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Use of an industrial by-product as a liming source[1]

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ABSTRACT

Calcium hydroxide [$Ca(OH)_2$], a by-product of the acetylene production process, is a potential liming source for acid agricultural soils. The material as generated has a moisture content of 80%, which decreases to about 50% after settling in a collecting pond. Air dried $Ca(OH)_2$ (2.63% moisture), ground to pass a 300 μm sieve, had a $CaCO_3$ equivalent of 120%. Commercial $CaCO_3$ (1.53% moisture) had a pure $CaCO_3$ equivalent of 84%. Both liming sources were evaluated in laboratory incubation studies using four acid soils: Corozal clay (Ultisol), Mariana (Inceptisol), Bayamón (Oxisol) and Alonso (Ultisol). The industrial waste [$Ca(OH)_2$] was as effective as $CaCO_3$ in neutralizing soil acidity. An application of 8.0 meq/100g of both liming sources increased the pH of Mariana soil from 4.65 to 6.07, Corozal soil from 4.13 to 4.92 and Alonso soil from 4.74 to 6.48. The pH of Bayamón soil increased from 4.39 to 6.65 with the application of 8.0 meq of $CaCO_3$; however, the same amount of $Ca(OH)_2$ increased the pH to 6.92. Exchangeable Al^{3+} levels were close to zero in Mariana, Bayamón and Alonso soils at pH values between 6.0-6.3. Exchangeable Al^{3+} in Corozal soil decreased from 934.37 mg/kg to 269.79 mg/kg as the pH increased from 4.13 to 4.92. In a short term incubation experiment (5 days), $Ca(OH)_2$ reacted faster than $CaCO_3$ to neutralize soil acidity. Samples of Mariana, Alonso and Bayamón soils treated with 8.0 meq/100g of $Ca(OH)_2$ reached pH values around 6.00 after one day of incubation, whereas $CaCO_3$-treated samples reached similar pH values only after the second or third day of incubation.

RESUMEN

Subproducto industrial como enmienda cálcica al terreno.

El hidróxido de calcio [$Ca(OH)_2$], un subproducto de la producción de acetileno, tiene buen potencial como fuente de encalado para suelos agríco-

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las ácidos. Inicialmente este material contiene un 80% de humedad, la que disminuye a aproximadamente 50% una vez asentado en la charca de recolección. El $Ca(OH)_2$ seco al aire (2.63% humedad), molido y pasado por un cedazo de 300 µm mostró una equivalencia a $CaCO_3$ puro de 120%. El $CaCO_3$ comercial (1.53% humedad) mostró una equivalencia a $CaCO_3$ puro de 84%. Las fuentes de encalado se evaluaron en estudios de laboratorio utilizando cuatro suelos ácidos: Corozal (Ultisol), Mariana (Inceptisol), Bayamón (Oxisol) y Alonso (Ultisol). El residuo industrial $Ca(OH)_2$ fue tan efectivo como el $CaCO_3$ en neutralizar la acidez de estos suelos. La aplicación de 8.0 meq/l00g de las fuentes de encalado aumentó el pH del suelo Mariana de 4.65 a 6.07, Corozal de 4.13 a 4.92 y Alonso de 4.74 a 6.48. En el caso del suelo Bayamón, la aplicación de 8.0 meq/l00g de $CaCO_3$ aumentó el pH de 4.39 a 6.65, mientras que la misma aplicación en forma de $Ca(OH)_2$ aumentó el pH a 6.92. El aluminio intercambiable de los suelos Mariana, Bayamón y Alonso alcanzó valores cercanos a cero cuando los valores de pH estaban entre 6.0 y 6.3. En el suelo Corozal se observó una reducción en Al^{3+} intercambiable de 934.37 a 269.79 mg/kg con un aumento en pH de 4.13 a 4.92. En un experimento de incubación a corto plazo (5 días) el $Ca(OH)_2$ neutralizó en menos tiempo la acidez de los suelos Mariana, Bayamón y Alonso que el $CaCO_3$. Las muestras tratadas con 8.0 meq de $Ca(OH)_2$ alcanzaron valores de pH cercanos a 6.00 al día siguiente de la aplicación. Sin embargo, con la aplicación de $CaCO_3$ se observaron valores similares de pH al segundo y tercer día de incubación.

INTRODUCTION

Soil acidity is a major constraint to crop production in tropical and subtropical areas where heavy rainfall results in the progressive leaching of soluble salts, the more soluble soil minerals, and basic cations such as Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}. As these weathering processes progress, the soil becomes acid, its fertility diminishes and its mineralogy becomes dominated by the presence of iron and aluminum oxides. Soil acidity significantly influences the availability of nutrients considered essential for optimum production. Most nutrients are in optimum concentration at pH values around 6.5 to 7.5. Very acid soils (pH <5.0) usually present a combination of conditions unfavorable for plant growth, such as Ca deficiency, aluminum toxicity and manganese toxicity (5, 6, 7, 11, 12).

