



MINING RESIDUE IN THE COMMERCIAL LIMESTONE BLENDING AND THE CHEMICAL ATTRIBUTES OF A LATOSOL

João Vidal de Negreiros Neto¹, Rubens Ribeiro da Silva², Gilson Araújo de Freitas³, Ângela Francieli Machado⁴, & Antônio Clementino dos Santos⁵

1 - Agronomist, Professor at UFT/Araguaína – TO, joao_vidal@uol.com.br

2 - Agronomist, Professor at UFT/ Gurupi-TO, rrs2002@uft.edu.br

3 - Agronomist, Post-Graduation Program (PNPD) of Plant Production Post-Graduation/UFT, Gurupi-TO, araujoagro@hotmail.com

4 - Environmental Chemistry, Soil Laboratory /UFT/Gurupi-TO, angelafrancieli@uft.edu.br

5 - Agronomist, Professor at UFT/Araguaína – TO, clementino@uft.edu.br

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ABSTRACT

The limestone mining activity causes environmental impacts due to the generation of waste. However, the reuse of these residues has been investigated with the objective of improving soil fertility and acidity correction. The objective of this work was to evaluate the potential for using mining residues in the commercial limestone blending and in the chemical attributes of a dystrophic Red Yellow Latosol. The experiment was carried out in three steps: the first corresponded to the sampling and characterization of the residues in the tailings pile; the second was the combination and characterization of the new soil acidity correction agents as well as the selection of treatments based on the Neutralization Power and doses of soil acidity correction agents (0.0; 0.5; 1.0; 2.0; 4.0 t ha⁻¹); in the third step, a test of the incubation and calibration of the application doses of the soil acidity correction agents was performed. It was found that even with the raise in the levels of Ca²⁺ and Mg²⁺ in the correction agents, it was not possible to provide an optimal supply of nutrients to the soil, a fact explained by the low constant solubility of CaCO₃ and MgCO₃. However, the commercial limestone blending with tailing was efficient, as it had a significant effect on raising the pH and neutralizing the soil moisture potential.

Palavras-chave:

constante de solubilidade
corretivo de acidez
poder de neutralização

REJEITO DA MINERAÇÃO NA BLENDAGEM DO CALCÁRIO COMERCIAL E NOS ATRIBUTOS QUÍMICOS DE UM LATOSSOLO¹

RESUMO

A atividade de mineração de calcário causa impactos ambientais pela geração de resíduos. Entretanto, tem-se buscado o reaproveitamento desses resíduos, visando o emprego na melhoria da fertilidade e correção de acidez do solo. O objetivo foi avaliar o potencial de uso do rejeito da mineração na blendagem do calcário comercial e nos atributos químicos de um Latossolo Vermelho Amarelo distrófico. O trabalho foi realizado em três etapas: a primeira correspondeu à amostragem e caracterização dos resíduos na pilha de rejeitos; a segunda foi a blendagem e caracterização dos novos corretivos de acidez do solo, bem como a escolha dos tratamentos baseados no valor de Poder de Neutralização e doses de corretivos de acidez do solo (0,0; 0,5; 1,0; 2,0; 4,0 t ha⁻¹); já na terceira etapa realizou-se o ensaio de incubação e calibração das doses de aplicação dos corretivos de acidez do solo. Observou-se que mesmo com incrementos nos teores de Ca²⁺ e Mg²⁺ nos corretivos, não foi possível o fornecimento ideal desses nutrientes para o solo, fato explicado pela baixa constante de solubilidade do CaCO₃ e MgCO₃. No entanto, a blendagem do calcário comercial com os rejeitos da mineração foi eficiente, pois tiveram efeito significativo na elevação do pH e neutralização da acidez potencial do solo.

INTRODUCTION

Mining is an activity that exploits natural resources, therefore causing environmental impacts not only in the mined area but also in the neighboring areas. In relation to the soil, it causes direct destruction by removing the vegetation cover. Regarding water, it changes its quality with the disposal of tailings and silting up of watercourses. Rock drilling associated with the detonation of explosives harms the air quality, as well as the flora and the fauna with the degradation and destruction of the faunal habitat (BEZERRA, MARIA 2015; CÉSAR, CARNEIRO 2017; ALBUQUERQUE, TAVARES 2018).

It is estimated that in Brazil, the production of by-product from the limestone mining in 2012 was in the order of 13.43 Megatonnes (Mt), with a perspective for the year 2030 in the order of 20.35 Mt (IPEA, 2011). The quantities generated from these residues are always very large and depend, among other factors, on the processes used to extract the ore and the location of the deposit in relation to the surface (IPEA, 2011). Traditionally, these residues are disposed in landfills and, very commonly, they are thrown directly into the environment, without any treatment process.

An alternative to ensure the reuse of the by-product is the uniformity of the mass through blending, which aims to obtain a mass with specific characteristics (SABEDOT *et al.*, 2014). Solid residues containing mineral substances have the potential to be used in other industrial activities or in farming (MANGIERI; FILHO, 2015; FERNÁNDEZ *et al.*, 2018).

