THE USE OF ATMOSPHERIC FLUIDIZED BED COMBUSTION WASTE AS A LIMING AGENT I: A GREENHOUSE STUDY[1]

by

R.I. Barnhisel and W.O. Thom[2]

Abstract - - The primary objective of this study was to evaluate atmospheric fluidized bed combustion (AFBC) waste as a substitute for calcium carbonate. Several factors were considered in this evaluation; however, the ones to be presented here have been limited to the effect wetting and drying had on changes in soil pH following mixing of various amounts of AFBC or $CaCO_3$ with an acidic soil collected from a surface mine reclamation project in western Kentucky and how these liming agents affected the growth of alfalfa and soybeans. Both materials rapidly raised the pH of this acidic soil to a value consistent with the amount applied. When rates of AFBC exceeded twice that needed to bring the soil to the target pH 6.4 value, the pH's were in the range that would likely produce adverse effects on plant growth.

Another objective of this study was to determine if AFBC waste had an adverse effect on alfalfa and soybean seed germination. Both AFBC and $CaCO_3$ were applied to the acidic soil at various rates. Even when excessive rates of AFBC waste were applied, there were no adverse effects on soybean germination, but decreases were observed for alfalfa. When the soil was allowed to equilibrate prior to planting the alfalfa seed, the effect of excessive rates of AFBC on alfalfa germination diminished significantly. It is likely that this observation was a function of the pH achieved and other associated chemical reactions when these excessive AFBC rates were applied.

Introduction

In the atmospheric fluidized bed combustion process, finely-ground limestone and coal are suspended, or fluidized, in the combustion chamber. The sulfur in the coal reacts with calcium in the limestone to form calcium sulfite; however, the resulting AFBC waste is a mixture of calcium sulfite, metal oxides, silicates, and unreacted calcium oxide. Following equilibration with moisture and air, $CaSO_4$ and $Ca(OH)_2$ are more likely to be the ingredients of the AFBC waste rather than CaO and $CaSO_3$. Research by Hern et al. (1977) has shown AFBC to have a neutralizing potential equivalent to about 50% that of ground Ag lime, although the potential may be as low as 33%. Terman et al. (1978) have shown that the finer fraction (<100 mesh) of AFBC had 47% and the coarse fraction 8% in relative effectiveness as compared to finely-ground calcium carbonate when mixed with Mountview silt loam soil of pH 5.2. Their research also indicated that the coarse fraction of AFBC was 44% as effective as fine calcium carbonate for changing pH of coal mine spoil sampled 10 months after mixing the materials with the spoil. The AFBC material has a potential for use as a source of Mg and S, and required two times the material when compared to calcium hydroxide in a study by Stout et al. (1979). In other research, Stout et al. (1982) indicated that the coarse size (0.5-2 mm) of the AFBC limited the effectiveness of the material as a liming agent by not raising soil pH as much as Ag lime. Having both fine and coarse fractions in AFBC may be important to allow some material to react faster while some material either reacts more slowly or is delayed, which will spread the effectiveness of the AFBC over a longer period. Certainly not all of the material should be fine, as this fraction may change soil pH too drastically and thus delay or prevent germination of some crop seeds.

Some concerns of heavy metal availability from the AFBC were addressed in research by Stout et al. (1982). They indicated that the resulting plant material from 5.2 and 10.4 tons AFBC/acre contained low levels of Zn, Cu, Cd, Pb, and Mn, while the extractable spoil level of Pb was the only element to be significantly increased. Spoil pH was increased from 4.5 to 5.1 and 5.6 for 5.2 and 10.4 tons AFBC/acre, respectively. This lack of a large pH change was due to the large size (0.5-2.0 mm) of the applied AFBC.

1 Contribution from the Ky. Agr. Exp. Sta., Dept. of Agronomy, Univ. of Kentucky, Lexington KY. Funded by a TVA Contract No. TV-60443A.

