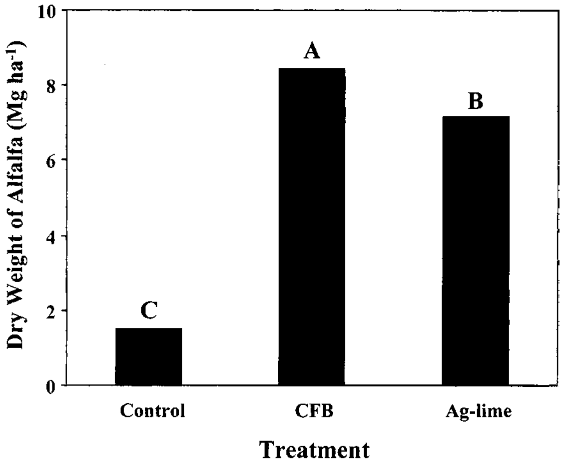

Figure 1. Cumulative dry weight of alfalfa (combining two harvests in 2004 and three harvests in 2005) as affected by CFB product or ag-lime treatments. Different letters over each bar represent a significant difference at $P \leq 0.05$.

and 7.15 Mg ha^{-1} by ag-lime treatments. These results clearly show a positive yield response when CFB product and ag-lime were applied to this site, indicating CFB product can be used as substitute for ag-lime in providing lime to soils.

Effects of CFB Product as a Lime Substitute on the Composition of Alfalfa Tissue. Concentrations in alfalfa of N, P, and K were generally increased by CFB product or ag-lime treatments compared to the untreated control (**Table 4**) because of the healthy growth of alfalfa under improved soil conditions. Concentrations of Ca, the major element in the CFB product and ag-lime, in the alfalfa tissue were not significantly different ($P \leq 0.05$) for CFB product as compared to the control plots. However, Ca concentrations in alfalfa tissue from the first harvest in 2004 were lower on ag-lime plots than the CFB product plots. Concentrations of Mg, the other major element in the ag-lime, were significantly greater in alfalfa when soil was treated with ag-lime compared to soil treated with CFB product. Magnesium concentration was decreased to below the adequate level of 2 g kg^{-1} for higher plants (*16*) by CFB product due to the Ca/Mg imbalance in this material (*14*). However, it did not reduce the growth of alfalfa (**Figure 1**), and there were no symptoms of Mg deficiency.

Concentrations in alfalfa of S, the other major element in CFB product, were generally increased by application of CFB product compared to ag-lime, especially in the first harvest in 2005. This is due to the increased availability for plant uptake of the added S in the CFB product (*17*). Deficiencies of S in crops is increasing due to reduced atmospheric inputs, use of more concentrated fertilizers containing little S, and increased S removal from soils caused by increased crop yields (*17*). The large input of S to soil by CFB product, as compared to ag-lime, is an additional benefit of the CFB product.

The concentration in alfalfa of Mo was greatly increased by the CFB product treatments (**Table 4**). It was 15−24 times greater when CFB product was applied at the 2× LR rate compared with the untreated control. This indicated that Mo in the CFB product (**Table 2**) was easily taken up by alfalfa. Plant

Table 4. Mean Concentrations in Alfalfa of Plant Essential Elements When Soil Was Treated with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

