Cultivos Tropicales, 2020, vol. 41, no. 2, e02
ISSN impreso: 0258-5936
ISSN digital: 1819-4087

abril-junio
Ministerio de Educación Superior. Cuba
Instituto Nacional de Ciencias Agrícolas

http://ediciones.inca.edu.cu

Original article

Characterization of solid waste to liming and fertilizing carrier calcium and nitrogen

Leonardo Rodríguez-Suárez[1*]

María del Carmen Falcón-Acosta[2]

Yan Carlos Ordoñez-Sánchez[1]

[1]Centro de Ingeniería e Investigación Química CIIQ. Vía Blanca s/n entre Infanta y Palatino, Cerro, La Habana, Cuba. Teléfono 7 648 91 88-92 ext. 112

[2]Universidad Agraria de La Habana "Fructuoso Rodríguez Pérez", carretera a Tapaste y Autopista Nacional, San José de las Lajas, Mayabeque, Cuba

[*]Author for correspondence: leonardo@ciiq.minem.cu

ABSTRACT

Liquid calcium nitrate is obtained from the reaction between nitric acid and lime hydrate, carriers of the nutrients nitrogen and calcium respectively; the latter coming from the Holguín and Pinar del Río limestone quarries. The generation of solid waste results in the greatest environmental impact of this process. In order to reduce the environmental damage in the Company of Fertilizers and Pesticides of Nuevitas, Camagüey, it is investigated and characterized the residues of the process of obtaining liquid calcium nitrate the objective is to use it as a carrier of nutrients for the crops. It known that these residues still contain nutrients easily assimilated by plants, therefore these can be useful as fertilizer or as an agricultural amendment. The chemical characterization of the residues was used the Cuban Norm 1121: 2016, Cuban Norm 1117: 2016 and American Chemical Society Specifications. The characterization of the sludge obtained in the sedimentation and the insoluble solid of the neutralization reaction give lower nitrogen and calcium values in the solid. Based on the results this waste can use in the agriculture.

Key words: fertilizers, agricultural amendments, acid soils, environmental impact, NPK

INTRODUCTION

Soil acidification is one of the negative processes that limit its productivity. In tropical or subtropical regions, where rainfall and temperatures are high, the soils are generally very acidic; this causes a cationic imbalance due to the leaching of bases [(1)]. There is a replacement of exchangeable bases by hydrogen and aluminum ions due to the percolation of water, extraction of basic cations by plants, and the use of acidic fertilizers [(2)]. The same source indicates that when the soils are strongly acidic (pH=4.5-5.5), the aluminum content increases markedly. It causes a series of chemical-physical processes that negatively affect the growth of plants, among which the following may be mentioned: (*i*) decrease in microbial activity, especially bacterial activity, (*ii*) low cation exchange capacity, (c) reduced amounts of phosphorus (P), calcium (Ca), magnesium (Mg), copper (Cu) and molybdenum (Mo) available. Recent studies indicate the influence of nitrogen fertilization on increasing acidity and the limited efficiency of fertilizers applied to coffee crops (*Coffea arabica* L.) in soils with acidity problems [(3)]. This acidity problem in coffee plantations has been counteracted with the application of agricultural lime in low doses (340 kg ha year^{-1}), which increased coffee production by 15 % [(4)].

The high acidity of the soils is highly influenced by human activity [(5)], with acid rains being one of these manifestations. However, other research indicates that soils are not always acidified [(6)]. These investigations present the results of the pH increase in Ferralitic Red and Ferralitic Red Leachate soils that is occurring in the last 20-25 years, with a hypothesis that it is due to soil degradation by continued agricultural management. Also, with the increase in the average temperature of the plains of Cuba of 0.9 ºC in the last 60 years. The pH increase that is occurring in these soils is also influenced by the agrogenic influence together with climate change.

In Cuba, this process is very harmful for agriculture due, among other things, to the area that is by some type of acidity affected and the unfavorable agro-productive distribution of the soil.

According to official figures, the area affected in Cuba by acidity in soils corresponds to 50.7 % of the agricultural area [(8)], taking into account the acidity values for pH KCl<6 and pH KCl <4.6. It means that 31 % of the total surface of the country is by acidity affected, that is, 3.4 million hectares. This situation affects an important part of the world's agricultural soils, where 40 % are acidic soils with a pH less than 5.5 [(7)].

When the agro-productive classification of Cuban soils is analyzed [(8)], along with the acidity of the soils, the serious problem of soil availability for crops can be seen. Only 33 % are classified as highly productive or productive soils, 21 % moderately productive and approximately half, 46 %, as little productive.