2 Professor of Agronomy and Geology and Associate Extinsion Professor of Agronomy, respectively.

Proceedings America Society of Mining and Reclamation, 1986 pp 65-70

DOI: 10.21000/JASMR86010065

https://doi.org/10.21000/JASMR86010065

Methods and Materials

The soil used in this study was taken from a stockpile on the Sinclair Surface Mine in western Kentucky operated by Peabody Coal Co. This was a mixture of Ap, B2 horizons of Sadler silt loam (Glossic Fragiudalf; fine-silty, mixed mesic), Belknap silt loam (Aeric Fluvaquent, coarse-silty, mixed, acid, mesic), and Zanesville silt loam (Typic Fragiudalf, fine-silty, mixed mesic), and was collected from the same stockpile as for other studies (Huntington et al., 1980; Boyle et al., 1982; and Barnhisel et al., 1985). This soil was highly acidic, with a SMP lime requirement of about 18 Mg ha^{-1}. This soil mixture also tested very low in phosphorus and medium in potassium. In cases where alfalfa or soybeans were planted, appropriate amounts of P and K fertilizers were used based on rates recommended in AGR 40 (Barnhisel, 1976).

Determination of $CaCO_3$ equivalence of AFBC Waste

AFBC waste, as received, encompassed a wide range of particle sizes. This material was passed over a series of sieves with the following openings: 10, 2, 1, and 0.5 mm. The bulk of the material passed through the 1 mm sieve and was retained on the 0.5 mm sieve. The calcium carbonate equivalence was determined on each fraction, i.e., >10, 10-2, 2-1, 1-0.5 and <0.5 mm, by weighing out 1-2 g of each fraction in triplicate on an analytical balance. These materials were placed in beakers, and standardized 0.1N HCl acid was added in excess to insure complete reaction. The samples were stirred overnight with a magnetic stirrer and the excess HCl back-titrated with standardized base. Except for the >10 mm fraction, all of these had a $CaCO_3$ of about 50%.In a similar way, the $CaCO_3$ used in the study was also evaluated. The amount of AFBC or $CaCO_3$ required to raise the pH of the acidic spoil to pH 6.4 was calculated. This quantity of AFBC or $CaCO_3$ will be referred as the 1X rate. The actual amount of liming agent varied between the three experiments reported here, since the amount of soil used was different in each of these cases. In all of the studies reported here, only the 1.0-0.5 mm size fraction of AFBC waste was used.

Effect of Wetting and Drying

Twenty-five grams of soil, crushed to pass a 2 mm sieve, were placed in a series of 100 ml plastic beakers. The following lime rates were used: 0, 0.5X, 1X, and 2X of pure $CaCO_3$ and 0.5X, 1X, 2X, 3X, and 4X of AFBC waste. A stirring rod was placed in each beaker and the lime thoroughly mixed with the soil in the dry state. Then 25 g of deionized water was added, the samples stirred to mix the water and soil, and the pH determined after 30 minutes. This treatment will be called zero equilibration time. These, as well as subsequently described conditions, were repeated in duplicate.

A second set of samples was prepared as above, however, following the addition of the 25 g of water, the samples were not stirred but were allowed to dry, which required about one week. Water was added and the drying sequence repeated. After the second week, 25 g of water was added, then the samples were stirred and the pH measured. Similar sets of samples were prepared, except the wetting-drying cycles were repeated 4 and 8 times. An identical series of samples was prepared as above, except in this case the samples were stirred following each addition of water.

Two additional sets of samples were prepared, except they were not allowed to dry. One set was stirred, the other was not stirred except just prior to measuring the pH. These samples were covered with plastic film and some water was added every 2-3 days to keep the water content near the 1:1 soil to water ratio.