		CFB product			ag-lime			
element	control	0.5× LR[a]	1.0× LR	2.0× LR	0.5× LR	1.0× LR	2.0× LR	$LSD_{0.05}$
				2004 First Harvest				
				g kg^{-1}				
N	23.3 e[b]	33.4 b	33.1 b	36.0 a	28.0 d	30.5 c	34.0 ab	2.3
P	2.57 b	2.72 ab	2.66 ab	2.67 ab	2.79 a	2.66 ab	2.63 ab	0.20
K	25.7 b	32.9 a	32.1 a	31.4 a	30.6 a	32.4 a	30.7 a	4.8
Ca	11.8 abc	12.6 ab	12.7 ab	13.4 a	11.5 abc	10.5 c	11.0 bc	1.9
Mg	2.47 a	1.61 cd	1.55 d	1.75 c	2.32 ab	2.27 b	2.32 ab	0.19
S	3.55 a	3.31 ab	3.38 ab	3.59 a	3.26 ab	3.01 b	3.01 b	0.48
				mg kg^{-1}				
B	78.9 a	58.9 cd	55.1 d	62.6 c	70.9 b	61.0 c	58.7 c	5.8
Cu	21.0	20.3	20.4	21.3	24.1	20.1	22.1	5.5
Fe	146 b	155 ab	168 ab	184 a	141 b	144 b	138 b	33
Mn	603 a	155 b	131 b	206 b	276 b	187 b	141 b	154
Mo	0.50 c	6.01 b	7.50 a	7.91 a	0.64 c	0.79 c	0.84 c	1.24
Ni	5.35 a	4.61 ab	4.57 ab	4.49 ab	4.57 ab	3.68 b	3.75 b	1.02
Zn	62.7 a	33.9 c	33.5 c	33.2 c	46.2 b	39.3 c	37.9 c	6.7
				2005 First Harvest				
				g kg^{-1}				
N	33.8 c	39.0 a	36.6 ab	36.2 bc	35.6 bc	34.9 bc	35.7 bc	2.5
P	2.29 b	2.89 a	2.77 a	2.88 a	2.77 a	2.85 a	2.94 a	0.36
K	34.7 ab	35.6 ab	37.8 a	36.1 ab	34.2 ab	32.8 ab	31.1 b	5.8
Ca	15.3	15.5	15.0	14.0	13.7	13.4	14.8	2.7
Mg	2.22 b	1.46 c	1.49 c	1.48 c	2.98 a	3.18 a	3.34 a	0.49
S	2.71 b	3.95 a	4.03 a	3.91 a	2.72 b	2.82 b	3.01 b	0.35
				mg kg^{-1}				
B	19.5 a	16.7 ab	16.2 ab	13.1 ab	1.5 cd	0.5 d	9.5 bc	8.5
Cu	7.68 ab	7.74 ab	6.98 b	7.22 ab	7.74 ab	7.80 ab	8.43 a	1.25
Fe	64.4 bc	79.3 ab	81.5 ab	73.8 abc	60.9 c	69.7 abc	83.7 a	17.5
Mn	118.9 a	48.7 bc	49.0 bc	49.5 b	50.9 b	39.9 c	42.7 bc	9.1
Mo	0.58 c	9.89 b	13.57 a	14.40 a	0.68 c	1.53 c	2.27 c	2.05
Ni	2.98 a	1.97 bc	2.23 b	2.12 b	1.62 bcd	1.13 d	1.37 cd	0.63
Zn	36.8 a	22.7 cd	21.8 d	22.1 d	26.2 bc	27.3 b	27.2 b	3.8

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \leq 0.05$.

Table 5. Mean Concentrations (Milligrams per Kilogram) in Alfalfa of Nonessential Plant Elements When Soil Was Treated with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