Brazilian agriculture has continuously investigated new inputs and raw materials to ensure the sustainability and sovereignty of the agricultural sector in the country (PASSOS *et al.*, 2015; ARAÚJO *et al.*, 2018). However, the search for reusing these residues in an economically feasible manner and that satisfactorily helps the environment, has been the subject of research in the last years, aiming at their use in fertility improvement and soil acidity correction. Thus, in view of the millions of tons of by-products that are daily produced in mining activities, the alternatives for recycling and or reuse should be investigated and implemented, as much as possible.

Thus, the objective of this study was to evaluate

the potential use of mining waste in commercial limestone blending and the chemical attributes of a dystrophic Red-Yellow Latosol.

MATERIAIS AND METHODS

The experiment was carried out in three steps in which the first one was performed in the facilities of the Caltins/JDemitto limestone mining company in the municipality of Bandeirantes, State of Tocantins and the following steps on the experimental station of the Federal University of Tocantins – UFT, Gurupi University Campus, southern region of the State of Tocantins, at 280 m altitude and within the coordinates 11°43'45" south latitude and 49°04'07" west longitude. According to the climatic classification of Köppen (1948), the regional climate is of the humid B1wA'a' type with a moderate water deficiency.

The average annual temperature is 29.5°C, with an annual rainfall of 1,804 mm. The first step corresponded to the sampling and characterization of the residues in the tailing pile. In the second step, the blending and characterization of the new soil acidity correction agents was carried out, as well as the selection of the treatments and doses of soil acidity correction agents to be used in the next step. In the third step, the incubation test and calibration of the application rates of the soil acidity correction agents were carried out.

Step 1: Sampling and characterization of the residues in the tailing pile

Sampling was carried out following a north-south and east-west oriented 5.0 m x 4.0 m net over the tailings pile, respectively. At each point in the net, sampling was also performed at depths of 0 – 1.5 m; 1.5 – 3.0 m; 3.0 – 4.5 m; 4.5 – 6.0 m; 6.0 – 7.5 m and 7.5 – 9.0 m, totaling six different depths. Sample collection at different depths was necessary to support a greater accuracy of the indicators of the tailing composition, which was carried with the aid of a pneumatic drill. Sampling was carried out at 37 different points on the net, totaling 222 samples. The chemical characterization of the samples was performed in x-ray diffraction equipment, where the percentages of the following oxides were determined: SiO₂, CaO, MgO, Al₂O₃ and Fe₂O₃, and the determination of the Neutralization Power (NP) shown in Equation 1.

$$NP = (\%CaO \times 1.78) + (\%MgO \times 2.48) \quad (1)$$

For the analysis of X-ray diffraction, the samples were subjected to grinding in a mortar and sieved in a 0.15-mm aperture mesh. Subsequently, they were analyzed using a Panalytical diffractometer, Epsilon3 series.

Step 2: Blending and characterization of new soil acidity correction agents

Once the step of sampling and characterization of the 222 samples of the tailings finished, 60 samples were separated based on the value of Neutralization Power (NP), and out of those, it was selected 20 samples of higher NP values, 20 of median values and 20 of lower values. The limestone blending was carried out with the 60 samples separated from the NP values; thus 60 new samples of blended acidity correction agents were obtained. The Relative Efficiency (RE) of the tailings was 93.16%. Thus, the Relative Power of Total Neutralization (RPTN) of the tailings was calculated according to Equation 2 and shown in Table 1.

$$RPTN = \frac{NP \times RE}{100}, \text{ where } RE = 93.16\% \quad (2)$$

The blending was done in order to obtain a soil

acidity correction agent with 90% NP and a final blended limestone mass of 20 g (Equations 3 and 4).

Blending was performed according to equations 3 and 4, where:

- m_a = commercial limestone mass;
- m_b = tailing mass
- x_a = commercial limestone PRNT; and
- x_b = tailing RPTN

The m_b was calculated to produce 20 g of blended acidity correction agent:

$$m_a = 20 - m_b \quad (3)$$

$$m_b = 0.2 \times \left(\frac{90 - 100X_a}{X_b - X_a} \right) \quad (4)$$

Based on these equations, two new soil acidity correction agents, denominated T1 and T2, were prepared. The samples were crushed in a ball mill and sieved in 0.355-mm mesh sieve to obtain a particle size smaller than 0.355 mm. Soil acidity correction agents T1 and T2 were prepared through limestone blending, with a tailing of less than 0.355 mm in order to obtain two new soil acidity correction agents with a NP equal to 90%. The mass ratio between commercial limestone and tailings at all points for the production of T1 and T2 is shown in Table 2.