Seed Germination Study

Alfalfa - - Three kilograms of soil were placed in a twin-shell mixer with appropriate amounts of either AFBC waste or pure $CaCO_3$. The lime rates used were 0, 1X $CaCO_3$, 1X AFBC, and 2X AFBC. In addition, P and K fertilizers were added as $CaHPO_4$ and KCl at the equivalent rates of 200 kg/ha P_2O_5 and 150 kg/ha K_2O, respectively. After mixing for 10 minutes, the soil was transferred to plastic pots and deionized water added to bring the soil to field capacity.

Samples were equilibrated 0, 1, or 2 weeks prior to seeding each pot with 25 alfalfa seeds. Four replications were prepared for each series. It was necessary to add water each day to maintain the soil at the desired moisture level. After five days, the number of emerged seedlings were counted and this was continued up to 14 days after planting, at which time soil samples were collected and analyzed for pH and exchangeable cations.

Pots which had been equilibrated 2 weeks prior to planting were thinned to 16 seedlings per pot and allowed to grow through five harvests. The first harvest was made when half the plants were in bloom and successive harvests were made each 35 days thereafter. Soil samples were collected from these alfalfa pots following the final harvest.

Soybeans - - A similar experiment as described for alfalfa was used to evaluate the effect of AFBC waste on the germination of soybeans. The only difference was that 16 seeds were planted per pot. This experiment was terminated after the last observation of seedling emergence on day 14 following planting, at which time soil samples were collected from each pot and analyzed for pH and exchangeable cations.

Soil Analyses

pH - - All pH measurements were made at a 1:1 water to soil ratio using a Fisher pH meter equipped with a gel-filled combination electrode. The lime requirement was determined by using the SMP buffer pH method proposed by Shoemaker et al. (1961).

Exchangeable cations - - Soils were extracted with 100 ml of neutral normal NH_4OAc following equilibration overnight. The levels of Ca, Mg, Na, and K were determined using atomic adsorption techniques. The total exchangeable acidic cations were extracted by leaching 50 g of soil with 200 ml of 1N KCl by the method proposed by Yuan (1963). This extract was titrated with standardized NaOH. Following this step, 25 ml of 0.5N NaF was added and if Al was present, as indicated by an increase in pH, the solution was back-titrated with standard acid to the same end point. The quantity of exchangeable H^+ was obtained by subtracting the amount of Al from the total acidity.

Results and Discussions

The pH of the highly acidic soil was increased significantly as a result of applying lime as either AFBC or pure $CaCO_3$. As one would expect, the pH increased as a function of the quantity of lime applied, and these data are presented graphically in Figure 1. If one were to plot pH versus lime rate, a linear relationship would result. There were significant differences as a result of wetting-drying cycles in many cases. When the pH values differed by 0.2-0.3 pH units, usually significant differences occurred between drying cycles. In general, pH's were lowest for the zero-cycle series, highest for the 2-cycle series, and intermediate for the 8-cycle series. A possible explanation for this general trend may be related to the fact sufficient time had not elapsed for the zero-cycle series to allow for the neutralization reaction to occur between the liming agent and the acid soil, hence, pH's were generally lower.

The pH of the 2-cycle series was always greater than the 8-cycle series for the AFBC liming agent when adequate lime had been applied, i.e., 1X and greater rates. The higher value obtained for the 2-cycle series may have been related to two factors: 1) insufficient equilibration time and 2) the fact that the source of base for the neutralization reaction for AFBC waste is largely $Ca(OH)_2$. Calcium hydroxide will support a higher pH than $CaCO_3$; the latter has a maximum equilibrium value of pH 8.3. With time, stirring, etc., $CaCO_3$ became the dominant base in these systems and the pH declined.

