

Liming and acidification kinetics of some acid, neutral and alkaline soils

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Introduction

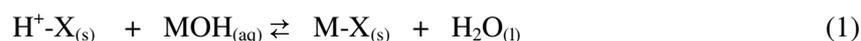
Liming (and acidification) of soils is a common agricultural practice to correct pH. The dose determination is based on traditional rapid methods (titratable acidity-alkalinity; single and double buffer methods, Exchangeable-Al (Thomas and Hargrove 1984; McLean 1982), which frequently under or overestimate the lime/acid requirements. The limitation can be amended if a correct quantitative understanding of the relationship between kinetics and the capacity-intensity acid-base chemistry.

Key Words

Lime requirement; acidification dose; neutralization kinetics

Kinetic-Buffering Theory

The equation governing the kinetic behavior of the neutralization reactions of soils are of the same nature of those found in other areas of chemistry (Frost and Pearson, 1961), soil (Sparks 1989) and environmental sciences (Stumm and Morgan 1996). Thus, as neutralization of a given soil proceeds via the direct reaction of OH⁻ ions with reactive species of the soil solids, here represented as X_(s), a general liming process can be visualized as follows:



where H⁺-X_(s) stands for the acid group to be neutralized, and M is the metal accompanying the liming material (*e.g.*, Ca, Na, etc.). A similar equation can be generated for alkaline soils.

The reaction rate for the OH⁻ consumption due to the neutralization can be expressed by

$$v = -d[\text{OH}^-]/dt = k [\text{OH}^-]^n = k \gamma^n (\text{OH}^-)^n = k' (\text{OH}^-)^n \quad (2)$$

where $-d[\text{OH}^-]/dt$ is the consumption rate of OH⁻ ions with respect to time as the neutralization reaction proceeds; v (moles/L), is the reaction speed; k (L¹⁻ⁿ molⁿ⁻¹ s⁻¹) is the rate constant of the process and n is the reaction order, whereas $[\text{OH}^-]$, (OH^-) , γ and k' stand for the molar concentration, the activity and the activity coefficient of OH⁻ ion, respectively. The log linearization of (2) results in:

$$\log v = \log \{-d[\text{OH}^-]/dt\} = \log k' + n \log(\text{OH}^-) \quad (3)$$

equation that can be plotted substituting $\Delta[\text{OH}^-]$ by $d[\text{OH}^-]$ and Δt by dt , for a series of diverse and several activity-values of OH⁻ ions in solutions to which the pH-value has been measured as a function of time. Thus, a $\log v$ vs. $\log(\text{OH}^-)$ plot should allow the evaluation of k' and n , from the ordinate and abscissa axes, respectively.

Materials and methods

Soil-water suspensions (10g:30dm³) of 5 substrates: humus-compost, MO, Vertisol VR (clay soil), Lixisol, LX (tropical oxidic soil), Luvisol, LV (temperate neutral-oxidic soil) and Sand, AR (inert neutral Arenosol), were acidified/alkalinized monitoring pH with time. Kinetic {pH-t and log r-log (OH⁻)} and Neutralization (Intensity-Capacity: pH-mmol H⁺/OH⁻ and Buffer intensity pH-β (=Δ[OH⁻]/ΔpH) curves were generated.

Results

Overall neutralization pH-time kinetic curves followed the order MO>SA>VR>LV>LX>AR) for pH-buffer. The pH-β [mol dm⁻³] curves resulted in maximum β-values (Figure 2). The significant log-linearized correlations obtained from the kinetic equations, $r = -d[\text{OH}^-]/dt = k'(\text{OH}^-)^n$ for liming and, $r = -d[\text{H}^+]/dt = k'(\text{H}^+)^n$ for acidification resulted in the rate constants, k' , and reaction orders, n , shown in Table 1. The (OH⁻) or (H⁺)-dependent reaction rates showed pseudo-first order kinetics for the mineral acid and neutral soils, and of second order for OM and SA. Rate constants were in the expected order of magnitude with regard to similar and different soil, environmental and chemical processes, as reported in the literature (Table 2). Figure 3 shows the increasing time depending liming requirement caused by slow reactions.