Exchangeable Al^{3+} is the major factor influencing soil acidity (8). Aluminum ions hydrolyze to monomeric and polymeric hydroxyaluminum complexes, releasing hydrogen (H^{+}) ions. Crop fertilization (1,2,16,17,18) and decomposition of plant residues and organic matter (10,11,18) can also contribute significantly to soil acidity. Abruña et al. (1) observed a significant reduction in pH and exchangeable bases in an Alfisol and a Mollisol within a year after beginning N applications in the form of ammonium sulfate. Samuels and Gonzalez-Vélez (19) reported that long term applications of ammonium sulfate to sugarcane increased the acidity of a variety of soils. A recent survey of the pH status of sugarcane fields of Puerto Rico (21) indicated that from a total of

14,331 ha sampled, 9,974 ha (69.6%) showed pH values below 5.5, and 8,555 ha (59.7%) showed pH values below 5.0.

Liming is a term used in agriculture to describe the addition to the soil of any calcium or calcium-magnesium compound to reduce acidity. The most common liming material is calcium carbonate ($CaCO_3$), but other compounds, such as calcium oxide (CaO), calcium hydroxide [$Ca(OH)_2$] and calcium-magnesium carbonates, are excellent liming materials. The neutralizing power of these materials depends on their purity, particle size and reactivity, and on the nature and amount of soil acidity.

The lime requirement of a soil is both a function of the deficit of basic cations and the accumulation of acidic cations (7, 12, 13). It can be defined as the amount of lime required to increase the soil pH from an initial acid condition to a near neutral condition or to decrease the content of toxic elements in the soil to levels not detrimental to the crop. An appropriate liming program will result in adequate soil base saturation, reduction in the concentration of toxic elements, enhanced availability of most plant essential nutrients and higher activity of beneficial microorganisms (13). Liming to pH values around 5.5 has been found to decrease toxic levels of exchangeable aluminum and manganese and increase yield of several crops (3,4,5).

The Department of Agriculture of Puerto Rico has implemented a program to supply lime at low cost to farmers. The price fluctuates between $5.00 and $12.00 per ton (14). The prices are far below the production costs, which amount to $46.00 per ton (14). The impact of the mining operations on the environment has not been evaluated. However, it clearly does not conform to present environmental protection standards. Finding an additional liming source, less costly and less damaging to the environment, would be of great benefit to the government, the farmers and the general public. A possible alternative to correct soil acidity problems is the use of an industrial by-product [$Ca(OH)_2$][4] generated from the production of acetylene.

Liquid Air of Puerto Rico, an acetylene production company located in the municipality of Cataño, Puerto Rico, has accumulated over 30,000 tons of this industrial by-product, which needs to be disposed of in a safe practical way. The use of the material as a liming source for agricultural soils can be a practical and profitable alternative for its disposal. The studies herein reported were conducted to evaluate the potential of the material as a liming source for agricultural soils and to compare its effectiveness with that of CaCO3, the commonly used liming material.

[4]Acetylene production reaction: $CaC_2 + 2H_2O \dashrightarrow C_2H_2 + Ca(OH)_2$.

MATERIALS AND METHODS

Composite samples of the $Ca(OH)_2$, as generated from the reactor and after settling in a pond, were collected at the acetylene plant. The moisture content of the material was determined by drying the samples in an oven at 105 °C for 72 h. The material used in the incubation studies was collected from the storage pond, air dried and ground to pass a 50 mesh sieve. Commercial calcium carbonate ($CaCO_3$) was also ground to pass a 50-mesh sieve, thus eliminating possible effects due to particle size differences. The moisture contents of air dried $Ca(OH)_2$ and commercial $CaCO_3$ were also determined. The total neutralizing power of both liming materials was determined by neutralization with *boiling standard $HN0_3$ followed by titration of the excess acid by stan*dard NaOH, with phenolphtalein as indicator.

Four acid soils, two Ultisols, one Inceptisol and an Oxisol were used in the studies. Some chemical properties of the soils are presented in table 1. Soil pH was measured in a 2:1 water: soil ratio. Exchangeable Al was extracted with 1 *N* KCl and exchangeable Ca, K and Mg with 1 *N* ammonium acetate buffer at pH 7 (15). Al, Ca and Mg were determined by atomic absorption; K by atomic emission (15). Organic matter content was determined by the Walkley and Black method, which involves oxidation with permanganate (15).

Two laboratory studies were conducted. In the first study, triplicate samples (150 g) of air-dried Mariana and Corozal soils were equilibrated for 13 days with increasing amounts of $CaCO_3$ (0, 2.20, 4.40, 6.60 and 8.80 meq/100g) and Ca(OH)2 (0, 2.97, 5.94 and 8.91 meq/100g). Triplicate samples of Bayamón and Alonso soils were equilibrated with 0, 2.00, 4.00, 6.00 and 8.00 meq/100g of each liming material. Each soil sample was treated individually and the corresponding amount of liming material thoroughly mixed to ensure uniform distribution. Forty-five milliliters of distilled water was added to each sample from a spray bottle to ensure uniform wetting. Soil samples were placed in 400-ml

TABLE 1.—*Soil chemical analysis.*

			Exchangeable cations				
Series	Order	p*H*	Al (mg/kg)	Ca -----	K $cmol_c kg^{-1}$	Mg -----	O.M. (%)
Mariana	Inceptisol	4.60	250.90	4.16	0.56	1.73	3.37
Corozal	Ultisol	4.19	934.37	1.25	0.62	0.30	2.34
Bayamón	Oxisol	4.35	323.75	0.63	0.23	0.08	0.45
Alonso	Ultisol	4.64	238.31	4.21	0.51	1.68	3.87

beakers and covered with a watch glass. The beakers were weighed and the weight was recorded to monitor moisture loss. At the end of the incubation period, soil pH and exchangeable Al content were determined.

