Limestone and Silicate Applications by Different Methods to Correct Soil Acidity

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Abstract

The study aimed to measure the variation in the values of pH, P, K, Ca, Mg, Al, H+Al, V, and Ca and Mg saturation after limestone and silicate applications as a function of different soil correction methods and incubation periods under a controlled environment. The research was carried out in a greenhouse at the FCA of the Federal University of Grande Dourados (UFGD). The experiment was completely randomized in a factorial scheme ($5 \times 3 \times 5$), with four replications. The main factors consisted of five incubation times: 0, 30, 60, 90, and 120 days; three soil classes: dystrophic Red Latosol (LVd), Dystroferric Red Latosol (LVdf), and dystrophic Gray Argisol (PACd); and five soil acidity correction methods: control, Ca/Mg balance for limestone and silicate, and 50% and 70% base saturation. Chemical analyses were performed after each incubation period. A regression analysis of variance, being adjusted to quadratic models for pH, P, Al, K, Ca, Mg, H+Al, and V. Statistical analyses were performed in the AgroStat software. The ideal soil incubation time to reach the maximum efficiency of correction of the chemical attributes of LVd, LVdf, and PACd soils by the studied methods ranges from 78 to 86 days. The application of limestone by balance of 60% Ca and 20% Mg and calcium and magnesium silicates achieved the best correction indexes of soil chemical attributes, enabling the proposed equation as a calcium and magnesium silicate calculation.

Keywords: base balance, soil incubation, soil attributes, silicon

1. Introduction

Brazilian soils have wide variability in their main chemical, physical attributes, and particle size. They are grouped into 13 classes according to the Brazilian Soil Classification System, with Latosols, Argisols, and Neosols being the most predominant (70%) (Santos et al., 2018). Latosols and Argisols represent 58%. They have low natural fertility, high acidity, high Al saturation, and low Ca, Mg, K, and P content. Neosols have medium natural fertility, limiting the cultivation on arable land (Ratke et al., 2018) and therefore,, are requiring correction.

Soil correction is usually performed by liming, a practice that transforms the chemical, physical, and even biological characteristics of the soil. Among numerous benefits, it provides the alteration of soil acidity; insolubility of toxic elements, mainly Al, Mn, and Fe; increases Ca, Mg, P, and Mo contents, but may interfere with the availability of K and other micronutrients; and improves soil physical properties by recycling Ca and Mg (Conradi Junior et al., 2020).

There are different methods for recommending liming, with empirical models based on the dose per area (Parecido et al., 2021) or base saturation (Raij, 1981). The latter is being the most used although criticized for the linearity between the soil pH and the limestone total neutralizing power (TNP) (Teixeira et al., 2020). Although the most common practice for acidity correction is liming, the application of Ca and Mg silicate in place of limestone has been carefully studied with satisfactory results (Deus et al., 2020).

Regardless of the methodology employed, amendment amounts should neither be low nor excessive to maintain a proper balance between soil chemical elements (Takala, 2020). In this context, the model of Albrecht (1996) for soil fertility correction, based on the base balance and P and micronutrient correction, can be an effective

method (Black, 2019) and can provide the amount of amendment required in the search for maximum economic efficiency of productivity (Guarçoni & Sobreira, 2017). Although there may be gaps that need to be better studied to understand limitations and competencies of soil balance (Chaganti & Culman, 2017). Many studies have been conducted in greenhouses with subsequent validation in the field, seeking the development of conceptual models (Forero et al., 2019). Among these studies, experiments evaluating various acidity neutralization methods and the effect of fertilizer and amendment applications to optimize the behavior of chemical attributes by incubating soils for a certain period are common (El-Naggar et al., 2018; Hirzel et al., 2021).

The present study aimed to measure the variation in pH, P, K, Ca, Mg, Al, H+Al, base saturation (V%), Ca saturation (SatCa%), and Mg saturation (SatMg%) after limestone and silicate applications as a function of the correction method and to determine the ideal incubation period under a controlled environment.