Table 1. Chemical characterization through X-ray diffraction of the tailings used in the commercial limestone blending for the production of T1 and T2 acidity correction agents

AC*	Point	%						
		SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	NP	RPTN
T1	25 (0 – 1.5 m)	16.62	25.31	14.19	0.95	0.94	80.24	74.75
	3 (3.0 – 4.5 m)	12.52	28.35	16.10	0.76	0.70	90.39	84.17
	33 (3.0 – 4.5 m)	16.03	26.04	14.09	0.89	0.87	81.29	75.73
	Mean T1	15.05	26.56	14.76	0.86	0.83	84.25	78.21
T2	3 (0 – 1.5 m)	12.40	27.37	14.73	0.51	0.58	85.25	79.42
	23 (0 – 1.5 m)	10.00	29.12	15.69	0.56	0.57	90.75	84.54
	35 (0 – 1.5 m)	10.28	29.41	15.24	0.50	0.61	90.14	83.97
	7 (3.0 – 4.5 m)	9.84	28.24	14.31	0.53	0.51	85.75	79.88
	8 (3.0 – 4.5 m)	12.41	27.57	15.11	0.64	0.68	86.54	80.62
	25 (3.0 – 4.5 m)	9.75	27.66	13.88	0.64	0.63	83.65	77.93
	35 (7.5 – 9.0 m)	10.75	28.03	14.09	0.59	0.59	84.83	79.03
Mean T2	10.77	28.20	14.72	0.56	0.59	86.98	80.77	
Commercial limestone		-	30.29	17.89	-	-	98.28	92.01

AC* - Acidity correction agented.

Table 2. Mass of the tailing and commercial limestone needed for blending for the formulation of T1 and T2 soil correction agents with 90% NP

Limestone	Point	Mineral mass (g)		
		Tailing mass	Commercial limestone mass	Total Mass
T1	25 (0 – 1.5 m)	2.3	17.7	20.0
	3 (3.0 – 4.5 m)	5.1	14.9	20.0
	33 (3.0 – 4.5 m)	2.5	17.5	20.0
T2	3 (0 – 1.5 m)	3.2	16.8	20.0
	23 (0 – 1.5 m)	5.4	14.6	20.0
	35 (0 – 1.5 m)	5.0	15.0	20.0
	7 (3.0 – 4.5 m)	3.3	16.6	20.0
	8 (3.0 – 4.5 m)	3.5	16.7	20.0
	25 (3,0 – 4.5 m)	2.8	17.2	20.0
	35 (7.5 – 9.0 m)	3.1	16.9	20.0

Next, samples at depths of 0 - 1.5 m; 3.0 - 4.5 m and 7.5 - 9.0 m were grouped according to their NP value in which the NP ranges of 92.50 - 94 were chosen for the soil acidity correction agent T1 and 95.50 - 98.5 for the soil acidity correction agent T2 for the execution of the incubation work. As we chose NP ranges that were greater than 90%, the 4.5-6.0 and 6.0-7.5 depths presented materials that showed low NP (Below 90%) in the analyses, so such depths were not used in the treatments to maintain the guarantees established by the company with the Ministry of Agriculture, Livestock and Supply (MAPA). Thus, the soil acidity correction agent T1 was composed of point 25 at 0 - 1.5 m depth and points 3 and 33 at 3.0 - 4.5 m depth. The T2 soil acidity correction agent was composed of points 3, 23 and 35 at 0 - 1.5 m; 7, 8 and 25 m at a depth of 3.0 - 4.5 m; and at point 35 in the 7.5 - 9.0 m depth. The new acidity correction agents T1 and T2 were subjected to X-ray diffraction analysis to determine the levels of SiO₂, CaO, MgO, Al₂O₃ e Fe₂O₃, and to determine the Neutralization Power (NP) shown in Equation 1.

Step 3: Test of incubation and calibration of the application doses of soil acidity correction agents

The incubation and calibration test was installed under a greenhouse located on the University Campus of Gurupi. The soil came from the horizon (A/B) of a dystrophic Red Yellow Latosol (Table 3). The samples were sieved in a 2.00-mm sieve to obtain the air-dried fine soil and sent to the Soil Laboratory - LABSOLO, for chemical and granulometric analysis.

The experimental design was a completely randomized with four replications. The 16 treatments were obtained in a 4X4 factorial scheme, which were four correction agents (T1: NP 92.50-94; T2: NP 95.50-98.50; Commercial limestone (without blending) and Calcium carbonate PA) and four doses of the correctives (0.5; 1.0; 2.0; 4.0 t ha⁻¹) plus the control 0.0 t ha⁻¹. Each treatment consisted of 0.5 kg of soil, plus the equivalent corrective dose for 0.5 kg of soil. Then, a volume of water equivalent to 70% of the field capacity (175 mL) was added to each of

Table 3. Chemical and textural characterization of the dystrophic Red-Yellow Latosol used in the incubation and calibration of soil acidity correction agents step

Ca ²⁺ +Mg ²⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	H+Al	K	CEC (T)	SB	CEC(t)	K	P
..... cmol _c dm ⁻³ mg dm ⁻³	
0.15	0.10	0.05	0.00	3.50	0.01	2.37	0.49	0.49	4.98	0.97
V	m	Org. Matter		pH _{H2O}	Sand	Silt	Clay	Sand	Silt	Clay
..... (%) %g dm ⁻³Texture (%).....		Texture (g kg ⁻¹).....		
20.76	0.00	1.53	15.31	5.84	50.9	6.67	42.39	509.49	66.66	423.9

these samples. The plastic bags were sealed and subjected to periodic openings for gas exchange. The incubation was performed for a period of 28 days, with pH readings taken at 7, 14, 21 and 28 days of incubation. The determination of Ca^{2+} , Mg^{2+} and potential acidity ($\text{H} + \text{Al}$) contents were carried out only after 28 days of incubation, and determined according to the methodology proposed by Embrapa (1997).