A second study was performed to measure the speed of reaction of both liming materials. Enough liming material, $CaCO_3$ or $Ca(OH)_2$, to attain 8.0 meq/100g of soil was added to triplicate soil samples (150 g) as previously described. Soil pH was measured daily for 5 days by using a 2:1 water:soil ratio. After 5 days, exchangeable Al was measured.

RESULTS AND DISCUSSION

The by-product $Ca(OH)_2$, as generated from the reactor, has a moisture content of 80% and after settling in the pond its moisture may decrease to 51%. The moisture content of the air dried $Ca(OH)_2$ was 2.63% and for commercial $CaCO_3$ it was 1. 53%. The $CaCO_3$ equivalent of the $Ca(OH)_2$ was 120%. For pure $Ca(OH)_2$ this value should be 136%; however, lower values were obtained because of the moisture content and impurities present in the material. Calcium carbonate, silicates, iron and aluminum oxides, sulfur, phosphorus and free carbon exist in small quantities in this material (table 2) (9). Commercial $CaCO_3$ showed a $CaCO_3$ equivalent of 84%, a value also influenced by the moisture content of the material and impurities, especially its clay content.

$CaCO_3$ and $Ca(OH)_2$ were equally effective in neutralizing the acidity of Mariana, Corozal and Alonso soils (fig. 1 and 2). The application of 8.0 meq/100 g of liming material increased the pH of Mariana soil from 4.65 to 6.07, the pH of Corozal soil from 4.13 to 4.92 and the pH of Alonso soil, from 4.74 to 6.48. The pH of Bayamón soil increased from 4.39 to 6.65 with the application of 8.0 meq/100 g of $CaCO_3$, whereas the same liming rate in the form of $Ca(OH)_2$ increased the pH to 6.92.

TABLE 2.—*Chemical analysis of the industrial by-product $Ca(OH)_2$.*

Component	(%)
$Ca(OH)_2$	92.22
$CaCO_3$	2.82
SiO_2	1.46
R_2O_3	2.66
$Mg(OH)_2$	0.16
S	0.17
P	0.01
Free carbon	0.50

Source: Compressed Gas Association Inc., 1970.

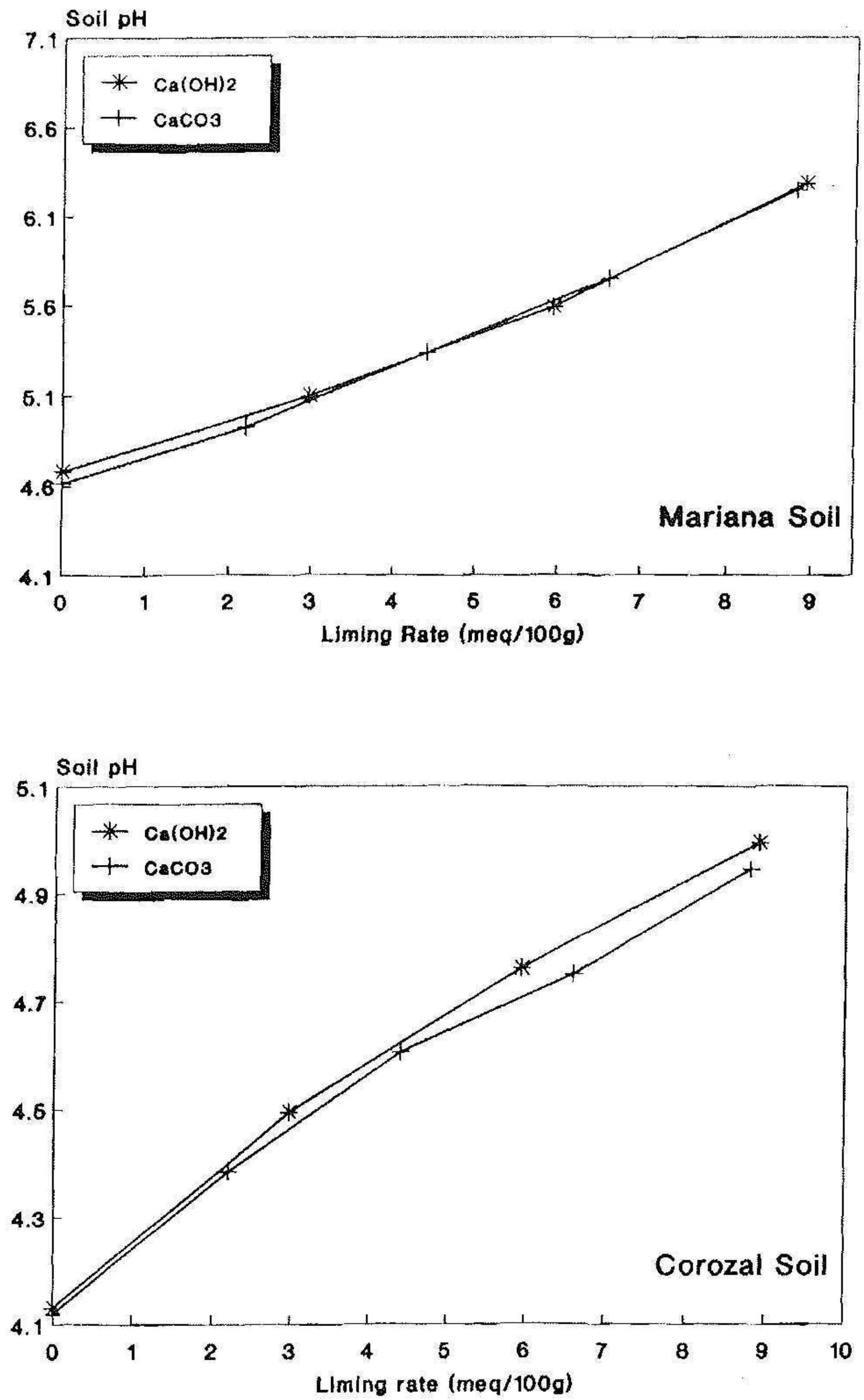
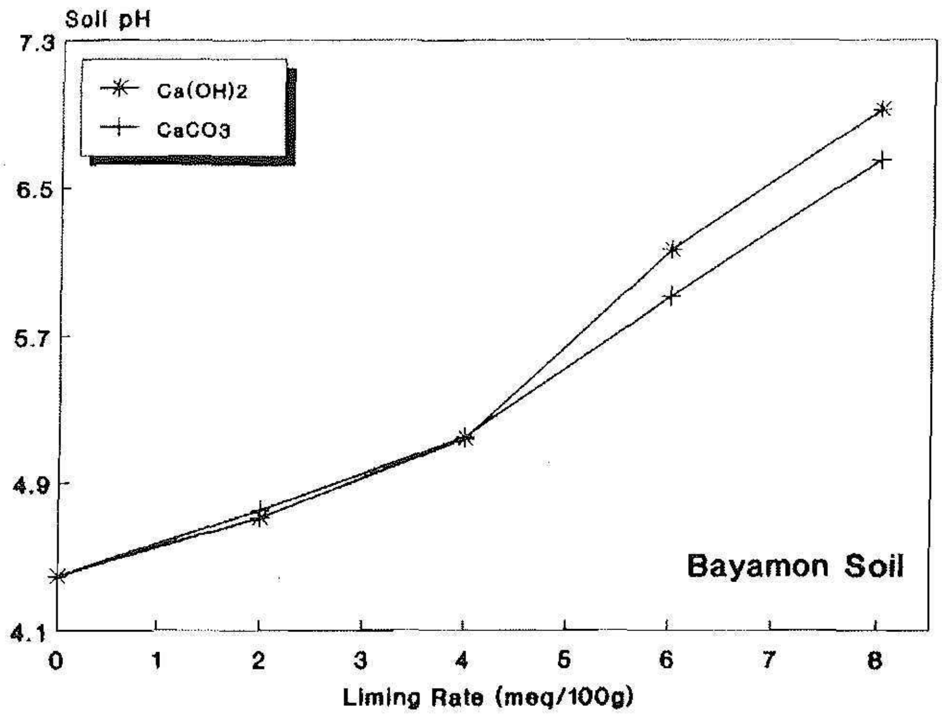


