Field Application of Reduced Crude Conversion Spent Lime

Brian H. Marsh, John H. Grove

Abstract—Gypsum is being applied to ameliorate subsoil acidity and to overcome the problem of very slow lime movement from surface lime applications. Reduced Crude Conversion Spent Lime (RCCSL) containing anhydrite was evaluated for use as a liming material with specific consideration given to the movement of sulfate into the acid subsoil. Agricultural lime and RCCSL were applied at 0, 0.5, 1.0, and 1.5 times the lime requirement of 6.72 Mg ha^{-1} to an acid Trappist silt loam (Typic Hapuldult). Corn [*Zea mays* (L.)]was grown following lime material application and soybean [*Glycine max* (L.) Merr.]was grown in the second year. Soil pH increased rapidly with the addition of the RCCSL material. Over time there was no difference in soil pH between the materials but there was with increasing rate. None of the observed changes in plant nutrient concentration had an impact on yield. Grain yield was higher for the RCCSL amended treatments in the first year but not in the second. There was a significant increase in soybean grain yield from the full lime requirement treatments over no lime.

Keywords—Soil acidity, corn, soybean, liming materials.

I. INTRODUCTION

FLUIDIZED bed combustion is a method for scrubbing sulfur (S) from refinery emissions. It contains Ca and Mg oxides and sulfates that can be used as a liming material. Liming acid soils improves base cation (Ca, Mg) status and reduces excessive Al and Mn availability. However, the lime reaction is generally limited to the depth of incorporation. Gypsum and by-product gypsum have been used to increase Ca and SO_4^{2-} movement into the subsoil in an effort to ameliorate acidity effects [1], [2]. Improved root growth has be attributed to improved soil Ca status or to the formation of less toxic Al species ($AlSO_4^+$) or Al^{3+} precipitation [3]. Greater root development and subsequent increased water extraction within the soil profile has been observed where gypsum had been surface applied [4].

Root growth has been related to Al activity [5], Ca activity [6], or a combination of Ca and Al activity [7] in greenhouse and nutrient solution experiments. Field verification of the relationship between root growth and solution chemistry is very limited [8].

The objectives of this research were to evaluate the efficacy of RCCSL in soil acidity control over time and monitor effects on the yield and elemental composition of corn and soybean with special emphasis on potential heavy metal accumulation.

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II. MATERIALS AND METHODS

The study was conducted near Bardstown, Kentucky on a Trappist silt loam (clayey, mixed, mesic Typic Hapuldult). The field had been in grass pasture for several years prior to moldboard plowing for this study. The experiment consisted of a two by four factorial combinations of treatments laid out in a randomized complete blocks with four replications. Plots were 3.6m (four 0.91m rows) wide by 9.1m long with a 6m border between replications. Two lime sources at four rates {0, 0.5, 1.0 and 1.5 times the lime requirement (LR) of 6.72 Mg ha^{-1}} were hand-spread and incorporated with a disc prior to planting. The soil lime requirement was determined by the method of Shoemaker et al. [9]. Lime sources were traditional dolomitic agricultural limestone (ag lime) and Reduced Crude Conversion Spent Lime (RCCSL). Calcium carbonate equivalent values were 94% and 105%, respectively. Ag lime contained 660 g kg^{-1} Ca and 220 g kg^{-1} Mg as carbonates and had a particle diameter size distribution of 64 g kg^{-1}> 1.65mm (10 mesh), 335 g kg^{-1}, 1.65 mm and > 0.25 mm (40 mesh) and 579 g kg^{-1}< 0.25 mm. RCCSL is a refinery by-product containing 410 g kg^{-1} CaO, 190 g kg^{-1} MgO, and 310 g kg^{-1} anhydrite ($CaSO_4$). Additional physical and chemical properties are described elsewhere [10]. Phosphorus and K fertilizers were applied at 56 kg P ha^{-1} and 84 kg K ha^{-1} as $Ca(H_2PO_4)_2$ and KCl, respectively, according to University of Kentucky recommendations [11] before a second discing. Corn [*Zea mays* (L.) 'Pioneer 3233'] was planted on 13 May at 57,000 seeds ha^{-1}. Good pest control was achieved with appropriate and recommended insecticide and herbicide applications at planting. Nitrogen was applied at 168 kg N ha^{-1} as NH_4NO_3. Ear leaves (10 plot^{-1}) were taken on 2 August at mid-silk (R1). Two center rows (6.08 m in length) were hand harvested on 26 September. A subsample was collected for grain analysis. Soil cores (10 plot^{-1}) were taken on 9 January to a depth of 30 cm for surface soil analysis.