		CFB product			ag-lime			
element	control	0.5× LR[a]	1.0× LR	2.0× LR	0.5× LR	1.0× LR	2.0× LR	$LSD_{0.05}$
				2004 First Harvest				
Al	128 ab[b]	108 ab	125 ab	145 a	107 ab	104 ab	90.3 b	42.7
As	2.25	2.25	2.25	2.80	2.25	2.38	2.25	0.64
Ba	54.1 a	7.76 cd	7.01 d	6.39 d	33.5 b	18.9 c	12.6 cd	11.6
Cd	0.76	0.37	0.76	0.27	0.43	0.35	0.39	0.54
Cr	1.91 ab	1.83 ab	2.06 a	1.97 ab	1.86 ab	1.78 b	1.92 ab	0.25
Pb	2.40	2.21	1.66	1.79	1.86	2.05	1.92	1.34
Se	5.00 b	8.24 ab	5.00 b	5.00 b	5.22 b	6.32 b	11.5 a	4.52
Sr	49.4 b	16.6 c	15.8 c	13.6 c	68.6 a	67.2 a	68.3 a	13.0
V	1.39 bc	1.56 b	1.54 bc	1.92 a	1.30 c	1.31 bc	1.30 c	0.26
				2005 First Harvest				
Al	64.3 a	48.1 ab	48.1 ab	45.5 ab	31.0 b	40.4 b	43.3 ab	23.2
As	2.25 c	2.30 c	2.82 bc	2.25 c	4.32 a	3.66 ab	2.25 c	1.31
Ba	109 a	15.2 d	9.0 d	7.0 d	46.7 b	34.9 c	31.0 c	9.5
Cd	0.33 a	0.16 b	0.16 b	0.15 b	0.11 b	0.12 b	0.22 ab	0.15
Cr	0.48 ab	0.43 ab	0.39 ab	0.29 b	0.51 ab	0.51 ab	0.62 a	0.30
Pb	2.72 b	1.00 c	1.00 c	1.00 c	4.31 a	4.13 a	3.90 ab	1.29
Se	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
Sr	68.6 d	24.4 e	20.1 e	17.2 e	92.0 c	131.5 b	214.3 a	15.5
V	0.63 bc	0.99 a	0.83 ab	0.54 c	0.50 c	0.50 c	0.55 c	0.27

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \le 0.05$.

tissue Mo concentration in the range of 10−20 mg kg^{-1} can cause adverse effects on animals (*18*). Therefore, Mo concentration should be monitored carefully when high rates of CFB product are applied. Concentrations of Fe were slightly increased when CFB product was applied. Concentrations of B, Mn, Zn, and Ni in alfalfa were greatly decreased by both the CFB product and ag-lime treatments compared to the control. This was probably due to increased soil pH causing decreased plant availability (*19*).

Our results indicated that Ni concentrations were not increased in alfalfa tissue, even when CFB product containing 358 mg kg^{-1} Ni was applied to the acidic soil. Bache et al. (*20*) reported that Ni was accumulated 5 times higher in Swiss chard (*Beta vulgaris* L.) grown in soils amended with 2% oil bottom ash than in Swiss chard grown in the control. Nickel uptake by plant varies greatly by plant species and cultivars. Concentrations of Ni were increased in basil (*Ocimum basilicum*) tissue but decreased in zucchini (*Cucurbita pepo*) tissue when grown in a growth medium amended with coal combustion products (*21*). Nickel uptake is affected by pedological factors, especially soil pH (*22*, *23*). Increasing the soil pH from 4.5 to 6.5 decreased the Ni content of oat grain by a factor of ≈ 8 (*19*). This agreed with our result that Ni in alfalfa tissue was decreased when CFB product was applied to acidic soil. Nickel is an essential element for higher plants. Nickel deficiency, which causes mouse ear disorder in pecan (*Carya illioinensis*) (*24*) and river birch (*Betula nigra*) (*25*), was found in the southeastern United States because of low soil Ni (*26*). The concentrations in alfalfa tissue of Ni were higher when CFB product was applied than when ag-lime was applied (**Table 4**). This indicated that CFB product provided Ni for plant growth. Phytotoxic Ni concentrations vary from 40 to 246 mg kg^{-1} depending on plant species and cultivars (*27*). The concentrations of Ni in alfalfa tissue treated by CFB product were far below the toxic levels (**Table 4**).

Table 5 shows concentrations in alfalfa of other elements that are potentially toxic to plants or regulated by the Resource Conservation and Recovery Act (RCRA). Concentrations of Ba were decreased in alfalfa growing on plots treated with CFB product or ag-lime compared to the untreated control. Furthermore, concentrations of Ba were greatly decreased by CFB product compared to ag-lime. This was probably due to precipitation of $BaSO_4$ on CFB product plots. Concentrations of other RCRA elements such as As, Cd, Cr, Pb, and Se were slightly decreased or not affected by the CFB product treatments. However, concentrations of As, Pb, and Se were occasionally increased when ag-lime was applied. The increases in Pb can be attributed to the Pb levels found in the ag-lime (**Table 2**). We do not have an explanation for the concentration increases in As and Se. Concentrations of Sr were decreased by the CFB product treatments but increased by the ag-lime treatments.