2. Material and Methods

The study was carried out in a greenhouse at the School of Agricultural Sciences (FCA) of the Federal University of Grande Dourados (UFGD). The experimental design was completely randomized factorial design $(5 \times 3 \times 5)$, with four replications. The first factor consisted of five soil incubation time comprised of 5 levels: 0, 30, 60, 90, and 120 days; the second factor was the soil class including three soil classes: dystrophic Red Latosol (LVd), Dystroferric Red Latosol (LVdf), and dystrophic Gray Argisol (PACd) (Santos et al., 2018); and the third factor was soil acidity correction method for which 5 methods were considered (Table 1).

Trea	atment	Method description						
1	Ctrl	Control, no soil correction						
2	E-60/20	Calcium and magnesium balance-correction method adapted from Albrecht (1996), standardized for 60% Ca and						
2	2 Eq60/20	20% Mg of cation exchange capacity at pH 7 (T)						
		Steelworks calcium magnesium silicate-based on calculations to determine the limestone requirement by the						
		Ca/Mg balance method (Eq60/20). An equation for silicate (Equation 1) was elaborated:						
3	Plx	Equation 1: $Plx = \frac{42 \cdot T - 56 \cdot Ca - 40 \cdot Mg}{CaO + MgO silicate} \cdot f$						
		where Plx is the calcium magnesium silicate requirement (t ha ⁻¹), T is the cation exchange capacity at pH 7 (cmol _c						
		dm ⁻³), Ca and Mg are the calcium and magnesium contents (cmol _c dm ⁻³), and f is the 100/TNP silicate)						
4	Sat50	Base saturation (Raij, 1981), with $V_2 = 50\%$						
5	Sat70	Base saturation (Raij, 1981), with $V_2 = 70\%$						

Table 1. Soil acidity correction methods (or treatments) used in the experiment

Two types of limestone were used for soil amendments notably dolomitic (30.34% CaO, 19.03% MgO, and 85.98% TNP) and calcitic (50.92% CaO, 2.86% MgO, and 80.54% TNP) (Table 2).

Table 2 Dose of each soi	amendment for the three soil	classes and five treatments
Table 2. Dose of each sol	amenument for the three son	classes and five deadlients

Soil class/amendment		Treatmer	nts (soil corre	ection method)
Son class/amenument	Ctrl	Eq60/20	Plx	Sat50	Sat70
			kg ha ⁻¹		
LVd					
Calcitic limestone	-	2932	-	-	-
Dolomitic limestone	-	2568	-	2582	4327
Ca and Mg silicate	-	-	6196	-	-
LVdf					
Calcitic limestone	-	5314	-	-	-
Dolomitic limestone	-	3597	-	3309	6698
Ca and Mg silicate	-	-	10080	-	-
PACd					
Calcitic limestone	-	4728	-	-	-
Dolomitic limestone	-	4064	-	4862	7211
Ca and Mg silicate	-	-	9887	-	-

The soils were collected at a depth of 0-20 cm, air-dried, decloded, passed through a 2-mm opening sieve, and chemically analyzed (Table 3).

Chemical atributes		Soil classes					
Chemical atributes	8	LVd	LVdf	PACd			
pH (CaCl ₂)	-	4.53	4.79	3.92			
P (mehlich 1)	mg dm ⁻³	6.10	6.70	10.10			
Са		1.16	3.18	0.71			
Mg		0.29	1.15	0.10			
K	····· • 1 ····· - 3	0.08	0.11	0.06			
H+A1	cmol _c dm ⁻³	5.97	10.13	9.23			
Al		0.41	0.46	1.11			
SB		1.53	4.44	0.87			
Т		7.50	14.57	10.10			
V		2.40	30.47	8.61			
Ca	saturation (%)	15.47	21.83	7.03			
Mg		3.87	7.89	0.99			
Clay		250	598	68			
Sand	g kg ⁻¹	719	142	760			
Silt		31	260	172			
Bulk density	-	1.19	1.09	1.14			

Table 3. Soil chemical and particle size attributes at the sampling depth of 0-20 cm before the experiment was installed

Note. LVd: dystrophic Red Latosol (22°32′030″; 54°22′300″); LVdf: dystroferric Red Latosol (22°23′607″; 54°32′709″); PACd: dystrophic Gray Argisol (22°28′000″; 54°24′261″).