Another potentially influential reaction that may be affecting the pH's in all of the systems in which AFBC waste was used is the effect of $CaSO_4$. In general, the pH will be lower in the presence of $CaSO_4$ where equal amounts of $CaCO_3$ are present. The systems illustrated in Figure 1 are closed, i.e., leaching cannot occur. In the field where leaching occurs, this effect of $CaSO_4$ in surpressing the pH should be less and would diminish with time. In a field study in which large Ag lime rates (40 T/A) were applied to highly acidic spoils, $CaSO_4$ was formed and resulted in a pH suppression that lasted 1-2 years (Barnhisel et

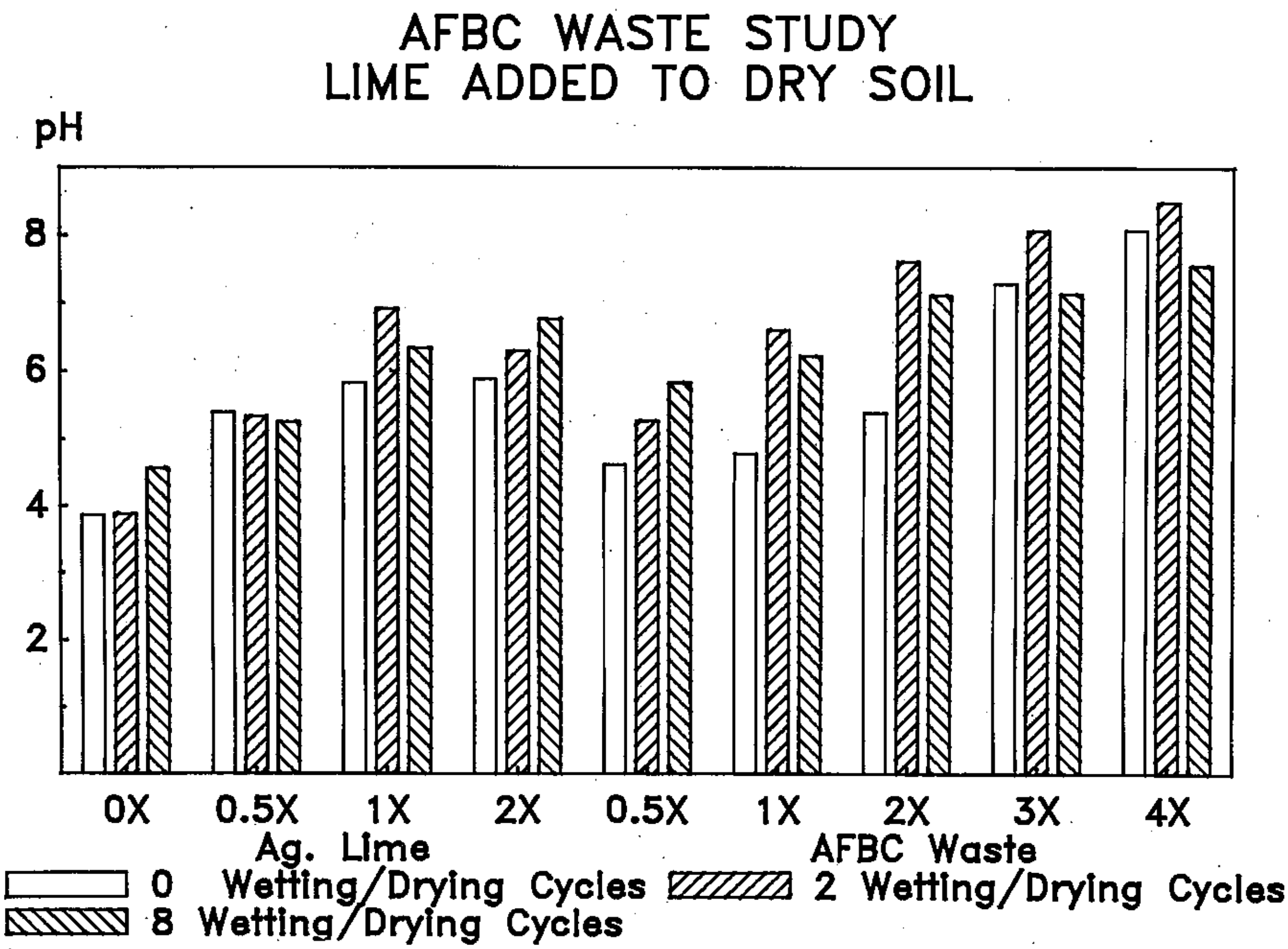

Figure 1. Effect of wetting-drying and lime amendments on pH.