Concentrations of V in alfalfa tissue were generally increased when the CFB product was applied. The mean concentration of V in higher plants is 1.0 mg kg^{-1} and varies greatly depending on species and environments (*19*). The concentration of V in clover (*Trifolium* spp.) was 0.38−2.7 mg kg^{-1} when grown in an unpolluted area and 13.0 mg kg^{-1} when grown in the vicinity of a crude oil refinery (*19*). Tomato (*Lycopersicon* spp.) grown in an unpolluted area contained 0.5 mg kg^{-1} V, and that grown in the vicinity of a thermal power station contained V within the range of 0.8−1.7 mg kg^{-1}. Bache et al. (*20*) reported that when soils were amended with 2% oil bottom ash, V concentration in Swiss chard was increased to 25.1 mg kg^{-1} from 1.3 mg kg^{-1} in the control. The V uptake by plants decreased with increased soil pH (*19*). Although the CFB product contained high levels of V, the V concentration in alfalfa tissue was only slightly increased and far below the ceiling level when CFB product was used as a lime substitute. Overall, the results in plant tissue indicated that CFB product could be safely used as a soil amendment to improve growth of alfalfa on acid soils even at the 2× LR rate.

Effects of CFB Product as a Lime Substitute on the Soil Quality of Alfalfa Plots. Three and 15 months after application, soil pH was increased as the rates of CFB product or ag-lime increased (**Figure 2**). Three months after application at the 1× and 2× LR rates, the increase of soil pH was significantly ($P \le 0.05$) greater with CFB product than with ag-lime. The soil pH values were 6.1 and 6.5 with CFB product treatments at the 1× LR and 2× LR rates, whereas they were only 5.5 and 5.9 with ag-lime at the corresponding rates. Fifteen months after application, the increase of soil pH was significantly greater

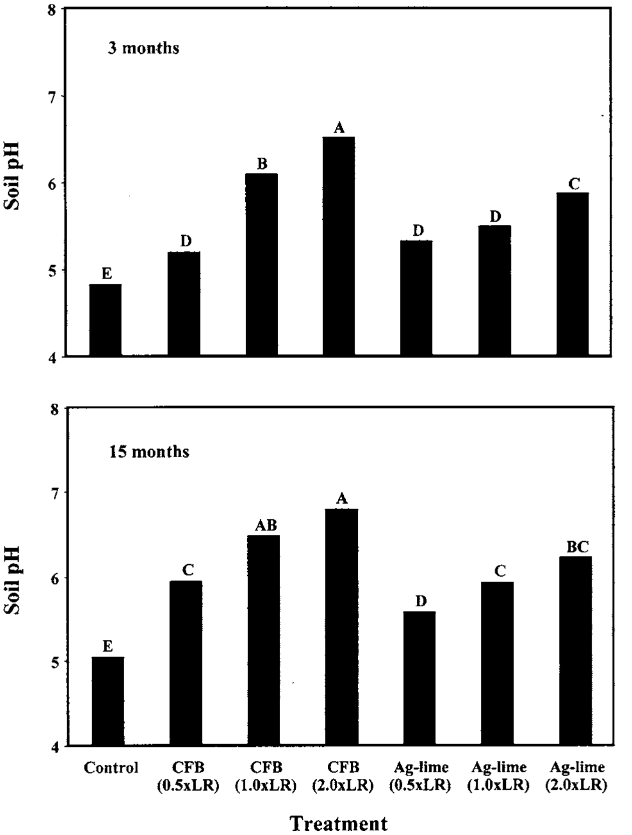

Figure 2. Effect of CFB product or ag-lime on soil pH at 3 and 15 months after application. Rates applied were 0.5, 1.0, and 2.0 times the LR of the soil. Different letters over each bar represent a significant difference at $P \leq 0.05$.

with CFB product than with ag-lime at the same LR rates. The soil pH values were 6.0, 6.5, and 6.8 with CFB treatments and 5.6, 5.9, and 6.2 with ag-lime treatments. This higher pH associated with the CFB treatment is because the primary source of alkalinity in the CFB product is portlandite [$Ca(OH)_2$] as compared to dolomite in the ag-lime. Portlandite is more soluble and reacts more rapidly than dolomite [$CaMg(CO_3)_2$]. Thus, for more rapid neutralization of surface soil acidity, the CFB product is more effective than ag-lime.