The treatments were placed in plastic bags with two kilograms of soil, homogenized with the dose of each amendment, and incubated in a greenhouse for 0, 30, 60, 90, and 120 days, with moisture content at a field capacity of 80% (Prado & Casali, 2006). The soils were air-dried after each incubation period for subsequent chemical analysis to determine the soil chemical attributes pH (CaCl₂), calcium (Ca), magnesium (Mg), potassium (K), aluminum (Al), and potential acidity (H+Al), which allowed the calculation of the base saturation (V%), calcium saturation (SatCa%), and magnesium saturation (SatMg%).

The data were submitted to analysis of variance (ANOVA) and, when significant by the F test (p < 0.01), the means were compared by the Tukey test and regression was performed for incubation time and soils, with quadratic models being adjusted when significant. The statistical analyzes were performed using the AgroEstat software (Barbosa & Maldonado, 2015).

3. Results and Discussion

Only dolomitic limestone was used in the base saturation method (50 and 70%) (Table 2) because it contains the bases as a whole. However, there was the need to use dolomitic and calcitic limestone in the method proposed by Albrecht to satisfy the 60:20% Ca and Mg balance.

The ANOVA revealed significant difference between mean values of attributes studied for incubation times, soil class, and liming methods. Moreover, a significant interaction was observed between incubation time and soil class as well as between incubation time and soil acidity correction methods (Table 4).

Causes of variation	DF	pН	Р	K	Al	Ca	Mg	H+A1	V	SatCa	SatMg
Time (A)	4	**	**	**	**	**	**	**	**	**	**
Soil (B)	2	**	**	**	**	**	**	**	**	**	**
Method (C)	4	**	**	**	**	**	**	**	**	**	**
Interaction A x B	8	**	**	**	**	**	**	**	**	**	**
Interaction A x C	16	**	**	**	**	**	**	**	**	**	**
Residual	225										
Mean		5.12	8.59	0.10	0.25	3.73	1.44	6.26	45.86	32.32	12.62
CV (%)		6.09	10.16	12.43	16.99	9.45	10.45	10.13	4.80	6.67	11.72

Table 4. ANOVA significance results for the chemical attributes studied

Note. ** Significant at the 1% probability level by the F-test.

The soil classes presented significant mean values (Table 5), with quadratic models for all chemical attributes, thus allowing determining the maximum values for pH, P, K, Ca, Mg, V, SatCa, and SatMg and minimum values for Al and H+Al during experiment incubation time (Table 6) in relation to time 0 (0 days).

Insubstian time (days)	Chemical atr	ibutes of soil analys	sis		
Incubation time (days)	pН	Р	K	Al	Ca
	CaCl ₂	mg dm ⁻³		$\operatorname{cmol}_{c} \operatorname{dm}^{-3}$	
0	4.41 b	7.63 b	0.08 c	0.66 a	1.68 c
30	5.27 a	8.80 a	0.10 b	0.15 c	4.10 b
60	5.39 a	9.04 a	0.11 a	0.13 c	4.34 a
90	5.28 a	8.78 a	0.10 b	0.15 c	4.30 a
120	5.27 a	8.69 a	0.11 a	0.17 b	4.24 ab
HSD (5%)	0.1567	0.4383	0.0063	0.0216	0.1770
Incubation time (days)	Mg	H+A1	V	SatCa	SatMg
		cmol _c dm ⁻³		%	
0	0.51 c	8.44 a	20 d	15 d	4 b
30	1.59 b	5.93 b	51 c	36 c	15 a
60	1.73 a	5.53 c	54 a	38 a	15 a
90	1.69 a	5.59 c	53 b	37 ab	15 a
120	1.67 a	5.78 bc	52 bc	36 bc	14 a
HSD (5%)	0.0756	0.3185	1.1061	1.0186	0.7424

Table 5. Means of soil chemical attributes in relation to the incubation time

Note. Means followed by the same lowercase letter in the columns differ from each other by Tukey's test (p < 0.05). HSD: honestly significant difference.