FIG. 1. Effect of liming source and rate on the pH of Mariana and Corozal soils.



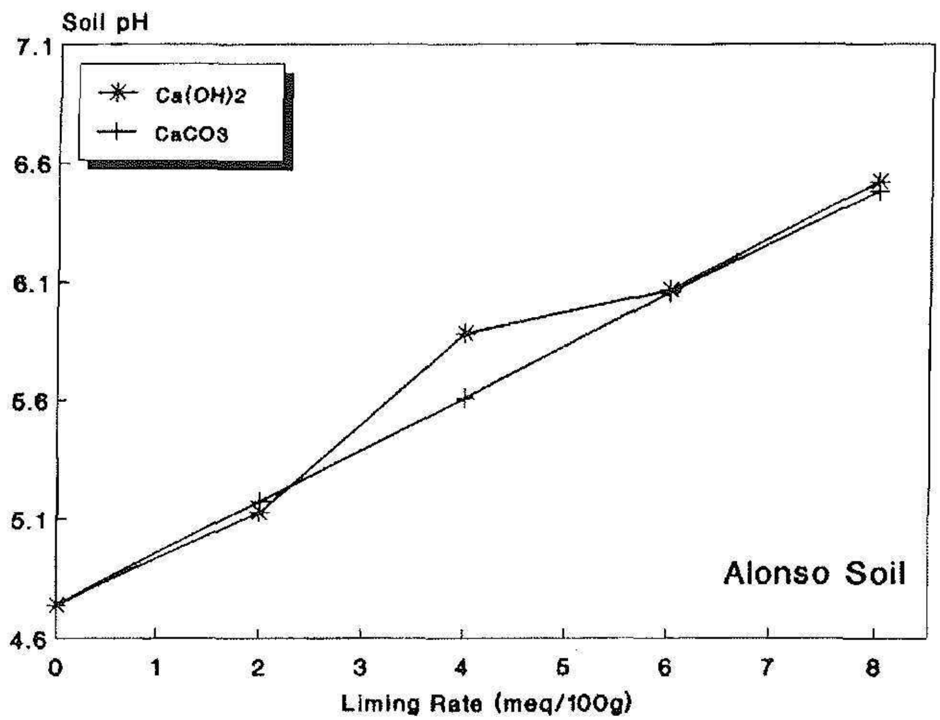


FIG. 2. Effects of liming source and rate on the pH of Bayamón and Alonso soils.