Mean concentrations of elements in Mehlich III extracts obtained from the 0−20-cm soil layer of the alfalfa plots 3 and 15 months after treatment of the soil with CFB product or ag-lime are presented in **Table 6**. Mehlich III is a weak acid extractant commonly used to estimate the availability of nutrients in the soil for plant uptake. Application of CFB product significantly ($P \leq 0.05$) increased the available concentrations of Ca, Mg, S, Cu, and Mo, whereas application of ag-lime significantly increased the concentration of only Mg and slightly increased the concentrations of Ca and Cu. When CFB product was applied at the 1× LR rate compared to the untreated control, available Ca concentration in the soil increased 4.4 times in 3 months and 5.3 times in 15 months, and available S increased 5.2 times in 3 months and 7.4 times in 15 months. All rates of CFB product application significantly decreased the extractable concentration of Al, whereas for ag-lime treatments, extractable Al decreased much less at the same application rates. In CFB product amended soil, Ca can reduce Al toxicity by replacing Al on exchange sites in the soil−plant root zone (*3*), and the SO_4^{2-} ion also can pair with Al in soil solution and increase leaching of the toxic Al. Sulfate pairing with Al has been reported to reduce its toxicity to plant roots (*28*) and increase root growth. CFB product or ag-lime also decreased the available concentrations of Fe because of high pH (*6*). Our results indicate that the CFB product not only effectively increased soil pH but also provided essential plant nutrients such as Ca, Mg, S, Cu, and Mo for plant growth, as well as ameliorated Al toxicity to plants.

Mean concentrations of plant essential or nonessential elements in soil (complete digest) from the 0−20-cm soil layer 3 and 15 months after treatments are presented in **Tables 7** and **8**. Application of CFB product significantly ($P \leq 0.05$) increased the concentrations of Ca, Mg, S, Mo, and Ni in the soil, whereas application of ag-lime increased the concentrations of only Ca and Mg. However, application of CFB product decreased the concentration of Zn. This was because Zn was released from soil particles and moved downward with water (**Table 9**) when CFB product was applied. Geometric mean Ni content in surface soil from major agricultural production areas of the United States is 16.5 mg kg^{-1}, ranging from 0.7 to 269 mg kg^{-1} (*26*). Even at the 2× LR rate of CFB product application, the concentration of Ni in the soil was 55.0 mg kg^{-1}, which was similar to the level in many untreated agricultural fields in California, Oregon, Washington, Maine, Louisiana, and Mississippi (*26*).

Compared to the untreated control, application of the CFB product at the 2× LR rate increased the concentration of V in soil by 1.3 times (**Table 8**). The V toxicity to plants varies with different soil types due to the variable phytoavailability. In sandy soil, 80 mg kg^{-1} V can reduce plant growth, whereas in loamy soil, concentrations >100 mg kg^{-1} do not affect plants (*19*). The concentration of V in the soil from our experimental plots did not reach toxic levels. Application of CFB product or ag-lime increased the soil concentrations of Sr due to both materials containing high levels of this element (**Table 2**).