Phosphorus and K were applied at 34 kg P ha^{-1} and 56 kg K ha^{-1} on 13 May in the second year of the study followed by moldboard plowing. Appropriate herbicides were applied and disc-incorporated to control the weed species present. 'Sparks' soybean [*Glycine max* (L.) Merr.] was planted on 19 June at 23 seeds m^{-1} of row. Trifoliate leaf samples (20 plot^{-1}) were taken on 9 August at growth stage R1. The two center rows were harvested with a small plot combine on 3 November. Soil samples were taken on 9 January as previously described. Plant tissue samples were force air dried and ground for analysis. Tissue N and P were determined simultaneously on a micro-Kjeldahl digest. Nitrogen was determined by phenol blue (Berthelot) reaction and P by the molybdenum blue reaction. Samples were wet-ashed with concentrated 9:1 nitric-perchloric acid, dried and dissolved 1*M*HCl for analysis

of cations by atomic absorption spectroscopy. Sulfur was determined using the same digest method as for cations with analysis by turbidimetric reaction with $BaCl_2$.

Soil cores were air dried at room temperature and crushed to pass a 2 mm screen. Soil pH was measured in deionized water and MKCl at a 2.5:1 solution to soil ratio. A soil extraction for water soluble constituents (0.075 kg soil: 0.075L water, four hour equilibration time) was performed. Cations were determined by atomic absorption spectroscopy. Anions were determined by ion chromatography. Electrical conductance (EC) was also measured. Adsorbed K, Ca, Mg and Na were determined by atomic absorption spectroscopy from a single extraction with MNH$_4$OAc using a solution to soil ratio of 5:1 and a shaking time of 30 minutes. A MKCl extraction was used with the same ratio and shaking time for extractable acidity, Al, Mn and NH_4^+. Manganese was analyzed by atomic absorption and NH_4^+ by the Berthelot reaction. Extractable acidity and Al were determined by titration in the presence and absence of F [12].

III. RESULTS AND DISCUSSION

The pH is the most widely used measurement of soil acidity. The lime source by rate interaction for soil pH, measured in H_2O or MKCl, was significantly different when measured eight months after application (Table I). The change in pH$_{KCl}$ was less for all ag lime rates than for 0.5 LR RCCSL. Twenty months following lime application more of the ag lime had reacted. As a result, though the main effect of source or rate was significant, the lime source by rate interaction was not significant (Table II). Higher application rates of either source raised soil pH, and pH$_{KCl}$ increased more by RCCSL than ag lime, but the divergence in the pH versus rate function between the two sources was not evident.

A significant source by rate interaction was observed for various water extractable soil ions. Calcium and Mg levels increased with increasing rate in ag lime amended plots, however the increase was greater with increasing RCCSL rates. Sulfate and EC displayed similar significant source by rate interaction effects. A significant source by rate interaction was still evident for EC and water extractable Ca, Mg and SO_4^{2-} one year later.

TABLE I
SOIL CHEMICAL CHARACTERISTICS (YEAR 1)

	pH		Water Extractable			
	H_2O	KCl	EC†	Ca	Mg	SO_4^{2-}
			S m^{-1}	------ mg kg^{-1} ------		
Ag Lime						
0.0 LR	5.2	4.8	0.09	8.6	1.5	3.9
0.5 LR	5.5	5.2	0.11	10.3	2.5	5.0
1.0 LR	5.8	5.4	0.12	10.4	3.5	5.0
1.5 LR	6.0	5.4	0.15	13.6	4.4	5.4
RCCSL						
0.0 LR	5.5	5.1	0.11	9.7	2.4	3.9
0.5 LR	6.2	6.1	0.29	29.1	8.5	20.3
1.0 LR	6.4	6.3	0.46	49.1	16.4	39.1
1.5 LR	6.2	6.1	1.39	43.4	13.5	38.7
LSD$_{0.05}$	0.3	0.3	0.13	14.9	5.6	15.9