Bayamón soil has a lower buffer capacity than the other soils. For example, the application of 8.0 meq/100 g as $Ca(OH)_2$ increased the pH of Bayamón soil by 2.53 units, whereas a change of 1.78 units was observed for Alonso soil. In the case of Mariana and Corozal soils, an application of 8.91 meq/100g of $Ca(OH)_2$ increased the pH by 1.60 and 0.86 units, respectively. A factor that may contribute to a lower buffer capacity in Bayamón soil is its low organic matter content. Bayamón soil has an organic matter content of 0.45%, far below that of the Mariana, Corozal and Alonso soils, which contain 3.37, 2.34 and 3.87%, respectively (table 1).

The importance of exchangeable Al^{3+} as an acidity factor is clearly seen in the behavior of the Corozal soil. A liming rate of 8.0 meq/100 g increased the pH just to 4.92, whereas for the other soils pH values above 6.00 were obtained. All exchangeable A^{3+} in the Mariana, Bayamón and Alonso soils was neutralized at pH values between 6.00 and 6.50. Figures 3 and 4 present the relationship between exchangeable Al^{3+} and soil pH. $CaCO_3$ and $Ca(OH)_2$ were equally effective in neutralizing Al^{3+}. Exchangeable Al^{3+} content of the Corozal soil decreased from 864.22 mg/kg to 296.77 mg/kg as the pH increased from 4.13 to 4.94. A liming rate of 1.5 times the amount of exchangeable Al^{3+} has been recommended for tropical acid soils (20). This rate allows for the neutralization of all the exchangeable Al^{3+} plus 50% more to neutralize the acidity generated from organic matter and other sources.

Although in terms of meq/100 g both liming materials are equally effective, because of a lower molecular weight and a higher $CaCO_3$ equivalent, less $Ca(OH)_2$ has to be applied to attain a desired pH. For example, to achieve a pH of 4.95-5.00 the Corozal soil would require 9.88 t/ha $CaCO_3$ but only 7.41 t/ha of the $Ca(OH)_2$. If about 2.47 t/ha less liming material will be needed when using $Ca(OH)_2$, the farmers may save money from hand labor and transportation costs.

The short term incubation experiment indicated a faster increase in soil pH with the application of the industrial by-product $Ca(OH)_2$ (fig. 5, 6). Soil pH values around 6.00 were observed for Mariana, Alonso and Bayamón soils after the first day of incubation with the application of 8.0 meq of $Ca(OH)_2$, whereas $CaCO_3$-treated samples reached pH values around 6.00 only after the second day of incubation. Calcium carbonate treated samples maintained an increasing pH trend up to the fifth day of incubation. On the fifth day of incubation a pH value of 4.92 was observed for the Corozal soil limed with $CaCO_3$, whereas a pH value of 5.12 was observed for the $Ca(OH)_2$-treated samples. The high exchangeable aluminum content of Corozal soil (934.37 mg/kg) seems to foster a faster reaction of the $CaCO_3$ than that which occurs in the

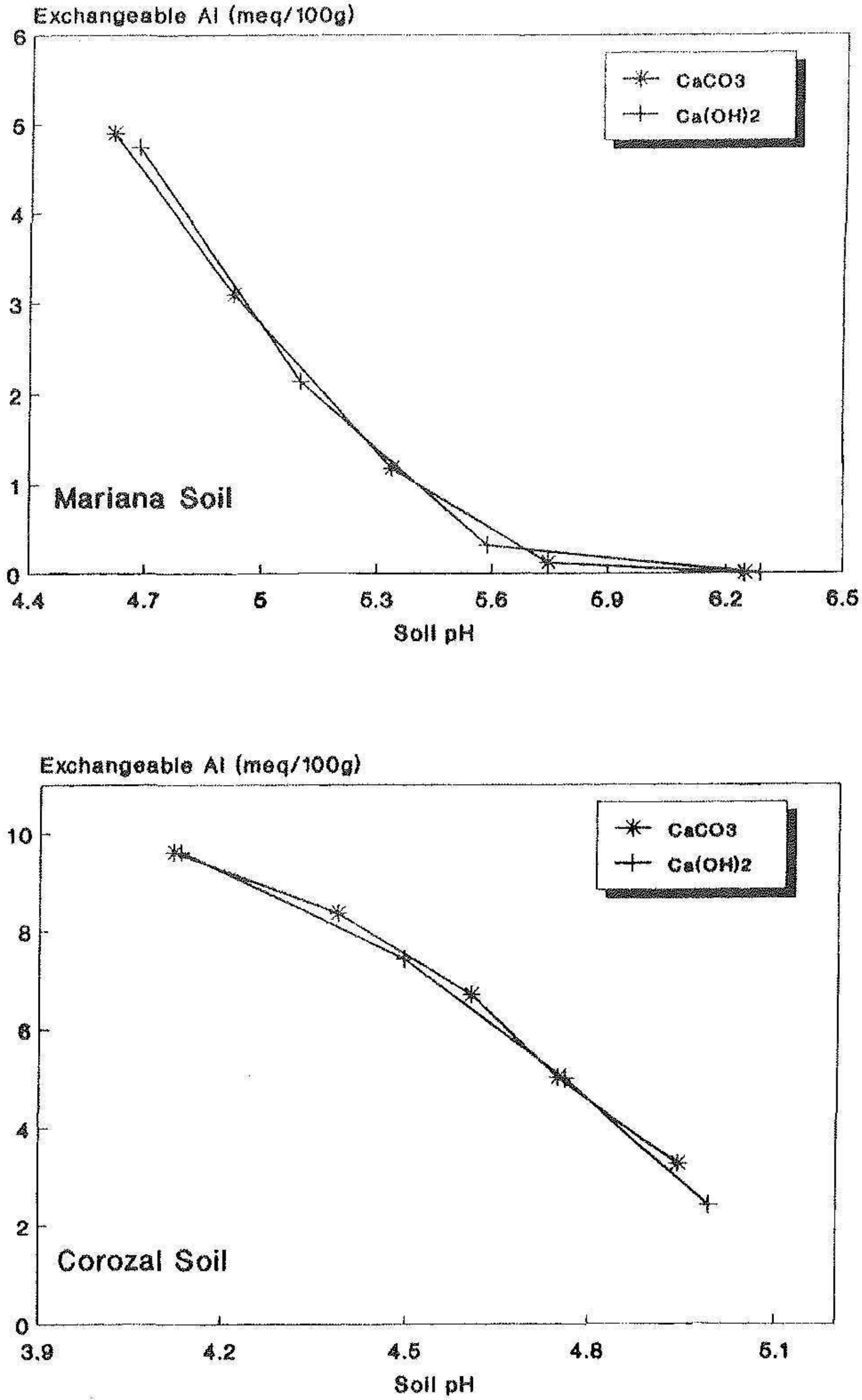
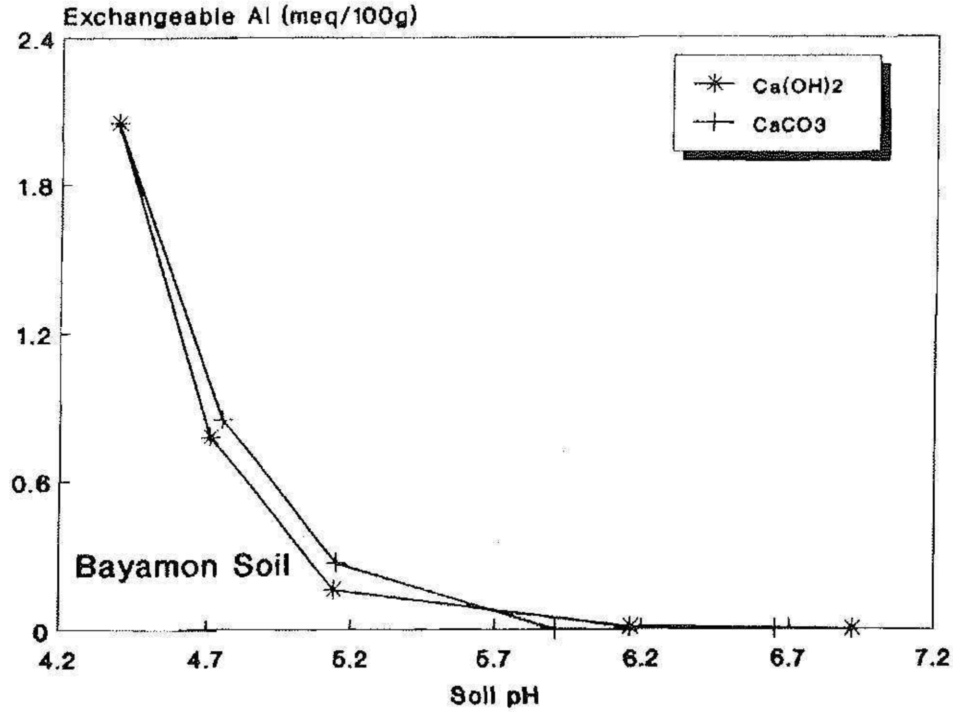


FIG. 3. Relationship between soil pH and exchangeable aluminum content of Mariana and Corozal soils.