Effects of CFB Product as a Lime Substitute on the Soil Water of Alfalfa Plots. Application of CFB product at 2× LR significantly increased the concentrations of macronutrients N (NO_3-N), K, Ca, Mg, and S (including SO_4-S) and micronutrients Fe, Mn, Ni, and Zn in soil water (**Table 9**). Concentrations of K, Ca, and Mg were increased 7−8 times compared to untreated control. Concentrations of NO_3-N and SO_4-S were increased 6.5 and 13.4 times, respectively, by CFB product. Because CFB product and ag-lime did not provide N, and soil water from plots with either CFB product or ag-lime treatment contained elevated concentrations of NO_3-N (**Table 9**), it is believed that this NO_3-N was released to soil water from alfalfa plants having improved growth and nodulation due to soil treatment. Manganese concentrations were increased 14.5 times. Soil water concentrations of Fe, Ni, and Zn were still very low, although they were increased by CFB product. Ca, Mg, and S (mostly SO_4-S) were probably from CFB product that moved downward, as observed by von Willert and Stehouwer (*29*) for gypsum and by Stehouwer et al. (*30*) for Mg-containing fluidized bed combustion byproduct. K, Fe, Mn, and Zn were released by cation exchange because Ca and Mg moved downward and replaced the ions of these elements on the adsorption complex (*4*). Nickel was probably from CFB product due to its high content in this material (**Table 2**).

The plant nonessential elements, Al and Sr, in soil water were increased by CFB product (**Table 9**). However, concentrations of RCRA-regulated elements such as As, Ba, Cd, Cr, Pb, Se, and V, an element with high concentration in CFB product, were not increased. Aluminum was probably released from soil particles because of Ca and Mg replacement as observed by Marsh and Grove (*31*) and Stehouwer et al. (*30*). This suggests that the the CFB product could reduce Al toxicity by leaching

Table 6. Mean Concentrations (Milligrams per Kilogram) of Elements in Mehlich-III Extract Obtained from the 0–20-cm Soil Layer of Alfalfa Field 3 and 15 Months after Treatment of the Soil with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

		CFB product			ag-lime			
element	control	0.5× LR[a]	1.0× LR	2.0× LR	0.5× LR	1.0× LR	2.0× LR	LSD$_{0.05}$
				3 Months				
Al	983 a[b]	910 ab	803 c	675 d	965 ab	934 ab	894 b	79
B	1.35 b	1.41 b	1.52 a	1.40 b	1.38 b	1.38 b	1.38 b	0.14
Ca	510 d	1370 c	2770 b	4120 a	622 d	658 d	938 cd	461
Cu	1.08 d	1.18 bc	1.38 a	1.22 b	1.12 cd	1.12 cd	1.18 bc	0.08
Fe	209 a	201 a	178 b	157 c	213 a	204 a	212 a	16
K	210 ab	248 a	216 ab	213 ab	191 ab	201 ab	162 b	62
Mg	71.8 d	92.1 d	123.8 c	148.9 b	121.9 c	157.6 b	229.1 a	22.3
Mn	69.6	63.8	65.4	71.5	69.9	62.7	66.1	14.7
Mo[c]	<0.10	0.14	0.20	0.12	<0.10	<0.10	<0.10	-
P	31.1 ab	38.2 ab	40.1 ab	41.2 a	35.1 ab	30.2 b	35.3 ab	10.9
S	58.5 c	329 b	361 ab	378 a	63.1 c	78.0 c	105 c	47.1
Zn	6.43	5.24	3.63	5.96	5.98	4.41	3.62	4.17
				15 Months				
Al	929 a	770 bc	720 c	499 d	869 ab	829 b	782 bc	100
B	2.64	2.79	2.90	3.08	2.68	3.63	2.88	1.01
Ca	506 e	1930 c	3210 b	4920 a	719 e	828 de	1110 d	325
Cu	1.03 c	1.23 a	1.25 a	1.20 ab	1.06 bc	1.10 abc	1.13 abc	0.15
Fe	199 a	155 bc	147 cd	130 d	167 b	164 bc	173 b	20
K	190	169	181	158	161	155	152	43
Mg	92.9 f	97.0 f	138 e	189 d	230 c	310 b	376 a	37.0
Mn	57.0	58.6	63.9	60.2	53.8	54.6	57.7	12.6
Mo	0.007 d	0.041 c	0.081 b	0.137 a	0.004 d	0.008 d	0.011 d	0.013
P	35.8	31.9	35.4	34.6	29.5	28.8	29.9	13.4
S	61.2 d	314 c	512 b	801 a	71.9 d	75.2 d	95.6 d	82.6
Zn	2.00 ab	2.16 ab	3.38 ab	5.35 a	1.09 b	1.02 b	0.98 b	3.66

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \leq 0.05$. [c] The 3 and 15 month samples were analyzed using different instruments and thus the differences in the reported levels of Mo in the two sets of samples.