		Soil classes						
Chemical atributes		LVd		LVdf		PACd		
		VM	days	VM	days	VM	days	
pH (caCl ₂)	-	5.44	78	5.56	78	5.37	79	
Р	mg dm ⁻³	7.03	67	8.25	104	12.11	66	
K		0.10	97	0.15	89	0.08	79	
Al		0.05	76	0.02	80	0.12	79	
Ca	cmolc cm ⁻³	3.23	84	6.52	81	4.25	81	
Mg		1.30	81	2.48	83	1.82	80	
H+Al		2.89	76	8.52	96	4.22	79	
V		62	78	51	84	60	80	
SatCa	%	43	79	37	83	41	80	
SatMg		18	77	14	86	18	79	
Mean			79		86		78	

Note. LVd: dystrophic Red Latosol; LVdf: dystroferric Red Latosol; PACd: dystrophic Gray Argisol.

VM: maximum values for pH, P, K, Ca, Mg, V, SatCa, and SatMg or (MV) minimum values for Al and H+Al.

The mean soil incubation time as a function of correction methods for each chemical attribute (Table 6) showed significant results for the corrective effect at 30 days for pH (CaCl₂), P, Al, and SatMg and at 60 days for K, Ca, Mg, H+Al, V, and SatCa. This result is similar to that obtained by Lima Filho (2011) at 40 days of incubation with three soil classes, with both slag (silicate) and limestone application.

Soil classes showed a variation from 66 to 104 days to change the chemical characteristics, with a mean time from 78 to 86 days for the effective maximum correction (Table 6), that is, 86 days is the residual time of amendments applied to the soil to maximize the assimilation of the analyzed chemical elements.

Amendment application in different soils showed significant differences for the correction methods (Table 7).

Correction methods		Chen	nical atributes of s	oil analysis	
Concention methods	pH	Р	K	Al	Ca
	CaCl ₂	mg dm ⁻³		cmol _c dm ⁻³	
Ctrl	4.36 d	7.71 c	0.09 c	0.61 a	1.84 d
Eq60/20	5.75 a	8.76 b	0.09 c	0.13 c	5.39 a
Plx	5.77 a	10.28 a	0.12 a	0.13 c	5.31 a
Sat50	4.76 c	7.79 c	0.10 b	0.24 b	2.51 c
Sat70	4.99 b	8.41 b	0.09 c	0.15 c	3.61 b
HSD (5%)	0.1567	0.4383	0.0063	0.0216	0.1770
Correction methods	Mg	H+A1	V	SatCa	SatMg
	(cmol _c dm ⁻³		%	
Ctrl	0.55 d	8.73 a	21 e	16 d	4 d
Eq60/20	1.62 b	4.96 d	60 b	46 a	14 b
Plx	1.87 a	4.27 e	64 a	47 a	16 a
Sat50	1.35 c	7.23 b	36 d	22 c	12 c
Sat70	1.81 b	6.11 c	49 c	31 b	17 a
HSD (5%)	0.0756	0.3185	1.1061	1.0816	0.7424

Table 7. Means of soil chemical attributes relative to soil correction methods during the incubation period.

Note. Means followed by the same lowercase letter in the columns differ from each other by Tukey's test (p < 0.05). HSD: honestly significant difference.

The application of calcium and magnesium silicate (Plx) had slightly superior responses to the balance treatment (Eq60/20), which showed significantly superior responses to the other liming methods for all the analyzed

chemical attributes.