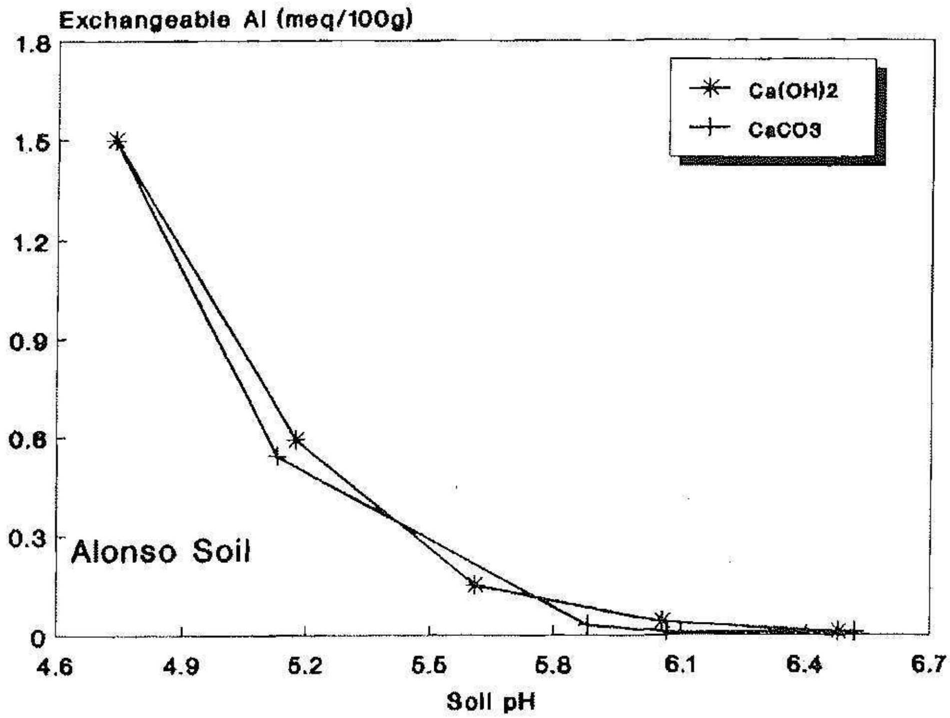


FIG. 4. Relationship between soil pH and exchangeable aluminum content of Bayamón and Alonso soils.

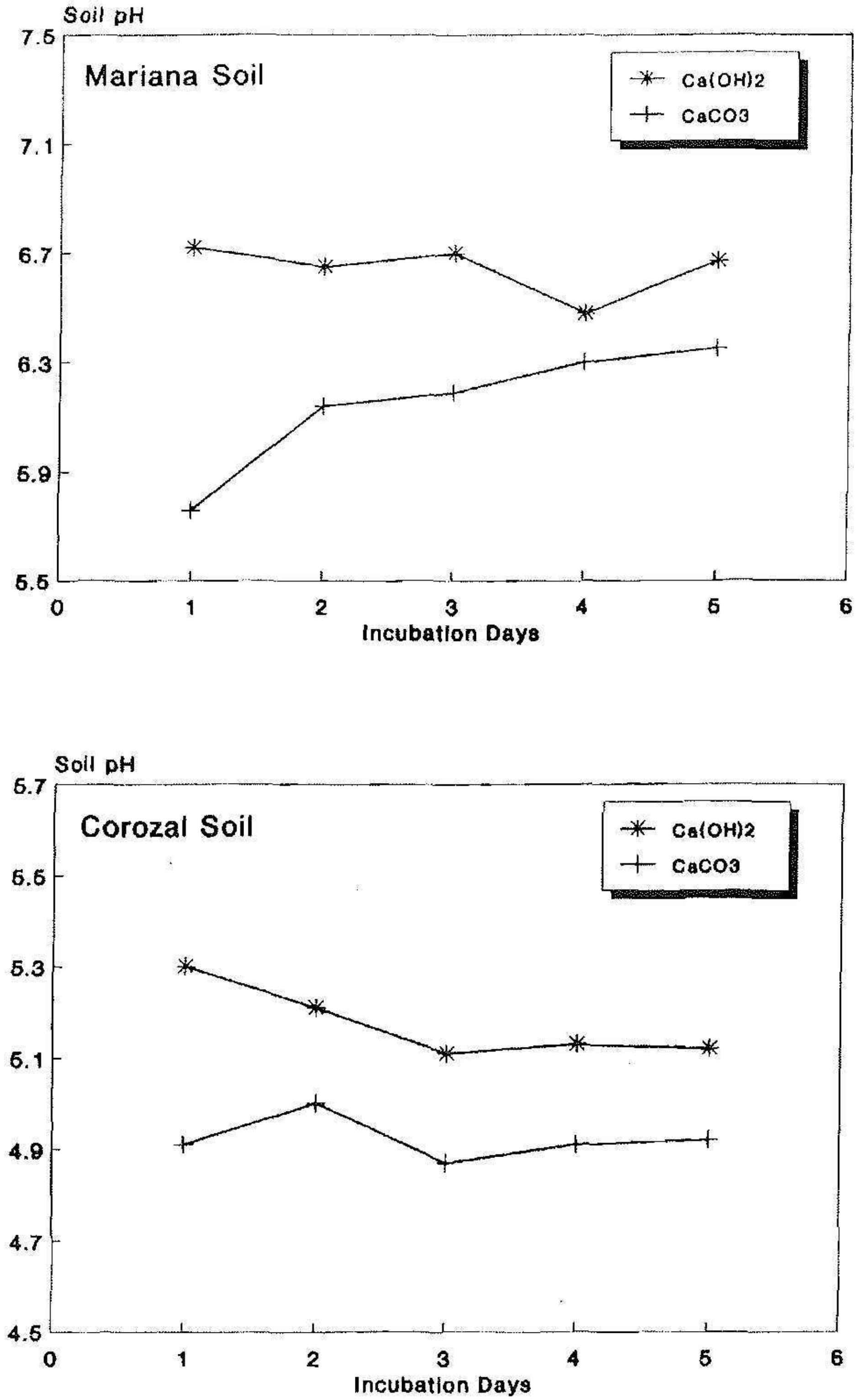


FIG. 5. pH of Mariana and Corozal soils as affected by liming source and time of incubation.

