

# Soil Water

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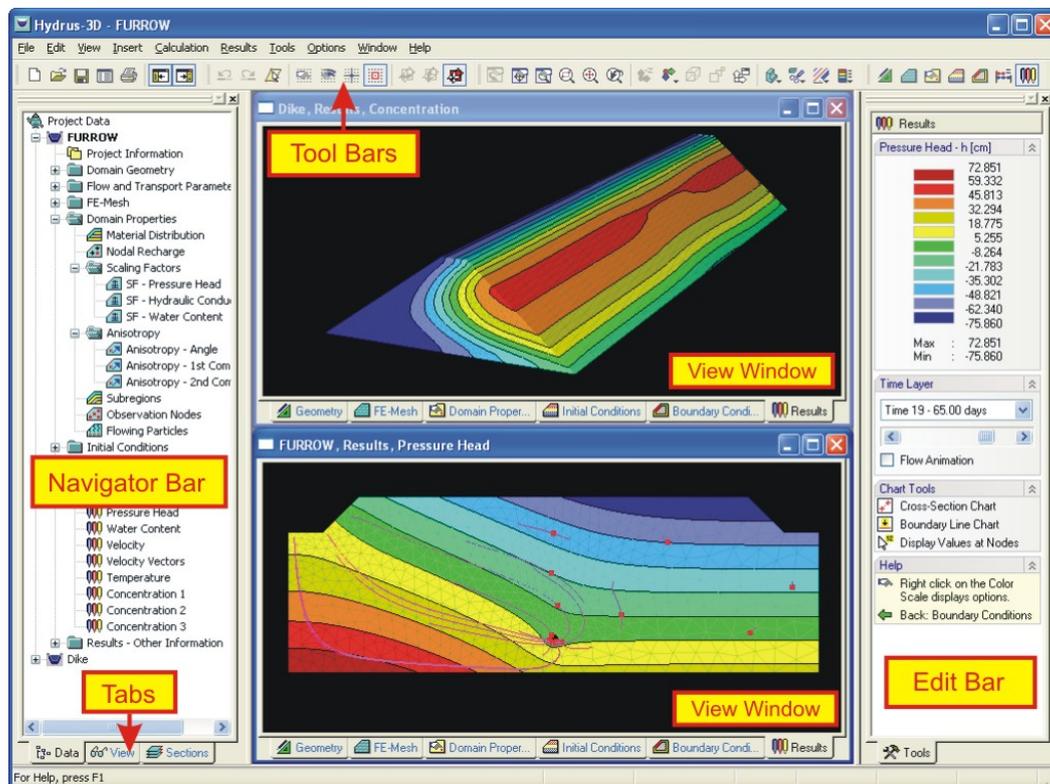
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# Calcium Hydroxide Leaching through a Well-Buffered Volcanic-Ash Soil with pH Dependent Charges

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**ABSTRACT:** Soils have a buffering capacity to moderate pH changes in soil solutions because of the pH dependent charges. A variable charge model is proposed assuming dissociation and attachment reactions of hydrogen with the hydroxyl reactive groups in soils to evaluate the soil buffering capacity. A titration experiment is conducted for a volcanic-ash soil by adding acid and alkaline solutions to estimate parameter values for the variable charge model using the PHREEQC geochemical database code (Parkhurst and Appelo, 1999). Calcium hydroxide leaching process through the well-buffered volcanic-ash soil is then simulated in accordance with the proposed variable charge model using a numerical code HP1 (Jacques and Šimůnek, 2005), which couples HYDRUS-1D for flow and transport and PHREEQC for chemical reactions. When we take into account a suitable buffering capacity based on the variable charge model, HP 1 is a promising tool for quantitative evaluation of the acid or alkaline contaminant transport through well-buffered soils.

## 1 INTRODUCTION

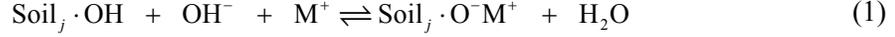
Construction sludge is usually dehydrated with a coagulant material such as lime hydrate for recycling the sludge as a soil foundation. A volcanic-ash soil is often used at the bottom of the landfill sites because of its high buffering capacity to minimize adverse effects of high pH solutions of the coagulant material to the surrounding area. For evaluating a soil buffering capacity, it is necessary properly to take into account the soil variable charges

The variable cation exchange capacity ( $CEC_v$ ) and anion exchange capacity ( $AEC_v$ ) of volcanic-ash soils for different pH and electrolyte concentrations have been experimentally determined by Japanese soil scientists (Wada and Ataka, 1958; Wada, 1980). Okamura and Wada (1983) proposed a general regression equation to describe the observed pH dependent CEC and AEC. Although the empirical regression formula can be used to predict the  $CEC_v$  and  $AEC_v$  at certain pH and concentration, it is necessary to describe explicit reactions of hydrogen or hydroxyl ions with soil hydroxyl reactive groups to predict transport of acid or alkaline solutes in soils.

In this study, a variable charge model is firstly proposed to describe the pH dependent charges and to evaluate the soil buffering capacity. Then, a titration experiment is conducted for a volcanic-ash soil by adding acid and alkaline solutions to the soil-water suspension. Parameter values for the variable charge model are determined based on the titration curve using the PHREEQC geochemical database code (Parkhurst and Appelo, 1999). