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## DICALCIUM SILICATE (BROWN MUD) AS AN AGRICULTURAL LIMING MATERIAL<sup>1</sup>

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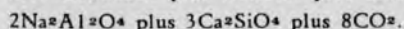
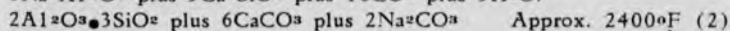
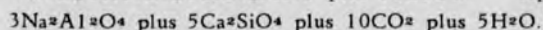
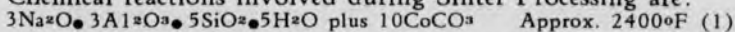
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### INTRODUCTION

"Brown Mud" (sometimes called Brown Lime) is a waste by-product of the alumina industry. The processes involved in aluminum production consist of first digesting bauxite ore with caustic soda (Bayer Process) to extract alumina that is present in bauxite as gibbsite ( $Al_2O_3 \cdot 3H_2O$ ). Also prevalent in Arkansas bauxite is aluminum silicate that is not attacked by the Bayer Process. During the Bayer digestion a desilication product, identified in equation 1 below, is formed. This desilication product and aluminum silicate, collectively called "red mud", are separated from the soluble sodium aluminate solution by settling. The red mud is then treated through the Sinter Process, which involves the addition of limestone, soda ash, and red mud in the necessary proportions to form dicalcium silicate and soluble sodium aluminate. This three-component mixture is ground and mixed in ball mills and fed through kilns where thermal reactions take place. The soluble sodium aluminate is removed by leaching and the insoluble dicalcium silicate is filtered, repugged and pumped to a waste lake. This insoluble "brown mud" has as its main constituent dicalcium silicate, with lesser quantities of iron, aluminum, titanium and sodium oxides; its calcium carbonate equivalent varies from approximately 80 to 90 (pure calcium carbonate—100).

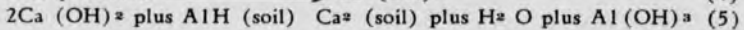
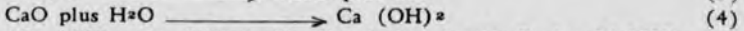
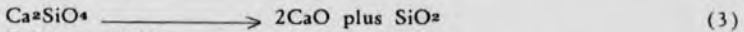
Chemical reactions involved during Sinter Processing are:



During the last several years an estimated 450,000 tons of brown mud have been produced in Arkansas annually. When this production is compared with Arkansas' annual limestone use of 440,000 tons (in 1962), and with an estimated annual maintenance need of 700,000 to 800,000 tons, it is immediately apparent that brown mud has a tremendous potential value as an agricultural liming material in this state.

<sup>1</sup>Approved by the director of the Arkansas Agricultural Experiment Station.

When dicalcium silicate is added to an acid soil it undergoes the following reactions which result in the neutralization of soil acidity:



Whittaker et al. (5), and others (2), have grown and analyzed plants in a greenhouse experiment, using brown mud as an amendment. Volk, Harding and Evans (3), and others (1,4) have reported on the value of the steel industry's blast furnace slag as an agricultural liming material.

The factors that have kept brown mud from having a more immediate value as a soil amendment are:

- (a) The alumina industry's main purpose was to produce alumina; in the past they have tended to disregard the value of their waste products.
- (b) Technological changes had to be made for further treatment of brown mud before it could be effectively utilized as a soil amendment.
- (c) The alumina industries, and hence the suppliers of brown mud, are not decentralized through the agricultural region of Arkansas.

## MATERIALS AND METHODS

In the spring of 1963 an experiment was established on an acid Taloka-Parsons-Johnsburg silt loam complex on the University of Arkansas Main Agricultural Experiment Station Agronomy Farm, at Fayetteville, to evaluate brown mud as a liming material. Dolomitic limestone and brown mud were applied and disked into the soil in late March; the experimental design was a randomized block with 5 replications. Hood variety soybeans were seeded on June 6 in the experimental area, but a serious drought negated the yield values. On August 6, eight composite soil cores, to a depth of 6 inches, were taken from each individual plot. The soil samples were dried, crushed, and analyzed for pH and exchangeable cations.

## RESULTS AND DISCUSSION

The analysis of brown mud may vary within rather narrow limits from batch to batch. The data in Table 1 encompass the outside limits of most samples of brown mud.

Table 2 gives the quantities of Ca, Mg, and Na applied to the soil as calculated from the analysis of the materials and the rates applied. Table 3 gives the results of the analysis of the ex-

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perimental plots five months after the amendments were applied. Because of the nature of field experiments such as this, it would be impossible to quantitatively account for, in Table 3, all the material that was applied as given in Table 2.

A study of the data in Table 3, and a comparison of the data in Tables 2 and 3, will show that the brown mud com-

TABLE 1

Chemical composition of brown mud

Oxide	low	high	typical	Element	typical
CaO	45%	52%	48.5%	Mg	.X-X
SiO <sub>2</sub>	24	27	25.5	Mn	.X
Fe <sub>2</sub> O <sub>3</sub>	6	12	9	S	.X
Al <sub>2</sub> O <sub>3</sub>	4	6	5	K	.OX
TiO <sub>2</sub>	3	5	4	P	.OX
Na <sub>2</sub> O	2.5	3.5	3	Li	.OX
				Ga	.OX
				B	.OX-.OOX
CaCO <sub>3</sub> equivalent	80	93	86.5	Zn	.OOX-.OOOX
Lost on ignition	2.5	6.0	4.2	Mo	.OOOX
				Others	.OOOX or less each

TABLE 2

Pounds per acre of calcium, magnesium and sodium applied

Treatment	Ca	Mg	Na
1 ton dol. limestone <sup>1</sup>	464	217	0
1 ton brown mud	637	-	40
2 tons brown mud	1274	-	80
4 tons brown mud	2548	-	160

<sup>1</sup>The calcium equivalent of Ca plus Mg in this ton of dolomitic limestone is 826 pounds.

TABLE 3

Effect of dolomitic limestone and brown mud applied in March on the analysis of the soil five months later

Treatment	pHw <sup>1</sup>	pHs <sup>2</sup>	lb/acre of exchangeable		
			Ca	Mg	Na
Check	4.9	4.3	1550	65	160
1 ton dol. lime	5.1	4.7	1710	130	190
1 ton brown mud	5.3	4.8	2030	80	185
2 tons brown mud	5.9	5.6	2430	55	245
4 tons brown mud	6.2	5.9	2650	50	270

<sup>1</sup>pHw is soil pH in a 1:1 soil-water mixture.

<sup>2</sup>pHs is salt pH in a 1:1 soil - 0.01 M CaCl<sub>2</sub> mixture.

pares very favorably with the limestone. The calcium carbonate

equivalent of the limestone was 103 while that of the brown mud was 80. Yet the brown mud was more effective in decreasing the soil acidity (increasing pH) and in increasing the exchangeable calcium content of the soil than an equivalent tonnage of the limestone. The greater effectiveness of the brown mud can be attributed to the smaller particle size and the increased surface area.

Some of the trace elements in the brown mud could have an extra value for certain crops on some soils; specifically, there may be sufficient Mo, S, Zn, and B present to be a nutritional aid to plants. However, since blanket applications of trace element mixtures are not generally recommended, brown mud should be evaluated on the basis of its liming value only.

It will be noted that brown mud contains more sodium than is contained in agricultural limestone. However, the quantity of sodium applied in an application of brown mud is not high; it is similar to the quantity of sodium applied in normal applications of sodium nitrate fertilizer.

Unreported greenhouse tests by the senior author are in agreement with the field work reported here and have shown that brown mud increased soybean yields when used on an acid soil.

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