The pH was obtained through the potentiometric method using the pH-meter of the brand MS Tecnopon Instrumentação, model mPA210, with an Ag/AgCl electrode. The reading of the Ca^{2+} and Mg^{2+} attributes were performed on Agilent Technologies Spectrophotometric Atomic Absorption equipment, model 55AA with flame atomizer and hollow cathode lamps, in a 1: 9 dilution (KCl extract: La_2O_3). On the other hand, potential acidity was obtained by titration using a Brand digital burette and the Digital Buret™ Easy Calibration model.

The calibration was based on theoretical liming recommendations for rice, eucalyptus, corn, pasture and soybean crops in a dystrophic Red-Yellow Latosol with pH 7 (CFSEMG, 1999) using the standard method which is based on the incubation of calcium carbonate PA. The crops of rice, eucalyptus, pasture and soybean are the main crops in the state of Tocantins, and their recommendations were based on two methods.

The Al^{3+} neutralization method and increasing the levels of Ca^{2+} and Mg^{2+} considers the tolerance of the crop to the high potential acidity and the buffering capacity of the soil and, on the other hand, the raise in availability of Ca^{2+} and Mg^{2+} is wanted. The base saturation method considers the relationship between pH and base saturation.

The data obtained were submitted to regression analysis to evaluate the significance of the betas and the determination coefficients using the software Statística version 7.0 (STATSOFT, 2014). The regression graphs were plotted using the statistical program Sigma Plot version 13.0®, where the model was chosen based on the best significance of the equations (SYSTAT, 2014).

RESULTS AND DISCUSSION

The correction agents T1 and T2 obtained from blending of the commercial limestone with tailings from limestone mining were characterized by means of X-ray diffraction, obtaining new percentages of oxides SiO_2 , CaO , MgO , Al_2O_3 and Fe_2O_3 and the determination of the Power Neutralization (NP) from CaO and MgO values (Table 4).

The new values of chemical characterization of blended limestones T1 and T2 showed that the blending was efficient, showing NP values above the expected 90%. The lowest NP value (92.80) corresponded to point 33 at a 3.0-4.5 m depth and

Table 4. Chemical characterization of soil acidity correction agents T1 and T2 through X-ray diffraction.

Limestone	Point	%						
		SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	PN	PRNT
T1	25 (0 – 1.5 m)	8.37	29.35	16.78	0.40	0.34	93.86	87.87
	3 (3.0 – 4.5 m)	8.80	29.23	16.75	0.43	0.39	93.57	87.60
	33 (3.0 – 4.5m)	9.36	28.88	16.69	0.41	0.40	92.80	86.88
	Mean T1	8.84	29.15	16.74	0.41	0.37	93.40	87.44
T2	3 (0 – 1.5 m)	8.58	30.14	17.04	0.35	0.30	95.91	89.79
	23 (0 – 1.5 m)	8.54	29.91	17.25	0.37	0.34	96.02	89.89
	35 (0 – 1.5 m)	8.42	30.12	17.27	0.34	0.31	96.44	90.29
	7 (3.0 – 4.5 m)	6.99	30.83	17.04	0.36	0.29	97.14	90.94
	8 (3.0 – 4.5 m)	8.54	30.00	17.11	0.37	0.33	95.83	89.72
	25(3.0 – 4.5m)	6.20	31.03	17.42	0.37	0.29	98.44	92.15
	35(7.5 – 9.0m)	6.95	30.77	17.02	0.36	0.30	96.98	90.79
Mean T2	7.75	30.40	17.16	0.36	0.31	96.67	90.50	

the highest value NP (98.44) was at point 25 also at a depth of 3.0-4.5 m. These NP values obtained in the blending can be explained by the high levels of CaO and MgO in the new blended soil acidity correction agents T1 and T2. The Brazilian legislation determines that to be commercialized, limestones must have at least 38% CaO + MgO. The acidity correction agent traded by the company has this CaO and MgO sum of 48.18%.

The blended acidity correction agents T1 and T2 obtained values of this sum of 45.89 and 47, 56 respectively. These values in the CaO and MgO contents may explain the fact that the blending NP was higher than the expected 90%, thus reaching an average of 93.40% for T1 and 96.67% for T2.

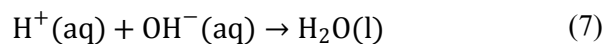
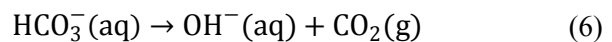
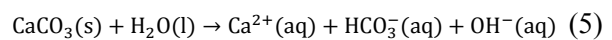
It was observed in the evaluation of the effect of the incubation time that the pH attribute showed a significant quadratic response ($P \leq 0.05$) due to the increasing doses of acidity correction agents PA (98% CaCO₃), Commercial, T1 (NP 92.50-94) and T2 (NP 95.50-98.50) over the incubation period (Figure 1). In the first week of evaluation, regardless of the dose or correction agent, the pH values were greater than 6.5, a value considered ideal for most crops.