The correction methods also presented quadratic models, thus determining the maximum values (MV) and minimum values (MV) for each chemical attribute during the incubation time of the experiment (Table 8) in relation to time 0 (0 days). A variation was observed in the incubation time of the correction methods between 73 and 97 days, with a mean time between 78 and 82 days, which are within the mean period obtained when the soil incubation time was analyzed.

Table 8. Incubation time in which the correction methods presented their highest values for each studied chemical attribute

			Correction methods								
Chemical atributes		Ctrl Eq60/20		0/20	Plx		Sat50		Sat70		
		VM	Т	VM	Т	VM	Т	VM	Т	VM	Т
pH CaCl ₂	-	4.33	-	6.37	79	6.40	77	4.93	79	5.27	79
P Mehlic1	Mg dm ⁻³	7.94	-	9.28	80	11.58	78	7.92	77	8.81	74
К		0.10	-	0.10	80	0.14	95	0.11	89	0.10	97
Al		0.59	-	0.00	81	0.00	81	0.03	73	0.00	78
Ca	cmol.dm ⁻³	1.92	-	7.07	82	6.94	81	2.90	79	4.50	81
Mg		0.57	-	2.14	85	2.48	82	1.75	79	2.41	79
H+A1		8.86	-	3.26	79	2.39	82	6.61	75	5.02	83
V		21	-	79	81	83	81	43	76	62	79
Sat Ca	%	16	-	60	80	61	81	26	76	39	81
Sat Mg		4	-	18	83	21	82	16	76	22	77
Mean time			-		81		82		78		81

Note. T: incubation time (days); VM: maximum values for pH, P, K, Ca, Mg, V, SatCa, and SatMg or (MV) minimum values for Al and H+Al.

The data obtained allowed drawing correction curves for the parameters pH (CaCl₂) (Figure 1), P (Figure 2), K (Figure 3), Al (Figure 4), Ca (Figure 5), Mg (Figure 6), H+Al (Figure 7), and V (Figure 8) in relation to the soil amendments applied by the correction methods Crtl, Eq60/20, Plx, Sat50, and Sat70.

The application of soil amendments increases the concentration of anions (OH⁻), which neutralize the acidic protons (H⁺) (Nolla et al., 2013), increasing soil pH. The increase in pH was observed with limestone and silicate applications (Figure 1).

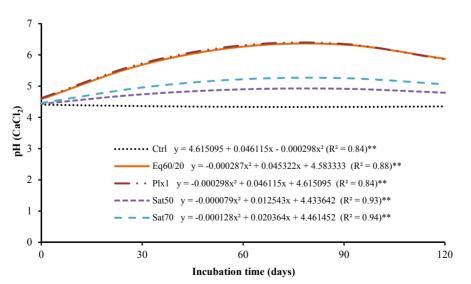


Figure 1. Regression curves of soil correction methods for pH (CaCl₂) during the incubation period in the studied soils

The 50% and 70% base saturation liming methods reduced soil acidity by raising the pH (CaCl₂) from 4.44 to 4.93 and 5.27, respectively. However, the Eq60/20 and Plx methods were significantly more efficient to correct the soil by raising the pH (CaCl₂) to 6.39 and 6.40, respectively (Table 8), since they introduced a higher dose of amendments to the soil (Table 2). Numerous studies have shown that the application of these two soil amendments improves soil chemical attributes, especially pH (Sarto et al., 2014; Holland et al., 2019; Silva et al., 2021).

P determined by the Mehlich1 extractor showed a significant increase when calcium and magnesium silicate was applied (Figure 2), with a value 45.8% higher than the control treatment at 77 days of incubation (Table 8).