Table 7. Mean Concentrations (Milligrams per Kilogram) of Plant Essential Elements in Soil (Complete Digestion) from the 0–20-cm Soil Layer 3 and 15 Months after Treatment of the Soil with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

		CFB product			ag-lime			
element	control	0.5× LR[a]	1.0× LR	2.0× LR	0.5× LR	1.0× LR	2.0× LR	LSD$_{0.05}$
				3 Months				
B	2.16 ab[b]	1.76 b	1.59 b	1.95 ab	2.51 ab	2.79 ab	3.13 a	1.24
Ca	672 d	2440 cd	7190 b	11400 a	1370 d	2100 cd	3800 c	2040
Cu	12.1	12.2	12.2	11.9	11.8	11.6	12.2	1.6
Fe	21000	20100	21100	19700	19600	20600	20400	3060
K	903	1017	859	822	944	934	899	210
Mg	1860 d	1910 cd	2120 cd	2100 cd	2210 c	2680 b	3590 a	320
Mn	561	564	569	561	560	555	550	47
Mo	1.04 c	1.45 bc	1.90 ab	2.53 a	1.43b c	1.21 bc	1.59 bc	0.85
Ni	23.4 d	28.4 bc	31.3 b	38.3 a	22.8 d	22.8 d	23.9 cd	4.6
P	455	452	420	439	448	436	451	53
S	275 c	1090 c	3190 b	5110 a	322 c	325 c	401 c	1080
Zn	61.2 a	56.6 ab	55.7 b	54.9 b	57.9 ab	58.2 ab	57.4 ab	5.5
				15 Months				
B	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	-
Ca	700 e	3160 cd	5770 b	13200 a	1480 de	2270 cde	3740 bc	2070
Cu	10.4 a	10.2 ab	9.8 abc	8.3 c	9.8 abc	8.3 bc	9.4 abc	1.9
Fe	20900 b	19800 b	23400 a	20000 b	20500 b	19700 b	21600 b	2280
K	1150	1340	1350	1130	1020	1280	1090	431
Mg	2310 d	2350 d	2630 cd	2780 c	2830 c	3260 b	4040 a	378
Mn	690	690	763	672	745	700	744	112
Mo	0.74 c	1.13 c	2.02b	3.19 a	1.10 c	0.75 c	1.07 c	0.61
Ni	33.3 c	36.8 c	47.5 b	55.0 a	30.5 c	30.6 c	34.5 c	6.3
P	521	499	554	482	494	483	524	74
S	332 c	994 bc	2090 b	5790 a	328 c	352 c	457 c	1210
Zn	88.0 ab	87.5 ab	94.3 a	87.3 ab	84.9 b	83.7 b	90.6 ab	8.9

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \leq 0.05$.

Al out of the rooting zone and is an effective subsoil acidity ameliorant. Strontium might come from CFB product that moved downward. However, none of the elements listed in **Table 9**, except for NO_3-N, were increased by ag-lime treatment.

Table 8. Mean Concentrations (Milligrams per Kilogram) of Plant Nonessential Elements in Soil (Complete Digestion) from the 0–20-cm Soil Layer 3 and 15 Months after Treatment of the Soil with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