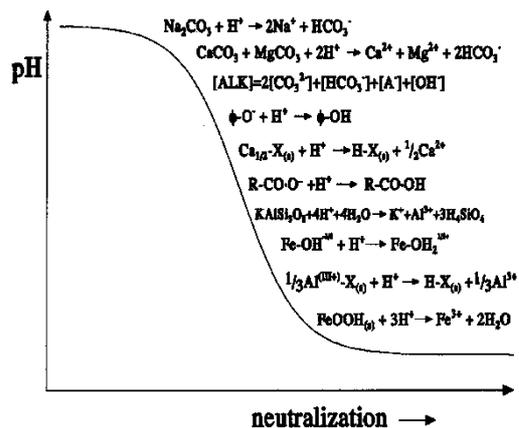


Figure 1. Schematic intensity-capacity neutralization curve of the main acidic-basic functional groups of soil materials

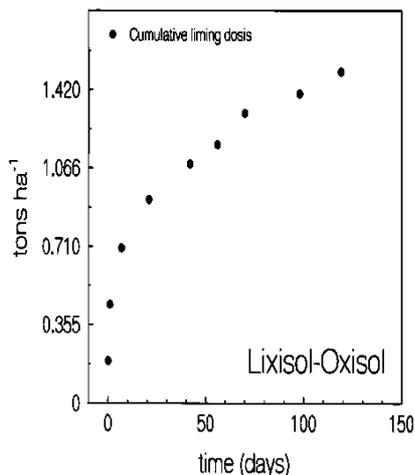


Figure 3. Increasing time dependence of the liming requirement caused by the slow neutralization reactions of functional groups, for $\Delta pH=1$