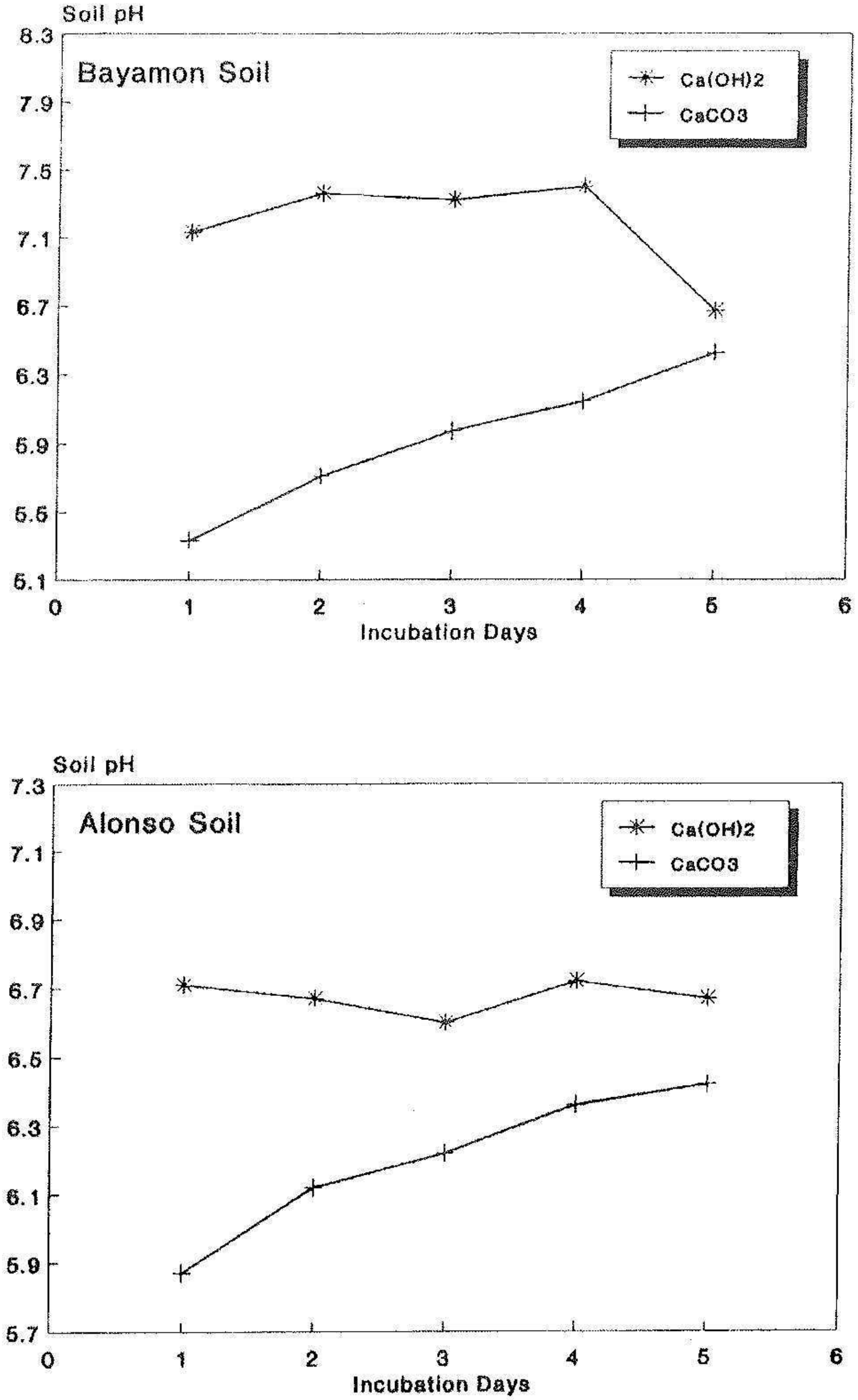


FIG. 6. pH of Bayamón and Alonso soils as affected by liming source and time of incubation.

TABLE 3.—*Soil exchangeable Al after 5 days of incubation.*

Treatments[1]	Soils			
	Mariana	Corozal	Bayamón	Alonso
	mg/kg			
Control	250.90	934.37	323.75	238.31
$Ca(OH)_2$	0.90	331.84	2.70	1.80
$CaCO_3$	2.70	496.41	4.50	1.80

[1]The liming material was applied at rate of 8.0 meq/100g of soil.

other soils. The $Ca(OH)_2$ samples showed a slight decrease in pH from 5.30 the first day to 5.12 the fifth day. This tendency suggests a strong buffering capacity in this soil.

Table 3 presents levels of exchangeable Al^{3+} after five days of incubation. The application of 8.0 meq/100g of liming material, $CaCO_3$ or $Ca(OH)_2$, neutralized almost completely the exchangeable Al^{3+} of Mariana, Bayamón and Alonso soils. Exchangeable Al^{3+} in Corozal soil decreased from 934.37 mg/kg in the control to 331.84 and 496.41 mg/kg for $Ca(OH)_2$ - and $CaCO_3$- treated samples, respectively. The lower exchangeable Al^{3+} observed for the $Ca(OH)_2$ agrees with the faster increase in pH observed.

The faster reaction of $Ca(OH)_2$ presents an advantage when immediate planting is required. The neutralization of soil acidity may be achieved in a shorter period of time. Also, the farmer will have to apply smaller amounts of liming material and then reduce labor costs. However, the long term effect of the liming of application may be shortened because of the faster reaction of $Ca(OH)_2$.

The high moisture content of the $Ca(OH)_2$ is a limitation for its use as liming material. However, if spread in a thin layer (8 to 10 cm thick), the moisture content decreases to 3 to 4% in five to six days and the material can be easily ground to appropriate fineness. In addition to its use as pure $Ca(OH)_2$, the alternative of processing and mixing it with the commercially produced $CaCO_3$ should be explored.

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