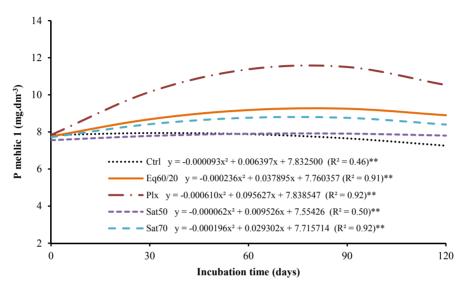


Figure 2. Regression curves of soil correction methods for P during the incubation period in the studied soils

Silicate application led to a competition between the silicate ($H_3SiO_4^-$) and phosphate ions ($H_2PO_4^-$) for the same adsorption sites (Schaller et al., 2019), resulting in a reduction of phosphate adsorption and the reversion of the adsorbed phosphate, releasing more P available in the soil. Therefore, the use of silicate can be an option to improve the availability of phosphorus in soils. However, the increase in P was low with limestone, that is, 9% and 13% under base saturation (70%) and balance (Eq60/20) methods, respectively (Table 8), probably because the soils had low P contents and acidic pH, conditions under which phosphate ions are fixed by Al and Fe (Antoniadis et al., 2015).

K contents were not much affected by the amendment application. Although silicate application increased K content (Figure 3), the change was only $0.03 \text{ cmol}_{c} \text{ dm}^{-3}$, from 0.09 to 0.12 (Table 7), as limestone and silicate applications resulted in increased soil Ca and Mg concentrations compared to K, also favoring the exchangeable K content in the soil by reducing leaching losses and even increasing it due to the lower degree of K attraction by the negative soil charges (Greger et al., 2018).

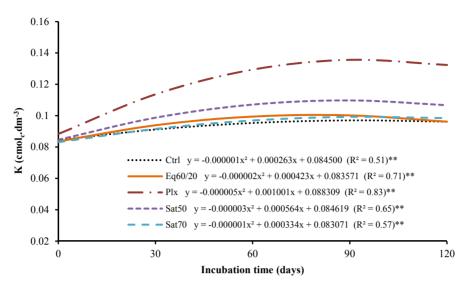


Figure 3. Regression curves of soil correction methods for K during the incubation period in the studied soils

The exchangeable Al content in the soil has a phytotoxic potential, becoming a limiting factor for plant growth usually at pH below 5.5, as the aluminosilicate of clays and Al hydroxide minerals dissolve, releasing $Al(OH)^{2+}$ and $Al(H_2O)_6^{3+}(Al^{3+})$ cations, which react with other cations (Sathyaseelan & Karthika, 2019). In the study, limestone and silicate applications considerably reduced Al contents (Figure 4), even reaching zero around 78 to 81 days of incubation (Table 8). Limestone and silicate with the same particle size have the same ability to correct soil acidity (Ramos et al., 2006), resulting in the decrease or neutralization of Al. Crusciol et al. (2014) obtained similar results when evaluating the surface application of calcium, magnesium silicate, and gypsum in ratoon sugarcane.

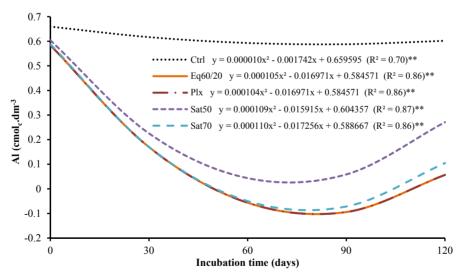


Figure 4. Regression curves of soil correction methods for Al during the incubation period in the studied soils

Considerable differences were observed in the increase in Ca (Figure 5) and Mg (Figure 6) contents in the soil as a function of the correction method. The methods based on Ca/Mg balance and silicate (Plx) were more efficient for Ca supply, while the correction by base saturation at 70% and silicate were superior for Mg (Table 7). These results were due to the higher dose of these soil amendments (Table 2), with Eq60/20 providing more Ca, while Sat70 released more Mg to the soil because it uses dolomitic limestone. Silicate is more soluble than carbonate and hence has a higher potential for releasing Ca and Mg to the soil (Alcarde & Rodella, 2003). Ramos et al. (2006) obtained similar results when working with these soil amendments in leach columns.