† Electrical Conductance

TABLE II
SOIL PH, EC AND EXTRACTABLE CA, MG AND SULFATE (YEAR 2)

	pH		Water Extractable			
	H_2O	KCl	EC†	Ca	Mg	SO_4^{2-}
			S m^{-1}	-------- mg kg^{-1} --------		
Ag Lime	5.0	4.6	0.15	10.6	3.0	3.9
RCCSL	5.2	4.9	0.20	16.4	6.2	12.7
	Ns	*	*	*	*	*
0.0 LR	4.8	4.5	0.15	10.5	1.9	3.0
0.5 LR	5.0	4.6	0.16	13.5	2.6	6.4
1.0 LR	5.2	4.7	0.20	15.1	3.7	11.9
1.5 LR	5.3	5.1	0.20	15.2	3.9	11.7
	0.3	0.4	ns	3.9	1.0	5.6
Ag Lime						
0.0 LR	5.4	4.3	0.15	10.9	1.9	2.6
0.5 LR	5.9	4.8	0.12	9.5	1.6	3.2
1.0 LR	6.3	5.3	0.16	11.4	3.1	4.5
1.5 LR	6.2	5.3	0.15	10.8	2.7	5.1
RCCSL						
0.0 LR	5.6	4.6	0.14	9.9	1.9	3.4
0.5 LR	6.0	5.0	0.20	17.4	3.6	9.6
1.0 LR	7.0	5.9	0.23	18.7	4.2	19.4
1.5 LR	7.0	6.0	0.24	19.5	5.1	18.2
LSD$_{0.05}$	ns	ns	0.05	4.3	1.1	5.8

A significant main effect was observed after year one for water extractable K, NH$_4$OAc extractable CA and Mg, which were higher in RCCSL amended plots (Table III). Water extractable K increased in RCCSL amended plots because of the greater solubility of RCCSL which supplied more Ca and Mg to the soil solution followed by exchange reaction of Ca and Mg for K and Al. KCl extractable Mn decreased with RCCSL usage because of the greater solubility and reactivity of the RCCSL material causing a precipitation of Mn with the pH change. NH$_4$OAc extractable Ca and Mg increased and KCl extractable Mn declined as the rate of either source increased through mass action exchange and precipitation, respectively, as pH increase with increasing lime rate.

TABLE III
EXTRACTABLE CATIONS (YEAR 1)

	Extraction Solution			
	H_2O	KCl	NH$_4$OAc	
	K	Mn	Ca	Mg
	------------------------- mg kg^{-1} -------------------------			
Ag Lime	2.2	1.8	670	120
RCCSL	3.1	0.8	762	131
	*	*	*	Ns
0.0 LR	2.2	2.4	685	106
0.5 LR	2.4	1.1	691	110
1.0 LR	2.9	0.8	709	138
1.5 LR	3.0	0.9	780	148
LSD$_{0.05}$	ns	0.5	230	21

Many of these effects were still evident 20 months following application (Table IV). Significant decreases in KCl extractable Mn and acidity (Al+H) were observed as application rate increased. NH$_4$OAc extractable Mg increased significantly with increasing rate average across lime sources. NH$_4$OAc extractable Ca was higher in RCCSL amended plots

while KCl extractable Mn was lower in the same plots. There was a trend for higher levels of NH_4OAc extractable Ca as the application rate of either source increased.

TABLE IV
SOURCE AND RATE MAIN EFFECT ON SOIL CHEMICAL CHARACTERISTICS (YEAR 2)

	Extraction Solution				
	H_2O	KCl		NH_4OAc	
	K	Mn	Al + H	Ca	Mg
	--- mg kg^{-1} ---		cmol$_c$ kg^{-1}	------- mg kg^{-1} ------	
Ag Lime	3.2	9.1	0.48	670	120
RCCSL	3.9	6.8	0.37	762	131
	ns	*	ns	*	ns
0.0 LR	3.6	10.6	0.68	685	106
0.5 LR	3.5	7.7	0.38	691	110
1.0 LR	3.9	7.5	0.28	709	138
1.5 LR	3.3	5.8	0.35	780	148
LSD$_{0.05}$	ns	2.5	0.22	ns	21

Plant tissue composition was only moderately affected by the different lime sources. Corn ear leaf S concentration was significantly affected by the source by rate interaction (Table IX). Unlimed plots and those receiving ag lime had a constant, adequate S level [13]. Ear leaf S levels increased as the RCCSL rate increased because of the higher soil solution S levels from the sulfate component of RCCSL.