Cultivos Tropicales, 2020, vol. 41, no. 2, e02
ISSN impreso: 0258-5936
ISSN digital: 1819-4087

abril-junio
Ministerio de Educación Superior. Cuba
Instituto Nacional de Ciencias Agrícolas

http://ediciones.inca.edu.cu

The pH of the irrigation water is another factor to consider, it must be between 5.5 - 7.0 as well as the pH of the soil (9). A pH less than 5.5 in the soil increases Al^{+3} levels. Interchangeable H^{+} is the main source of H^{+} until the soil pH reaches 5.3 when the Al^{+3} of the octahedral sheets of the clays becomes unstable and is absorbed as interchangeable Al^{+3} (10), the toxicity being to this element the most important limiting factor of growth in acidic soils (11). On the other hand, in the presence of a pH higher than 7.5, the absorption capacity of iron (Fe), manganese (Mn) and zinc (Zn) is limited (12).

At the Nuevitas Fertilizer and Pesticide Company in Camagüey, calcium nitrate [$Ca(NO_3)_2$] is by neutralizing nitric acid and lime hydrate obtained. This reaction produces calcium nitrate in solution and a volume of solid waste. These solid residues are formed, on the one hand, by the lime hydrate that did not react in the reactor, which are collected in the primary filter and, on the other hand, by the sludge obtained in the sedimentation process.

There is no unique strategy to control the acidity of the soil due to their particularities; the application of the same calcium source in different types of soils generates different responses in terms of the concentration of available calcium and potassium, pH value, among others (13). Many factors are involved in the correction of acidity. The solution of this problem implies a comprehensive approach that ranges from the analysis of soil, water and the use of amendments, among others (14). Experiences in Cuba have shown that, by establishing an integrated system of sustainable soil management technologies (15), it helps to improve the intercationic imbalance and the chemical properties of the soil, among other aspects.

The main purpose of this work is to characterize the solid residues obtained in this process. Confirmation of nutrients in these residues would allow the entity to market it as a material intended for liming acidic soils and carrying nutrients.

MATERIALS AND METHODS

The tests were carried out in the Inorganic Chemistry Laboratory of the Center for Chemical Engineering and Research (CIIQ), located in Havana and belonging to the Business Group of the Chemical Industry (GEIQ) of the Ministry of Industries (MINDUS).

One kilogram of the solid residue from the primary filter was weighed, dried in the Merck brand stove ULM-500, of German origin, at a temperature of 105 °C for one hour. Subsequently, without receiving any size reduction treatment, it was passed through a MRC Scientific Instruments Model TSS-200 sieve shaker to determine the sample size.

One liter of the residual sludge from the sedimentation process was separated. For filtering the sludge, a funnel was used with the filter paper F-2041, at a vacuum pressure of -0.6 atm, from this filtration a solid residue and a clear liquid were obtained.

Both samples were characterized according to standards: NC 1117: 2016; NC 1119: 2016; NC 1121: 2016; NC 54-279 and Reagent Chemicals, 8th American Chemical Society Specifications. The granulometry, the insoluble residue, the percentage of nitrogen and calcium, the density of the liquid and the acidity were determined, the latter being determined with pH indicator paper, range from 1-14.

RESULTS AND DISCUSSION

Table 1 and 2 present the characterization of the solid residues of this process with the purpose of evaluating the feasibility of being used as amendments or liming material.

Table 1. Physical-chemical analysis of the solid residue from the primary filter

Test		Values
H_2O, %		18.92
Granulometry , %	< 1 mm	29.5
	1 - 2 mm	25,0
	2 – 3.36 mm	6.2
	3.36 – 4	19.4
	> 4 mm	19.9
pH		12.0
Insoluble residue		8.95
Nitrogen		1.43%
Calcium		4.0%

In Table 1, it can be seen that the solid residue leaving the reactor has a high pH, so there is still calcium hydroxide [$Ca(OH)_2$].

Table 2. Chemical analysis of the mud and clear liquid obtained in the settler

Liquid residue (227.4 g)		Clear liquid (490 mL)			
N_2 (%)	Ca (%)	N_2 (%)	Ca (%)	Density, (g mL)	Free acidity
5.65	11.79	8.58	12.50	1.497	0

In Table 2, it is observed that there is a certain amount of calcium nitrate in the solid residue of the settler, although with lower values than that of the clear liquid.