Because of its 98% CaCO₃ purity, the PA soil acidity correction agent showed higher pH values when compared to the other correction agents. The lowest pH obtained by using the PA was 6.33, corresponding to the dose of 0.5 t ha⁻¹ on the 21st incubation day. The highest pH value of 7.78 was related to the dose of 2 t ha⁻¹ on the 7th day. The Commercial acidity correction agent when evaluated at the dose 0.5 t ha⁻¹ on days 14, 21 and 28, and at the dose 1 t ha⁻¹ on days 21 and 28 of incubation proved to be satisfactory in the ideal pH range for the soil. Nevertheless, at the doses 2 t ha⁻¹ and 4 t ha⁻¹ during all incubation days, the pH remained above the ideal of 6.5 for most crops.

The soil acidity correction agent T1 (NP 92.50-94) was acceptable with the values of 6.25 and 6.23 at the dose 0.5 t ha⁻¹ on days 21 and 28 of incubation, respectively. In the other doses on the days of incubation, the pH remained above the

ideal. In relation to correction agent T2 (NP 95.50-98.50), the application dose of 0.5 t ha⁻¹ in the last three weeks was favorable to the appropriate pH for most crops. In the first week of incubation, the pH values ranged from 6.68 for the dose 0.5 t ha⁻¹ to 7.24 for the dose 2 t ha⁻¹, which was considered above the ideal pH, which ranges from 5.7 to 6.5.

The weekly assessment of the influence of different soil acidity correction agents on the pH of the dystrophic Red-Yellow Latosol revealed a decrease in pH until day 21 and a stabilization at the end of the incubation (28 days) for all soil acidity correction agents. This behavior can be explained by the consumption of limestone in the soil, where calcium carbonate reacts with water, releasing the Ca²⁺ cation and two OH⁻ anions (Equations 5, 6 and 7). The HCO₃⁻ anion directly neutralizes H₃O⁺, resulting in the release of water and carbon dioxide. The hydroxyl ion, in turn, binds to potential sources of acidity, such as Al³⁺ (exchangeable aluminum).



Callegari *et al.* (2011) demonstrated that a soil with alkaline pH had a negative effect on the content of soluble solids and a delay in the maturation of melon fruit caused by the deficiency of some elements induced by the soil alkalinity. Thus, the raise in the soil pH values greater than seven may more easily cause the negative effects on agricultural crops (MONTE SERRAT *et al.*, 2011). The pH range determined in water above 7.0 had a depressive effect on the productivity of crops such as corn, soybeans and wheat (MONTE SERRAT *et al.*, 2011) since this pH of 7.0 undermines the supply of nutrients such as Mn, Fe, Zn, Cu and B (MONTE SERRAT *et al.*, 2011).

The evaluation of the pH attribute of the dystrophic Red-Yellow Latosol at the end of the 28 days of incubation showed a significant quadratic