A slight increase in ear leaf K was observed with RCCSL usage (Table V) although levels averaged over rates for both sources were below accepted sufficiency levels despite the moderately high rate of fertilizer K applied. Water extractable K was higher in RCCSL amended plots but NH_4OAc extractable K was not. Increased exchangeable K following gypsum application has been reported [3]. It is not entirely known by what mechanism the RCCSL material played it small role in improved K nutrition; whether chemically by changing K availability or by improving root growth with resulting benefits to K uptake. Soybean root length density increased with RCCSL [14]. It is not known if the same occurred with corn roots. Positive correlation between root length density and K uptake has been reported [15].

TABLE V
CORN EAR LEAF COMPOSITION AT R1

	P	K	Ca	Mg	Mo	Mn	Zn
	--------------- mg g^{-1} ---------------				------ mg kg^{-1} ------		
Ag Lime	3.1	13	4.6	3.3	0.73	56	22
RCCSL	3.1	14	4.4	3.1	0.78	58	21
	ns	*	ns	ns	ns	ns	ns
0.0 LR	3.1	14	4.5	2.8	0.60	60	22
0.5 LR	3.1	13	4.7	3.3	0.80	55	23
1.0 LR	3.1	13	4.4	3.4	0.76	57	20
1.5 LR		14	4.4	3.6	0.87	55	23
LSD$_{0.05}$	0.2	ns	ns	ns	0.19	ns	ns

Corn ear leaf Mg and Mo concentrations were significantly and positively affected by lime rate (Table V). Magnesium concentrations continued to increase as rate increased. Both lime materials contained Mg. Molybdenum concentration increased with the initial lime addition then remained relatively constant. Molybdenum availability increases with pH increases. All other measured ear leaf elemental concentrations were not affected by lime rate. The elemental composition of corn grain was not affected by lime source or rate (Table VI). This included other heavy metals of concern (data not shown).

TABLE VI
CORN GRAIN COMPOSITION

	P	K	Ca	Mg	S	Mn	Zn	Pb
	--------------- mg g^{-1} ---------------					------ mg kg^{-1} ----		
Ag Lime	2.6	4.6	0.10	0.94	0.77	6.7	24	0.28
RCCSL	2.6	4.8	0.11	0.98	0.77	6.8	26	0.64
	ns	ns	ns	ns	ns	ns	ns	ns
0.0 LR	2.7	4.8	0.11	0.94	0.74	7.1	24	0.23
0.5 LR	2.7	4.8	0.11	0.97	0.76	6.6	25	0.60
1.0 LR	2.5	4.6	0.11	0.95	0.75	6.5	27	0.53
1.5 LR	2.6	4.8	0.10	0.98	0.73	6.7	25	0.49
LSD$_{0.05}$	ns	ns	ns	ns	ns	ns	ns	ns

Soybean trifoliate P concentrations were slightly higher in RCCSL amended plots (Table VII) but all were within sufficiency levels. Manganese and Zn levels declined as lime rate increased. The availability of Mn and Zn decreases with increases in pH. No other elements were affected by lime source or rate. Soybean grain composition was more responsive to treatments than was corn grain. No changes were observed due to lime source (Table VIII) but a significant main effect of rate was observed for several elements. Grain P increased with increasing lime rate, similar to trends in the trifoliate concentration response for these two elements. Grain Ni decreased with the first lime increment, then remained constant. Grain Pb rose as the lime rate increased.