The correction of the acidity consists, fundamentally, in neutralizing mainly the interchangeable aluminum. It is noteworthy that this reaction occurs only when there is moisture in the soil and only affects the volume of the soil where it is applied. The reaction occurs according to the following formula [1,11]:

$$2\,Al - suelo + 3\,CaCO_3 + 6\,H_2O \rightarrow 3\,Ca - suelo + 2\,Al\,(OH)_3 + 3\,H_2CO_3$$

The effect of liming extends to biodiversity by modifying the availability of nutrients that makes some species develop to the detriment of others. As the pH approaches 7, the number of species increases, as a large number of these have Its optimal development at this value, if the pH moves away from neutrality, others adapted to these special conditions appear [16]. An accepted opinion on the purpose of liming can be summarized in two fundamental aspects, i to suppress calcium and magnesium deficiency; (ii) correct the negative effects of acidity [1].

Table 3 shows the neutralization values of different chemical substances used for liming.

The agronomic efficiency of the materials used for liming is determined by analyzing the purity of the material, the chemical form, the size of the particles and the value of the neutralization that is expressed as an equivalent percentage in calcium carbonate [17,18].

Table 3. Substances that correct soil acidity and its neutralization value

Denomination	Neutralization value (VN)%	kg equivalent to 1000 kg of $CaCO_3$
Calcium carbonate	100	1000
Magnesium carbonate	119	840
Calcium oxide	179	560
Magnesium oxide	248	400
Calcium hydroxide	135	740
Magnesium hydroxide	172	580
Calcium silicate	86	1160
Magnesium silicate	100	1000

Source: [18]

The most common liming substances used are inorganic as shown in Table 4, although there are studies carried out with organic residues, specifically vermicompost of bovine manure, alone or mixed that have given good results [19]. Other materials such as phosphated limestone and combinations of organic fertilizers and *NPK* have given very good results in cane fields of

Vertisoles on the north coast of the province of Villa Clara. These combinations showed significant positive effects on the structure of the soil, both in the layer superficial as in the subsoil, with residual impact over time up to 36 months (20). The application of liquid limes in an Utisol, can rapidly decrease the acidity of the soil with a residual effect greater than 61 days, and increase the fertility of the soil, increasing the height of the plants, the length of the roots and the dry weight of corn biomass (21).

It should be borne in mind that it is necessary to carry out this operation in a controlled manner to avoid adverse effects, one of them being the increase in production costs.

The agronomic efficiency of the liming material depends on the particle size, the smaller it is, the greater its reaction. Therefore, its relative efficiency (ER) will depend on the degree of grinding of the material (17,18). Table 4 shows this relationship.

Table 4. Relative grain size efficiency of lime based on mesh type

Mesh number	Hole size	Relative efficiency, %
< 8	> 2,36	0
8 – 20	2.36 – 0.85	20
20 – 40	0.85 – 0.42	40
40 – 60	0.85 – 0.25	60
> 60	< 0.25	100

To assess these two factors together, chemical purity and particle size, a parameter called Relative Total Neutralization Power (PRNT) is used. This value indicates the amount of material that will react in the first three months (17) and it is calculated according to equation 1.

$$PRNT = \frac{VN*ER}{100} \quad (1)$$

The assessment of the solid residue of the primary filter as liming material is shown in Table 5.

176 kg of solid waste is obtained from the mass balance carried out in the reactor in one working day, which means that 95.92 kg has the required granulometry and can react efficiently with the acidity of the soil. From the initial value 27.0 kg would react in the first three months, and the rest, 68, 92 kg would react later. It is clear that a smaller particle size in the residue would have a higher PRNT value and a greater quantity of lime would react in the first three months, achieving greater neutralization of acidic soils in the first three months. These times may vary, studies carried out in strongly acidic soils cultivated with cocoa applied as lime material agricultural lime of 85 % purity

and dolomite lime with 55 % $CaCO_3$ and 33 % $MgCO_3$, the pH of the soils increased from 4.36 to 6.0 in 60 days [22].

Table 5. Assessment as material for liming of the residue obtained in the primary filter

Residue	Relative particle size efficiency ER, %	Neutralization value VN, %	$PRNT = (VN * ER)/100$, %
Solid residue grain size 2 - <1 mm (8 - 20 mesh) 54.5 % of the residue passes through this mesh	20	135	27,0

The residue from the primary filter was used without any particle reduction treatment to evaluate its *PRNT* and thus avoid increasing costs.