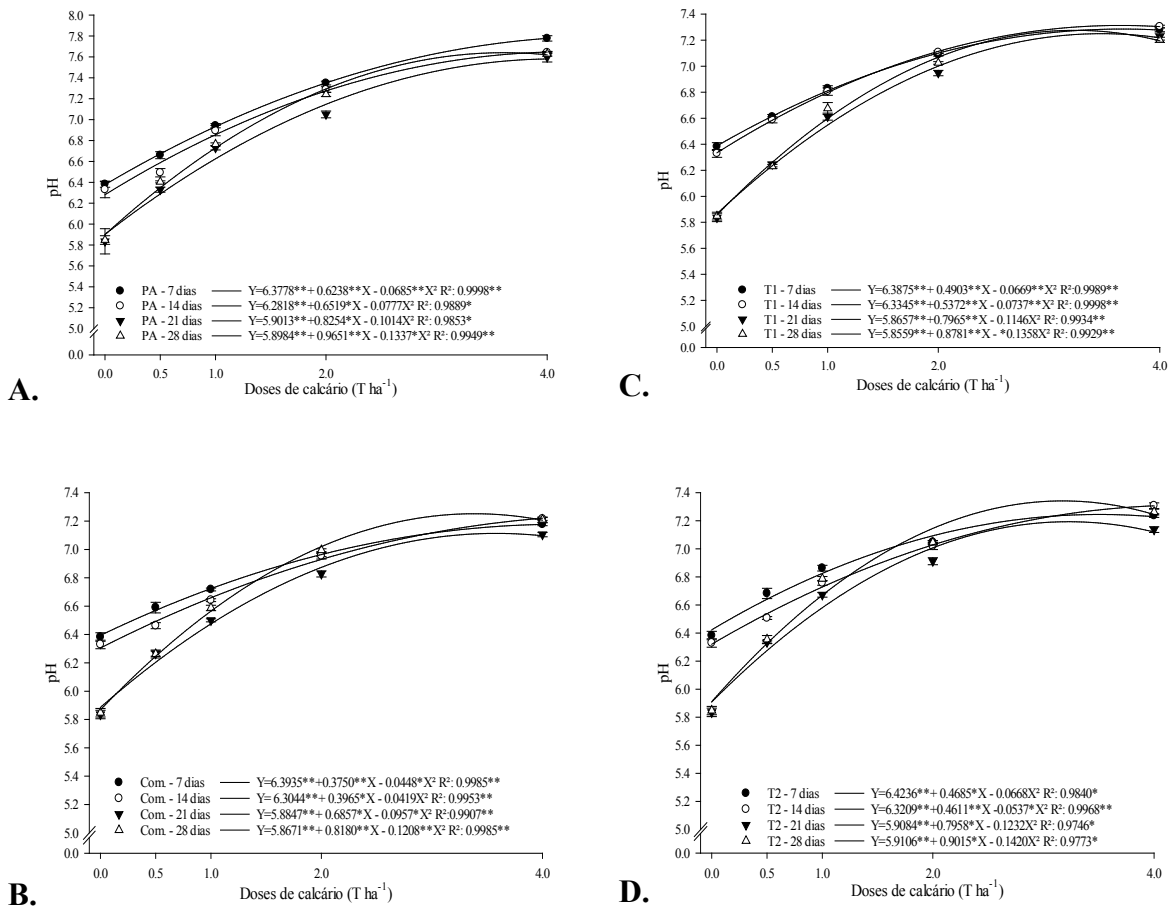


Figure 1. Alteration of the pH of a dystrophic Red-Yellow latosol as a function of doses of the correction agents PA, Commercial, T1 and T2, (A, B, C, D, respectively) in the 28-day incubation period

response ($P \leq 0.05$) as a result of the increasing doses for the correction agents PA (98% $CaCO_3$), Commercial, T1 (NP 92.50-94) and T2 (NP 95.50-98.50) (Figure 2).

At the end of the 28-day incubation period, the acidity correction agents evaluated were efficient in raising the pH when compared to the control treatment, 0 t ha⁻¹. The dose of 0.5 t ha⁻¹ of corrective was the dose in which the pH was within the recommended range for the agricultural cultivation of the different evaluated correctives. This ability shown by the acidity correction agents in promoting an increase in soil pH is important, because in addition to stimulating microbiological activity, it can reduce potassium losses by leaching, due to the creation of negative charges (SILVA *et al.*, 2012). Another importance of this efficiency is the fact that T1 and T2 are products used for

recycling the waste generated from limestone mining, with the confirmation of their potential for agronomic use.

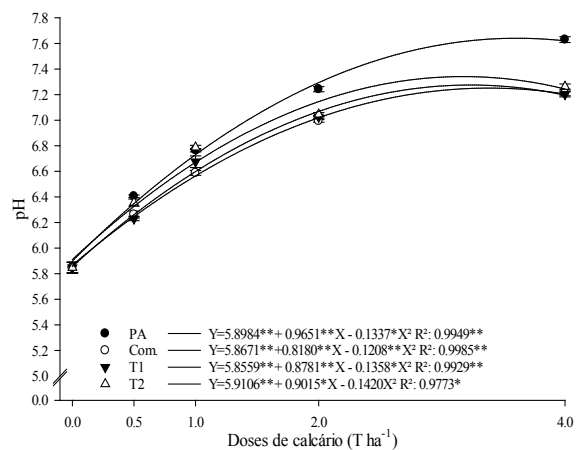


Figure 2. Alteration of the pH of the dystrophic Red-Yellow Latosol at the end of the incubation period as a function of the increasing doses of different limestones

From the dose of 2.0 t ha⁻¹, both the T1 and T2 correction agents, as well as the PA and Commercial correctives were able to promote pH close to neutrality or slightly alkaline in the dystrophic Red-Yellow Latosol at 28 days of incubation (Figure 2). Soil pH is the indicator that most influences the chemical balance of the metal partition between the soil and the soil solution, that is, its adsorption and desorption. Thus, in general, neutral or slightly alkaline pH, such as those obtained in this work from the dose of 2.0 t ha⁻¹, acts in the adsorption and immobilization of nutrient metallic cations such as Cu²⁺, Mn²⁺ e Zn²⁺, and pollutants such as Cd²⁺, Cr⁶⁺ e Pb²⁺. This immobilization occurs through the formation of poorly soluble compounds such as hydroxides, carbonates and phosphates (KEMERICH *et al.*, 2013).

An exponential reduction was observed in the evaluation of potential acidity as the recommended dose was incremented for all the correction agents used in the experiment (Figure 3). The application of the 4.0 t ha⁻¹ dose resulted in more efficient T1 and T2 correction agents in comparison to the Commercial acidity correction, once again indicating the potential for agricultural use of limestone-mining tailings. The values of potential acidity provided by these two limestones are considered very low and ideal for the soil (CFSEMG, 1999).

Besides influencing the solubility of carbonates, the pH of the soil also influenced the potential acidity (H + Al). Soil acidity controls the Al³⁺ dissolution reaction, and its solubility is minimal at pH greater than 5.5 (ROSADO *et al.*, 2014). Overall, the Al₃₊ activity in the solution decreases as pH increases.