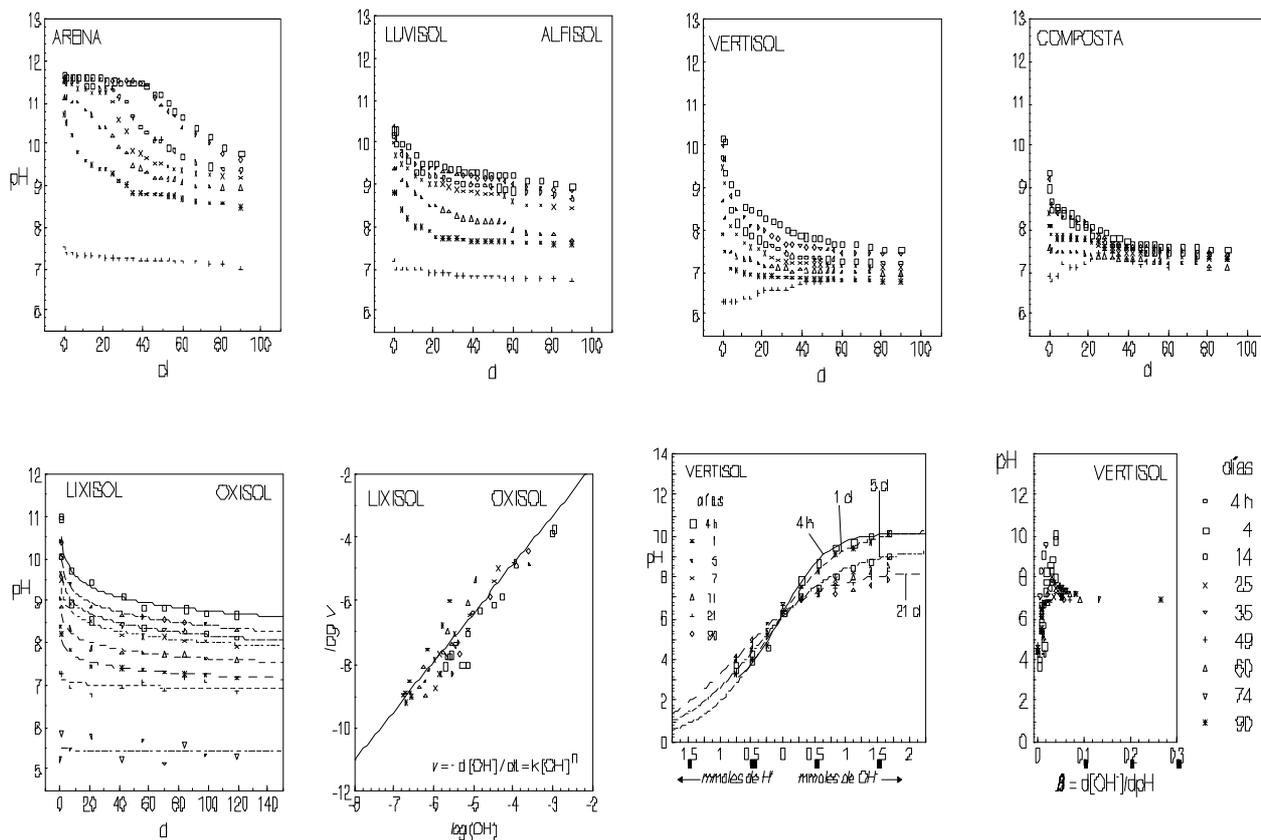


Figure 2. Schematic intensity-capacity neutralization curve of the main acidic-basic functional groups of soil materials

Table 1. Buffer intensity, pH of maximum buffering and kinetic parameters.

Soil	β_{\max}	pH_{β}	n reaction order	$k(\text{s}^{-1})$ rate constant	$\log k(\text{s}^{-1})$	k_s/k_{AR}	$r =$ $-\frac{d[\text{OH}^-]}{dt}$ $\text{mmolOH}^- \text{d}^{-1}$ for $\Delta\text{pH}=1$
MO	1.87	7.54	2.10	2.9	0.46	6.3E5	0.30
VR	0.27	6.88	1.75	2E-2	-1.7	4.3E3	0.26
LX	0.06	8.72	1.55	2.6E-4	-3.6	56	2.5E-2
LV	0.08	9.34	1.32	1.6E-5	-4.8	3.5	4.2E-3
AR	0.08	9.70	1.21	4.6E-6	-5.3	1	9.4E-4
SA	0.83	8.50	2.03	26.5	1.4	5.8E6	0.36*

Table 2. Rate constants of different chemical processes occurring in nature and laboratory experiments.

REACTIONS	$\log k (\text{s}^{-1})$ $\log (\text{rate constant})$
Dissolution of silicates ^a	-13.4 (Quartz), -12.6 (Kaolinite), -10.6 (Augite), -9.5 (Olivine)
Adsorption and ion exchange ^{a,b}	2-4
Gaseous reaction in the atmosphere ^c : $\text{O} + \text{O}_3 \rightleftharpoons 2\text{O}_2$	6
Oxidation ^a of Fe^{2+} and Mn^{2+} in solution with O_2	10
Neutralization in aqueous media ^d $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$	11
Complexation of metals ^e	-8 a 1 (Cr^{III} , Co^{III})
	1-4 (Al^{III} , Fe^{III})
	4-8 (Mg^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+})
	8-9 (Na^+ , K^+ , Ca^{2+} , Cu^{2+})
Neutralization of soils (this paper)	-5.3 (AR); -4.8 (LV); -3.6(LX); -1.7 (VR); 0.5 (MO); 1.5 (SA)

Conclusions

Whereas rapid methods recommended for evaluating liming or acidification requirements usually underestimate the neutralization dose, especially for soils of slow buffering reaction, the kinetic studies presented here show that the time dependence of the neutralization reaction of the acidic and basic functional groups of soils must be considered if a suitable correction of pH is to be attained. Neutralization kinetics and buffering reaction of soils are the key factors to be considered.

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