The objective of the calcium nitrate plant is to produce 2,800 m^3 $year^{-1}$ of liquid fertilizer, this would generate 123.2 t of solid waste, which, if used as a liming material, would avoid the generation of an environmental liability. Table 5 presents the quantities of purely divided fine limestone with the purpose of increasing the pH by 0.5 units, so it can get an idea of how much area this residue will cover. However, it is necessary to do a chemical analysis of the soil to determine its pH and buffer capacity [23].

Table 6. Average needs of finely divided pure limestone to increase 0.5 pH units to the soil based on its initial pH, texture and organic composition (t ha)

Type of soil	*pH* initial			
	4.5–5.0	5.0–5.5	5.5–6.0	6.0–6.5
Sandy	0.35	0.35	0.40	0.50
Frank – Sandy	0.50	0.60	0.70	0.90
Frank	0.85	0.95	1.05	1.25
Frank – silty	1.30	1.40	1.50	1.70
Frank – clayey	1.60	1.80	2.00	2.50
Organic	3.60	3.80	4.00	4.50

Source: [24]

The characteristics of the liming materials are variable and each one has its specifications. It is stated that a material has good quality to whitewash if it has an equivalent content of calcium carbonate of 80 % onwards. Materials whose ingredient is calcium and magnesium oxide and hydroxide are more effective in neutralizing acidity. Furthermore, the finer and higher the calcium and magnesium content, the faster your reaction will be in the soil [25].

However, an aspect that could provide an additional benefit when using this solid residue in agriculture is the amount of calcium nitrate that it retains and that can be used by plants as an easily assimilable source of nitrogen. Experiences have shown that the combination of liming material with macronutrients can be beneficial for increasing plant productivity among other benefits. In a work carried out it was used agricultural gypsum as a liming material and combined it with fertilizer 41-46-00 [26], which represented competitive advantages in the production of corn, increasing the yield of the leaf mass and the yield in grain, also the plants under This treatment turned out to have more robust stems and higher height. In another study carried out, sugar foam, a material with a high dry weight content of $CaCO_3$ and small amounts of NPK, produced an increase in the mean concentrations of *N-Kjendal*, *P-Olsen* and *K-available* from soils, as well as in the chemical and biochemical fertility of soils [27].

CONCLUSIONS

- It is possible to use the generated waste as an amendment to decrease the acidity of the soil and as a nutrient carrier.
- The Relative Neutralization Power of the solid residue of the primary filter without grinding is determined, which is equal to 27 %.
- 54.5 % of the residue from the primary filter has the required particle size and can react with the acidity of the soil in the first three months.
- The solid residue from the settler can be used as a carrier for the nutrients calcium and nitrogen.

RECOMMENDATIONS

Carry out a field test with this industrial residue to determine its agronomic efficiency in reducing the acidity of the soil.

BIBLIOGRAPHY

1. Machado A A. Efecto del encalado sobre las cargas eléctricas y otras propiedades de tres suelos de Costa Rica. Programa Conjunto Universidad de Costa Rica/Centro Agronómico Tropical de Investigación y Enseñanza(CATIE); 1977 p. 138.
2. Chaves Solera MarcoA. La acidez y el encalado de los suelos. Dirección de Investigación y Extención de la Caña de Azúcar(DIECA)); 1984 p. 1–5.