The reduction in the potential acidity and consequently the reduction of H⁺ contents promotes an enhancement in crop yield. Besides reducing root growth, the toxicity of the Al³⁺ cation decreases the absorption of water and nutrients, interferes with the absorption and transport of nutrients such as magnesium and calcium (SILVA *et al.*, 2013).

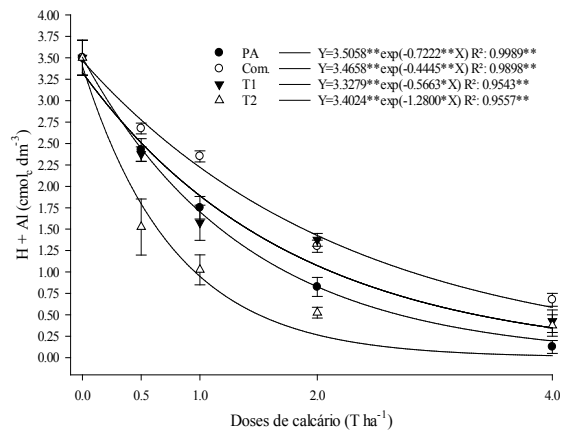
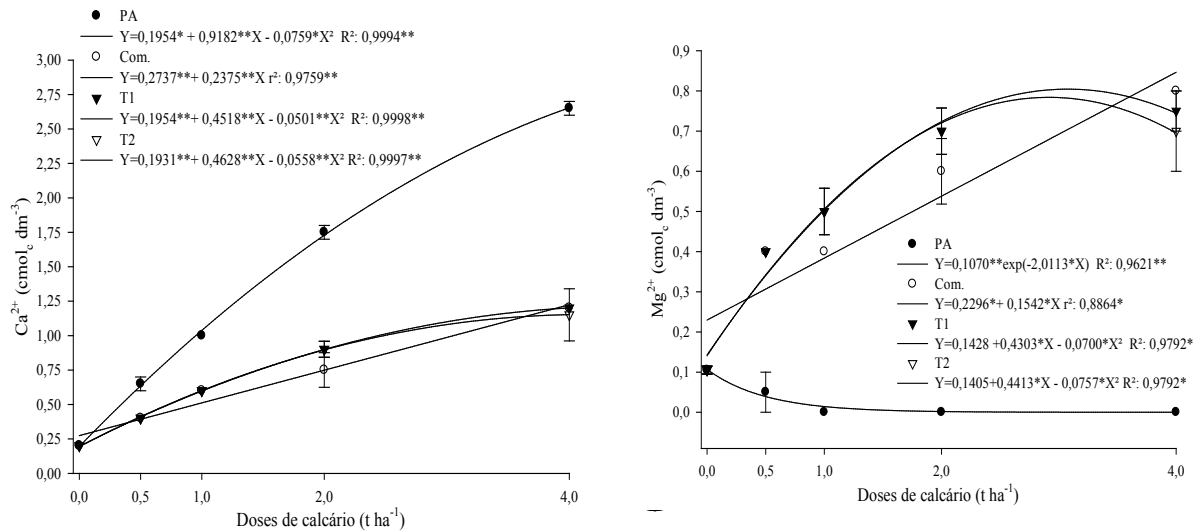


Figure 3. Contents of (H + Al) as a function of increasing doses of application of different acidity correction agents in the dystrophic Red-Yellow Latosol

In relation to the contents of Ca²⁺, because the soil pH did not reach values above 8.5, only calcium carbonate was solubilized. As a result, increases in Ca²⁺ levels were observed as the application rates were incremented. Regarding the levels of Ca²⁺ in the dystrophic Red-yellow Latosol at the end of the incubation period, it is possible to observe that there were no significant differences in the behavior of this attribute when comparing the T1, T2 and Commercial acidity correction agents (Figure 4 A). The Ca²⁺ attribute showed a significant quadratic response (P≤0.05) for the PA, T1 and T2 acidity correction agents and a linear significance response (P≤0.05) for the commercial soil acidity correction agent.

Even with the increments in the levels of Ca²⁺ with the raise in the application doses of these limestones, it was not possible to provide ideal levels of Ca²⁺ to the soil. At the highest application dose of 4.0 t ha⁻¹, the calcium content was approximately 1.20 cmol_c dm⁻³, a value considered low for most soils (CFSEMG, 1999). Soils with low content of calcium can cause serious damage to crop development. This nutrient is responsible for maintaining the structural integrity of cell walls and membranes. In addition, it acts in the regulation of various physiological and metabolic processes. Its deficiency results mainly in the reduction in the growth of meristemic and apical tissues and death



Doses de calcário = Limestone doses

Figure 4. Contents of Ca²⁺ (A) and Mg²⁺ (B) as a function of the increasing in the application rates of the different acidity correctives in the dystrophic Red-Yellow Latosol.

of the root system (DAFLON *et al.*, 2014).