		CFB product			ag-lime			
element	control	0.5× LR[a]	1.0× LR	2.0× LR	0.5× LR	1.0× LR	2.0× LR	$LSD_{0.05}$
				3 Months				
Al	11318	11304	10602	10150	11443	11467	11252	1453
As	21.2	17.2	20.3	14.1	19.8	20.0	19.5	9.5
Ba	92.7	92.7	87.3	88.7	93.9	92.3	89.9	12.4
Cd	1.01 ab[b]	1.10 a	0.99 ab	0.68 b	0.94 ab	0.92 ab	0.76 ab	0.34
Cr	23.3 ab	28.2 a	22.5 b	22.6 b	23.6 ab	23.1 ab	25.4 ab	5.3
Pb	20.2 ab	18.3 b	21.7 ab	19.3 ab	20.9 ab	20.2 ab	22.0 a	3.4
Se	10.0	10.8	15.3	12.6	13.1	10.0	15.5	8.2
Sr	7.2 c	7.9 c	10.0 bc	13.5 b	10.3 bc	13.6 b	22.4 a	4.8
V	26.7 c	32.4 c	46.3 b	61.3 a	25.8 c	27.0 c	26.6 c	8.0
				15 Months				
Al	16400	16500	17500	15100	15800	16200	15500	2630
As	14.6 a	8.90 b	12.5 ab	9.54 b	10.6 b	9.33 b	11.1 ab	3.66
Ba	98.8	106	111	100	104	103	98.8	16.8
Cd	0.56 b	0.53 b	0.68 a	0.56 b	0.57 b	0.50 b	0.60 ab	0.10
Cr	37.2 ab	34.9 ab	41.1 a	35.1 ab	31.1 b	34.0 ab	37.1 ab	7.8
Pb	18.5 abc	16.3 bcd	18.9 ab	17.0 bcd	16.1 cd	15.7 d	20.2 a	2.7
Se	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
Sr	9.91 d	11.7 d	12.8 cd	15.7 bc	13.1 cd	17.6 b	23.7 a	3.2
V	36.6 d	47.6 c	66.1 b	85.6 a	35.1 d	36.2 d	36.4 d	10.5

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \leq 0.05$.

Table 9. Mean Concentrations (Milligrams per Liter) of Elements in Soil Water from the 60-cm Soil Depth at 9 Months after Treatment of the Soil with the Circulating Fluidized Bed (CFB) Product or Agricultural Lime (ag-lime)

element	control	2.0× LR[a] CFB product	2.0× LR ag-lime	$LSD_{0.05}$
		Plant Essential Elements		
B	0.029	0.027	0.026	0.013
Cu	<0.01	<0.01	<0.01	
Fe	0.012 b[b]	0.027 a	0.010 b	0.015
K	0.99 b	7.28 a	1.67 b	2.89
Mg	8.0 b	56.4 a	13.7 b	11.9
Mn	0.19 b	2.92 a	0.09 b	1.84
Mo	<0.01	<0.01	<0.01	
N (NO_3-N)[c]	0.37	3.14	2.33	1.05
Ni	0.015 b	0.090 a	0.015 b	0.036
P	<0.10	<0.10	<0.10	
S	31.6 b	353.4 a	64.3 b	65.3
SO_4-S	29.5 b	390 a	66.9 b	80.2
Zn	0.016 b	0.074 a	0.011 b	0.038
		Plant Nonessential Element		
Al[d]	0.19	2.80	<0.04	
As	<0.045	<0.045	<0.045	
Ba	0.11	0.03	0.10	0.09
Cd	<0.002	<0.002	<0.002	
Cr	<0.005	<0.005	<0.005	
Pb	<0.06	<0.06	<0.06	
Se	0.100	0.100	0.105	0.007
Sr	0.23 b	0.71 a	0.33 b	0.21
V	0.030	0.020	0.024	0.022

[a] Lime requirement. See **Table 3** for definition. [b] Different letters in the same row represent a significant difference at $P \leq 0.05$. [c] N concentration in two control samples, one CFB product treatment sample and one ag-lime treatment sample, was below determination limit (0.10 mg L^{-1}). Data shown are means using 0.10 mg L^{-1} for those samples having N concentrations below the detection limit. [d] Al concentration was below determination limit (<0.04) in two control plot samples and four ag-lime plot samples. Data shown for the control are the mean of the four samples using 0.04 for the two samples below determination limit.

These results suggested that CFB product affected both the topsoil and subsoil layers but that ag-lime affected only the topsoil.

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