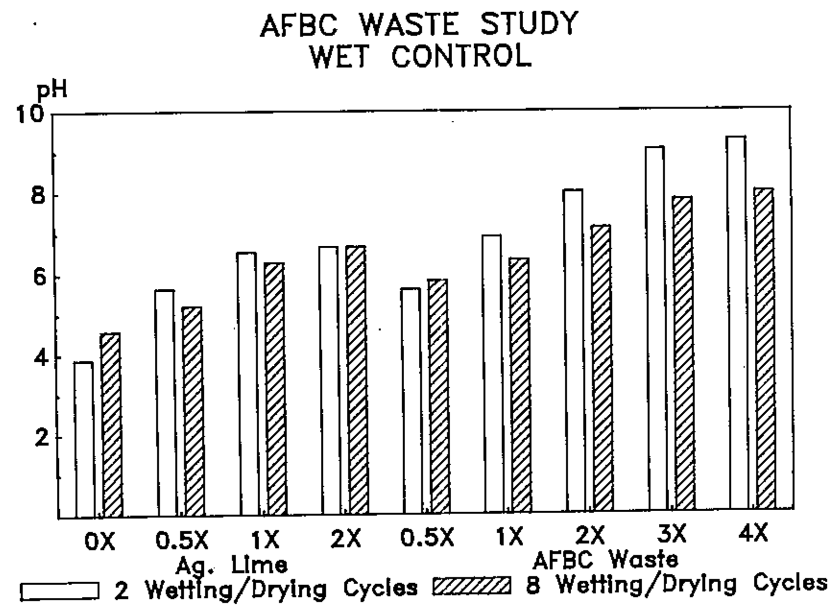

Figure 2. Effect of lime amendments on pH - systems remained wet, pH's measured at same time intervals as wetting/drying cycles in Figure 1.

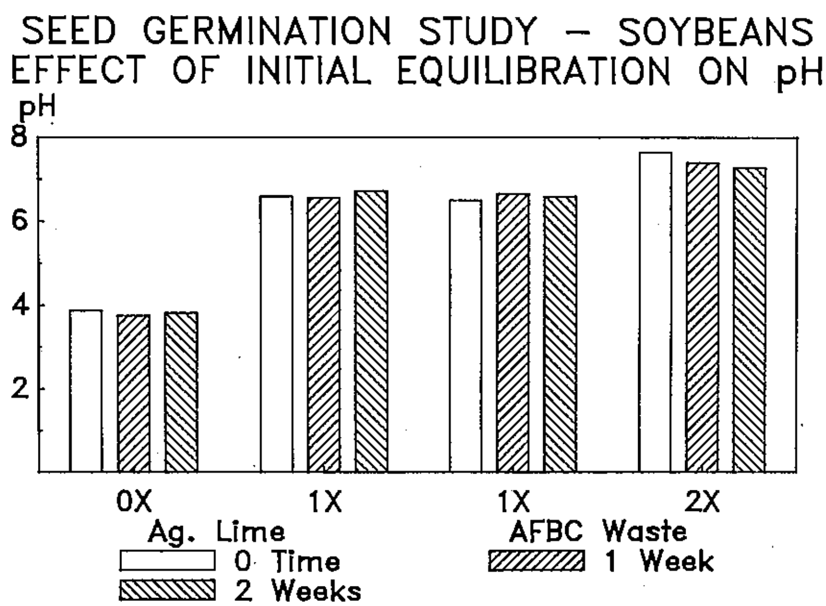

Figure 3. Effect of lime amendments and initial equilibration soybean seed germination test.

al., 1985). Then the pH increased about 0.5 when the $CaSO_4$ had been removed by leaching.