The Mg²⁺ showed a significant quadratic response (P≤0.05) for correction agents T1 and T2, while for the corrective PA, it significantly responded to the exponential model (P≤0.05). The commercial acidity correction agent showed a significance response to the linear model (P≤0.05) (Figure 4 B). As for the content of Mg²⁺, increases were also observed with the increase in the doses of acidity correction agents. This was a general trend, except for the PA limestone, as it does not have relevant levels of MgCO₃. Similar to the calcium nutrient, the contents of magnesium are also not considered ideal. For the T1 and T2 commercial correctives, at the application rates 0.5 and 1.0 t ha⁻¹, the highest magnesium content was approximately 0.5 cmol_c dm⁻³, which is considered a low value. In the doses of 2.0 and 4.0 t ha⁻¹, the levels are considered median, since they are within the range of 0.46 to 0.90 cmol_c dm⁻³ (CFSEMG, 1999). The higher magnesium content obtained with the use of commercial limestone is consistent with the greater input of MgO (17.89%).

Similar to the calcium deficiency, low levels of magnesium reduce crop yields. Mg²⁺ plays important roles in plant physiology, as it takes part in the processes of oxidative phosphorylation,

CO₂ fixation, protein synthesis and generation of reactive oxygen species (free radicals) and also in the leaf photo-oxidation. Thus, deficiencies of Mg²⁺ deregulate several physiological and biochemical processes in the plants (MOREIRA *et al.*, 2013).

The calibration of the methods Al³⁺ neutralization and the raise in the levels of Ca²⁺ + Mg²⁺ and the base saturation for correction recommendations for rice, eucalyptus, corn, pasture and soybean crops was performed using the standard method as reference, which is from the incubation of calcium carbonate in a dystrophic Red-Yellow Latosol. It was observed in this calibration that the theoretical value of 1.02 t ha⁻¹ for the recommendation of the neutralization method for rice, eucalyptus and pasture crops must be submitted to a correction factor of 1.96; 1.77 and 1.58 for commercial acidity correction agents, T1 and T2, respectively, in order to achieve the recommended dose through the incubation method, which was 2.00; 1.81 and 1.62 t ha⁻¹ (Table 5).

On the other hand, the use of base saturation method in the rice, corn and soybean crops to achieve this same dose of recommendation by the standard incubation method must be subjected to a correction factor of 2.87; 2.60 and 2.33 for commercial acidity correction agents T1 and T2

Table 5. Calibration of the methods for the recommendation of soil acidity correction agents according to pH alteration

Corr*.	Crop	Methods						
		t ha ⁻¹			%			
		Incubation	I**	F.C.	Efficiency	II***	F.C.	Efficiency
PA	Rice	1.43	1.02	1.40	71.33	0.695	2.05	48.60
Com		2.00	1.02	1.96	51.00	0.695	2.87	34.75
T1		1.81	1.02	1.77	56.35	0.695	2.60	38.40
T2		1.62	1.02	1.58	62.96	0.695	2.33	42.90
Mean				1.67	60.41		2.46	41.16
PA	Eucalyptus	1.43	1.02	1.40	71.33	0.458	3.12	32.03
Com		2.00	1.02	1.96	51.00	0.458	4.36	22.90
T1		1.81	1.02	1.77	56.35	0.458	3.95	25.30
T2		1.62	1.02	1.58	62.96	0.458	3.53	28.27
Mean				1.67	60.41		3.74	27.12
PA	Corn	1.43	1.52	0.94	106.30	0.695	2.05	48.60
Com		2.00	1.52	1.31	76.00	0.695	2.87	34.75
T1		1.81	1.52	1.19	83.97	0.695	2.60	38.40
T2		1.62	1.52	1.06	93.83	0.695	2.33	42.90
Mean				1.12	90.02		2.46	41.16
PA	Pasture	1.43	1.02	1.40	71.33	0.576	2.48	40.28
Com		2.00	1.02	1.96	51.00	0.576	3.47	28.80
T1		1.81	1.02	1.77	56.35	0.576	3.14	31.82
T2		1.62	1.02	1.58	62.96	0.576	2.81	35.55
Mean				1.67	60.41		2.97	34.11
PA	Soybean	1.43	1.52	0.94	106.30	0.695	2.05	48.60
Com		2.00	1.52	1.31	76.00	0.695	2.87	34.75
T1		1.81	1.52	1.19	83.97	0.695	2.60	38.40
T2		1.62	1.52	1.06	93.83	0.695	2.33	42.90
Mean				1.12	90.02		2.46	41.16

* Corr. – corrective; I** → Al³⁺ neutralization and raise in Ca²⁺ and Mg²⁺ content method II*** → Base saturation method.

respectively. The efficiency values show that the Al³⁺ neutralization and raise in Ca²⁺+ Mg²⁺ level methods and the base saturation method underestimate the recommended liming values for rice, eucalyptus, corn, pasture and soybean crops. In relation to Eucalyptus, the base saturation method showed the average efficiency means that in this method the recommendation supplies only 27.12% of the demand.

CONCLUSIONS

- Mining tailings in the blending of commercial limestone showed a potential for improvement

in the levels of Ca²⁺ and Mg²⁺ of the new correction agents; however, it did not reach the ideal supply to the soil due to the low solubility constant of CaCO₃ and MgCO₃.

- Blending provided a significant effect on raising the pH and potential acidity neutralization of the soils.

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