3. López-Báez W, Urbina H L, Reinoso S R, Martínez S J. Efectos del encalado ensuelo ácido cultivado con café (*Coffea arabica L.*) en la Reserva de la Biosfera del Triunfo, Chiapas, México. AgroProductividad. 2018;11(4):55–60.
4. Sadeghian S. La acidez del suelo una limitante común para la producción de café. Centro Nacional de Investigaciones de Café (Cenicafé); 2016.
5. Osorno Henao H. Mitos y realidades de las cales y enmiendas en Colombia. Universidad Nacional de Colombia, Sede medellin; 2012.
6. Jiménez AH, Díaz MM, Benítez YB, Vargas Blandino D, Cabrera Rodríguez JA, Ascanio MO, et al. Degradación de las propiedades de los suelos ferralíticos rojos lixiviados de la" llanura roja de La Habana", por el cultivo continuado. Mayabeque: Ediciones INCA; 2014, 157p.
7. Đalović IG, Jocković ĐS, Dugalić GJ, Bekavac GF, Purar B, Šeremešić SI, et al. Soil acidity and mobile aluminum status in pseudogley soils in Čačak-Kraljevo basin. Journal of the Serbian Chemical Society. 2012;77(6):833–43.
8. ONEI. Oficina Nacional de Estadísticas e Información. Edición 2018. 2018.
9. Gómez JJC, Muñoz RB, Rodríguez M de LH. Calidad del agua para riego en la agricultura protegida en Tlaxcala. Ingeniería. 2015;19(1):39–50.
10. Oliva Escobar DP, Arévalo G. Determinación de la acidez intercambiable (Al^{+3}+ H^{+}) a partir del pH para la estimación de la capacidad de intercambio catiónico (CIC) en suelos de la cuenca del Pacífico en El Salvador, Honduras y Nicaragua. ESCUELA AGRÍCOLA PANAMERICANA; 2009.
11. Campillo R. Estrategias de corrección de suelos acidificados mediante enmiendas calcáreas. Producción de trigo harinero para el borde costero de La Araucanía. Capitulo. 2013;1:9–23.
12. Santos Rojas J, Orena Alvarado S. Manual de produccion de papa para la agricultura familiar campesina. Santiago de Chile: Instituto de Investigaiones Agropecuarias. 2006;(147):77.
13. Hirzel J, Toloza S, Novoa F. Evolución a corto plazo de las propiedades químicas en dos suelos de la zona centro sur de Chile fertilizados con diferentes fuentes de calcio. Chilean journal of agricultural & animal sciences. 2016;32(3):217–27.
14. Molina E. Acidez de suelos y uso de enmiendas. Centro de Investigaciones Agronómicas. 2014;1:1–7.
15. Carcedo EAC, Miranda YMM, Aroche EJA. Tecnologías de manejo sostenible de suelo en la cooperativa Jaime Vena, Pinar del Río. Avances. 2015;15(4):416–25.

16. Morán DK. Efecto del encalado y la fertilización con lodos de depuradora urbana sobre la evolución edáfica, productiva y biodiversidad de un sistema silvopastoral desarrollado bajo Populus x canadensis en el noroeste de España. [Tesis de Doctorado]. [España]: Universidad de Santiago de Compostela. Escuela Politécnica Superior. Departamento de Producción Vegetal; 2009. 221 p.
17. Molina E, Espinosa J. Acidez y encalado de los suelos. International Plant Nutrition Institute. CATIE, San José–Costa Rica. 1999;46.
18. Quiroga Martínez MJ. Efecto de la aplicación de materiales encalantes en el cultivo de la vid cv. Mencía en la DO Bierzo, incidencia sobre la composición fenólica y evolución en la crianza del vino. 2014;
19. Bárcenas J, Gascó-Guerrero G, López R, Hernández J, Larreal M, Bracho B. El equivalente de $CaCO_3$ como criterio para realizar mezclas de materiales para la enmienda de acidez en Ultisoles. Estudio en columnas simuladas de suelo. Rev. Fac. Agron. 2014;31(Supl 1):611–23.
20. Cairo Cairo P, Machado de Armas J, Torres Artiles P, Rodríguez Urrutia A, Rodríguez López O, Jiménez Carrazana R. Efectos de la caliza fosfatada sobre la estructura y calidad de vertisoles bajo caña de azúcar. Centro Agrícola. 2017;44(4):30–6.
21. Garbanzo-León G, Molina-Rojas E, Cabalceta-Aguilar G. Efecto de la aplicación de enmiendas líquidas en el suelo y en el crecimiento de maíz bajo condiciones de invernadero. Agronomía Costarricense. 2016;40(2):33–52.
22. Rosas-Patiño G, Puentes-Páramo YJ, Menjivar-Flores JC. Relación entre el pH y la disponibilidad de nutrientes para cacao en un entisol de la Amazonia colombiana. Ciencia y Tecnología Agropecuaria. 2017;18(3):529–41.
23. Hirzel J, Henríquez R. Uso de enmiendas calcáreas en viñedos. Vinos del Sur. 2018;(2).
24. López-Cabeza R. Comportamiento enantioselectivo de los plaguicidas Metalaxil e Imazaquín en suelos agrícolas. 2017;279.
25. Toledo M. Manejo de suelos acidos de las zonas altas de Honduras: Conceptos y metodos. Instituto Interamericano de Cooperación para la Agricultura (IICA),; 2016. 156 p.
26. Acosta L, Rivera J, Marza F, Claure T. Uso de yeso agrícola como enmienda en el cultivo de maíz forrajero en el valle central de Tarija. Revista Científica de Investigación INFO-INIAF. 2017;4:56.

27. Xiong J. Recuperación y rehabilitación de suelos contaminados con elementos traza mediante la aplicación de enmiendas y el establecimiento de una cubierta vegetal natural o de una planta de crecimiento rápido (Paulownia fortunei). 2016;180.