Similar results were obtained for the wet-control series as those observed when samples were wetted and dried, Figure 2. In actuality, these samples were not allowed to dry, however, both the 2-cycle and 8-cycle series were otherwise equilibrated at the same temperature and for the same lengths of time. Note, in most cases, the 2-cycle series had higher pH's than the 8-cycle series. These differences were significant for all but three comparisons, i.e, the 0.5X of the AFBC series and the 1X and 2X Ag lime or $CaCO_3$ series. At comparable liming rates, the AFBC pH values were significantly greater than their Ag lime counterparts in two of the three cases for both the 2-cycle and 8-cycle series, with the exceptions being 0.5X and 1X, respectively.

The pH's obtained following the soybean seed germination study are shown as Figure 3. The data from the alfalfa study were almost identical and therefore are not presented. These pH values were measured 2 weeks after planting, therefore, pH data for the zero-time series were actually collected 2 weeks after equilibration. In only the case where two times the recommended value of AFBC waste had been applied, did significant differences in pH occur. In this case, the zero-time had a significantly higher pH than the 2-week equilibration treatment. There was no significant difference between the 1X Ag lime or $CaCO_3$ and AFBC waste treatments, both having a mean pH of 6.6. We had applied lime at the rate expected to raise the pH to 6.4, however, in both cases, it was slightly higher. The average pH for the 2X AFBC treatment was pH 7.4, which also corresponds to the 1-week initial equilibration treatment.

The effect of initial equilibration time on the germination of alfalfa and soybean seed is given in Table 1 and Table 2, respectively. At zero-time, the germination of alfalfa for both the 1X and 2X rates of AFBC was significantly suppressed, by 14% and 37%, respectively. The suppression effect of AFBC on alfalfa germination was reduced by allowing the soil to equilibrate prior to planting. Following 1-week initial equilibration, the number of alfalfa seeds germinating for the 1X $CaCO_3$ and 1X AFBC treatments was not significantly different from each other and neither was it significantly different from the zero-lime treatment. However, the 2X AFBC treatment had 16% fewer seeds germinating. For some unknown reason, the alfalfa germination rates following 2-weeks equilibration prior to planting were reduced for all lime treatments as compared to those at 1 week. However, assuming the 1X $CaCO_3$ treatment as being the control, the 1X AFBC treatment had 8% more seeds to germinate, and the zero-lime control 2% fewer seeds germinating. The 2X AFBC treatment had 16% fewer seeds germinating than the 1X $CaCO_3$ control.

In addition to fewer alfalfa seeds germinating, it was apparent that the rate of germination was slower for the 2X AFBC lime treatment, then for all other treatments, especially when the soil was not equilibrated prior to planting, where there were 57% fewer plants at 5 days than from the zero lime treatment, and the 2X AFBC treatment always had the fewest number of plants at any period of time.

Neither the lime treatment nor the initial equilibration period had any significant effect on soybean germination rate, as all treatments had essentially the percent germination value listed on the seed tag (Table 2). These results are likely attributed to the relative seed size between soybeans and alfalfa. It would be expected that factors such as excessively low or high pH would exhibit a greater impact on small seeds, such as alfalfa, as compared to soybeans.

Table 1 Effect of initial equilibration time on germination of alfalfa following application of various rates of lime.