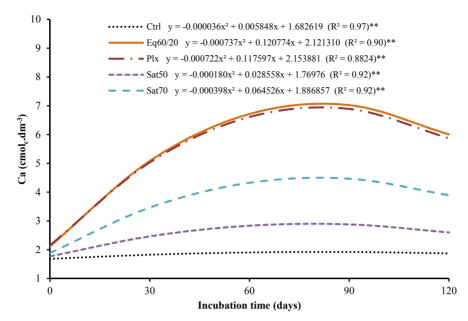


Figure 5. Regression curves of soil correction methods for Ca during the incubation period in the studied soils

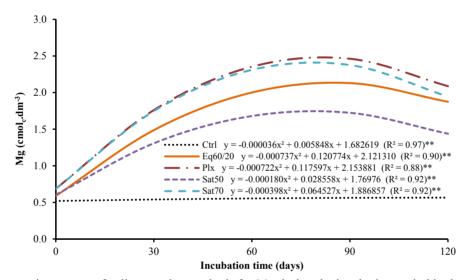


Figure 6. Regression curves of soil correction methods for Mg during the incubation period in the studied soils

Limestone (CO_3^{2-}) and silicate (SiO_3^{2-}) neutralizing agents in contact with water release hydroxide ions (OH⁻), neutralizing H⁺ and Al³⁺ (Aguiar et al., 2021), confirmed in the results obtained in this study for H+Al correction (Figure 7). The most efficient methods offered higher carbonate or silicate doses, reaching the highest correction value of H+Al between 75 and 83 days of incubation.

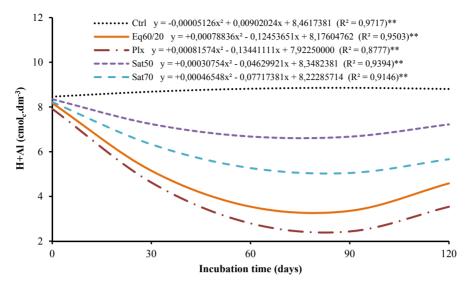


Figure 7. Regression curves of soil correction methods for H+Al during the incubation period in the studied soils

Base saturation was affected by the effects of increasing pH, reducing potential acidity (H+Al), and increasing exchangeable Ca, Mg, and K contents (Figure 8).

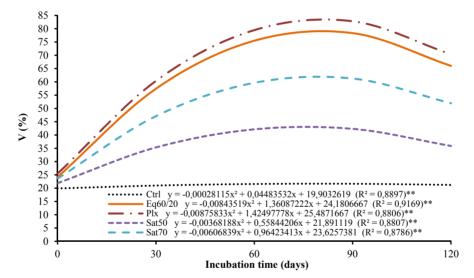


Figure 8. Regression curves of soil correction methods for V (%) during the incubation period in the studied soils

The mean saturation of the three soil classes (21% in Ctrl) reached values close to those intended by each amendment methodology, reaching maximum values of 79% for Eq60/20, 83% for Plx, 62% for Sat70, and 43% for Sat50 (Table 8), thus showing that soil correction by the Ca/Mg balance (Eq60/20) and silicate (Plx) methods were more efficient in increasing the bases of the tested soils.

4. Conclusion

The ideal incubation time of dystrophic Red Latosol (LVd), Dystroferric Red Latosol (LVdf), and dystrophic Gray Argisol (PACd) at a field capacity of 80% for maximum efficiency of correction of their chemical attributes by correction methods with limestone and calcium and magnesium silicates is between 78 and 86 days. Limestone application by 60% Ca and 20% Mg balance and calcium and magnesium silicates achieved the best correction indices of soil chemical attributes, thus enabling the equation (Plx = $(42T - 56Ca - 40)/(CaO + MgO silicate) \cdot f)$ as a proposal for calculating soil correction with calcium and magnesium silicate.

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