TABLE VII
SOYBEAN TRIFOLIATE COMPOSITION AT R1

	P	K	Ca	Mg	S	Mn	Zn
	----------------- mg g^{-1} -----------------					- mg kg^{-1} -	
Ag Lime	4.2	19.5	10.7	3.8	0.27	89	40
RCCSL	4.5	19.4	10.9	3.9	0.27	83	41
	*	ns	ns	ns	ns	ns	ns
0.0 LR	5.6	23	3.1	1.9	3.1	65	47
0.5 LR	5.8	23	3.2	1.9	3.1	48	48
1.0 LR	5.8	22	3.0	1.9	3.0	42	43
1.5 LR	6.1	23	3.1	1.9	3.1	39	43
LSD$_{0.05}$	0.2	ns	ns	ns	ns	14	4

TABLE VIII
SOYBEAN GRAIN COMPOSITION

	P	K	Ca	Mg	S	Mn	Zn	Ni	Pb
	---------- mg g^{-1} ----------					-------- mg kg^{-1} --------			
Ag Lime	5.8	23	3.1	1.8	3.0	53	46	8.5	6.2
RCCSL	5.9	23	3.1	1.9	3.1	44	44	7.9	5.6
	ns	ns	ns	ns	ns	ns	ns	ns	ns
0.0 LR	5.6	23	3.1	1.9	3.1	65	47	10.6	8.4
0.5 LR	5.8	23	3.2	1.9	3.1	48	48	7.8	4.4
1.0 LR	5.8	22	3.0	1.9	3.0	42	43	7.0	6.4
1.5 LR	6.1	23	3.1	1.9	3.1	39	43	7.1	7.2
LSD$_{0.05}$	0.2	ns	ns	ns	ns	14	4	2.5	3.0

Corn yields were severely affected by drought during the growing season. The yield variability increased as a result. RCCSL amended plots did yield 0.6 Mg ha^{-1} more than ag lime amended plots and this was significant at the 90% level of confidence (Table IX). The higher leaf K level observed in RCCSL amended plots may have been part of the reason for the yield response. Another reason may be related to the fact that lime materials were applied only one day before planting. The recommended timing for lime applications is 6 to 13 months prior to planting to allow the ag lime sufficient time to react. Early season rainfall was probably adequate of reaction of the fine particles of ag lime. The rapid reactivity of the oxides in the RCCSL material allowed for greater pH change early in the season when rainfall was adequate, whereas ag lime had only partially reacted. Corn yields increased 1.3 Mg ha^{-1} as the average lime rate was raised from unlimed to 1.5 LR, but because of variability, the yield was significant at only the 85% level of confidence. Soybean yields were not significantly different between lime sources. Soybean yields increased as rate increased up to 1.0 LR averaged across lime sources.

TABLE IX
YIELD AND S AS RELATED TO LIME SOURCE AND RATE

	Yield		Corn Ear Leaf	
	Corn	Soybean		S
	-- Mg ha^{-1} --			mg g^{-1}
Ag Lime	5.02	2.08	Ag Lime	
RCCSL	5.52	1.79	0.0 LR	2.3
	§	ns	0.5 LR	2.2
			1.0 LR	2.2
			1.5 LR	2.2
			RCCSL	
0.0 LR	4.77	1.65	0.0 LR	2.2
0.5 LR	5.20	1.96	0.5 LR	2.5
1.0 LR	5.20	2.33	1.0 LR	2.5
1.5 LR	5.83	2.14	1.5 LR	2.6
LSD$_{0.05}$	ns	0.43		0.1

§Significant at the 90 % level of confidence

IV. CONCLUSIONS

The changes in soil chemistry were a direct result of the solubility and reactivity of the two materials. Levels of water extractable CA, Mg, SO421, EC and pH were higher with RCCSL amended plots. The effect was diminished over time.

The use of RCCSL generally did not affect plant tissue composition in a manner different from that observed for ag lime. The few exceptions were for corn ear leaf S and K and soybean trifoliate leaf P. The small increases in S and P did not affect yield as all levels were above accepted sufficiency concentrations.

The results of yield varied due to vastly different weather conditions that were evident between the two cropping years. In the first growing season following material application, which was very dry, RCCSL usage improved corn yields over that achieved with ag lime. However, in the following season where rainfall was dwell distributed, no such increases in yield were observed.

The RCCSL material appears suitable for agricultural use as a liming material. However, other areas of concern need to be addressed. The highly reactive nature of the material may increase plant tissue levels of undesirable elements if these elements are natively high in the soil.

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