Lime Treatment	Days following Seeding* 5	8	11	14
	number of plants			
	Zero time equilibration prior to seeding			
0 lime	83a	90a	91a	92a
1X $CaCO_3$	90a	93a	93a	94a
1X AFBC	62b	64b	68b	79b
2X AFBC	33c	42c	49c	56c
	1 week equilibration prior to seeding			
0 lime	67ab	78a	81a	82ab
1X $CaCO_3$	80a	84a	85a	85a
1X AFBC	64b	72ab	77ab	81ab
2X AFBC	50c	62b	67b	69b
	2 weeks equilibration prior to seeding			
0 lime	66a	72ab	73ab	74ab
1X $CaCO_3$	72a	76ab	77a	77ab
1X AFBC	75a	81a	82a	84a
2X AFBC	54b	60b	60b	61b

* 100 seeds planted per lime treatment. Percent germination listed on seed tag was 94%.

Table 2 Effect of initial equilibration time on the germination of soybeans following application of various rates of lime.

Lime Treatment	Days following Seeding* 5	8	11	14
	number of plants			
	zero time equilibration prior to seeding			
0 lime	57ab	61a	63a	63a
1X $CaCO_3$	54b	61a	62a	63a
1X AFBC	60a	61a	61a	62a
2X AFBC	57ab	59a	62a	63a
	1 week equilibration prior to seeding			
0 lime	59a	61a	62a	62ab
1X $CaCO_3$	56a	59a	60a	60b
1X AFBC	60a	61a	62a	64a
2X AFBC	57a	59a	61a	62ab
	2 weeks equilibration prior to seeding			
0 lime	59a	60a	63a	63a
1X $CaCO_3$	59a	61a	62a	62a
1X AFBC	57a	60a	63a	64a
2X AFBC	55a	57a	61a	62a

* 64 seeds planted per lime treatment. Percent germination listed on seed tag was 98%.

Yield data of alfalfa forage as a function of liming agent over time are given in Table 3. These data indicate that both $CaCO_3$ and AFBC at the 1X rate significantly increased the yield levels of alfalfa over those obtained from the 0 lime treatment for all five harvests. The most important consideration with respect to these data concerns yield differences between the 1X rates of $CaCO_3$ and AFBC. The fact that they were not different suggest that AFBC may be used as a substitute for $CaCO_3$ in agricultural field applications.

Numerically, yields from the 2X AFBC rate were lower than those from the 1X rate in all cases, however, these differences were not significant. From the germination data presented earlier in Table 1, the number of alfalfa seeds germinating for the 2X rate was lower. Since these pots had been thinned to a constant number, the suppression in yield due to excessive application of AFBC could have been diminished. A reduced germination rate in the field could result in a reduced forage yield, provided the number of plants per square foot is less than 3-6. Under these greenhouse conditions, we had an excess number of plants per square foot to allow for sufficient biomass for chemical analyses. Unfortunately, these data were not completed at the time this manuscript was prepared.

Table 3 Effect of lime treatment on alfalfa yields as a function of harvest.

Harvest Number	0 lime	$CaCO_3$ 1X	AFBC 1X	AFBC 2X
	g/pot			
1	0.27Ca*	0.94Ad	0.93ABd	0.50BCd
2	0.09Bb	3.19Aab	3.00Ab	2.77Ab
3	0.01Bb	1.92Ac	2.20Ac	1.77Ac
4	0.02Bb	2.69Abc	2.56Abc	2.28Abc
5	0.17Ba	3.99Aa	4.00Aa	3.79Aa
Total	0.54 B	12.73 A	12.70 A	11.03 A

* Means with the same letters are not significantly different for LSD at alpha = 10. Capital letters are for significance between lime rates for each harvest, small letters are to be used to make comparisons between harvests for any given lime treatment.

Conclusions

1. The relative neutralization reaction rates of AFBC amd pure $CaCO_3$ measured in laboratory and greenhouse studies were similar.
2. AFBC waste can be utilized as a substitute for Ag lime provided recommended rates as a liming agent are used, and that the material does not contain toxic levels of some elements.
3. Reduced germination of some crops could occur when seeded directly following application of AFBC waste to the soil without allowing for equilibration.
4. Although this report is inconclusive, we did not visibly identify toxic levels of any element in either soybeans or alfalfa when AFBC was applied at the recommended rate equivalent to pure $CaCO_3$.
5. Excessive application of AFBC waste should be avoided as the high pH's that result could lead to yet undetected problems associated with the chemical composition of plants grown on such soils.
6. Germination of small legume seeds (alfalfa) was significantly reduced unless the AFBC waste and soil mixture was allowed to equilibrate. Under field capacity moisture levels, and under greenhouse conditions, at least one week was required.
7. Large-seeded legume (soybeans) germination was not affected by either the rate of AFBC on $CaCO_3$ nor eqilibration time before seeding.

Literature Cited

http://doi.org/10.21000/JASMR85010040

Barnhisel, R.I., J.L. Powell, M.L. Ellis, J.R. Armstrong, F.A. Craig, and S.K. Laue. 1985. Selection of grass and legume species and varieties for reclamation of mined land. In Proceedings of Am.Soc. Surface Mining and Reclamation. Denver, CO., pp 40-49.

Barnhisel, R.I., 1976. AGR 40-Lime and fertilizer recommendations for reclamation of surface-mined spoils. Ky. Agr. Exp. Sta., Department of Agronomy, Univ. of Kentucky, Lexington, KY. 4 p.

Barnhisel, R.I., J.L. Powell, J.S. Osborne, and S. Lakhakul. 1985. Estimating agricultural lime needs, and observed responses for surface-mined coal spoils. In Symposium on the Reclamation of Lands Disturbed by Surface Mining: A Cornerstone for Communication and Understanding. Science Reviews LTD, Northwood, England. pp. 318-344.

Boyle, P.L., R.I. Barnhisel, J.L. Powell, and J.H. Grove. 1982. Sulfur-coated phosphorus as a source of P for topsoiled mine land in western Kentucky. In Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Univ. of Kentucky, Lexington, KY. pp. 123-128.

Hern, J.L., W.L. Stout, R.C. Sidle, and O.L. Bennett. 1977. Characterization of fluidized bed combustion waste composition and variability as they relate to disposal on agricultural land. Proc. 5th Int. Conf. Fluidized Bed Combustion, Washington, DC pp. 833-841.

Huntington, T.G., R.I. Barnhisel, and J.L. Powell. 1980. The role of soil thickness, subsoiling, and lime incorporation methods on the reclamation of acid surface mine spoils. In Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Univ. of Kentucky, Lexington, KY. pp. 9-13.

Shoemaker, H.E., E.O. McLean, and P.F. Pratt. 1961. Buffer methods for determining lime requirement of soil with appreciable amounts of extractable aluminum. Soil Sci. Soc. Am. Proc. 25:274-277.

Stout, W.L., R.C. Sidle, J.L. Hern, and O.L. Bennett. 1979. Effects of fluidized bed combustion waste on the Ca, Mg, S, and Zn levels in red clover, tall fescue, oat, and buckwheat. Agron. J. 71:662-665.

Stout, W.L., H.A. Menser, O.L. Bennett, and W.M. Winant. 1982. Cover establishment on an acid mine soil using composted garbage mulch and fluidized bed combustion residue. Reclam. and Reveg. Res. 1:203-211.

Terman, G.L., V.J. Kilmer, C.M. Hunt, and W. Buchanan. 1978. Fluidized bed boiler waste as a source of nutrients and lime. J. Environ. Qual 7:147-150.

Yuan, T.L. 1963. Some relationships among hydrogen aluminum and pH in solution and soil systems. Soil Sci. 95:181-188.

Shoemaker http://dx.doi.org/10.2136/sssaj1961.03615995002500040014x

Stout Sidle etc http://dx.doi.org/10.2134/agronj1979.00021962007100040034x

Terman http://dx.doi.org/10.2134/jeq1978.00472425000700010031x

Yuan http://dx.doi.org/10.1097/00010694-196303000-00001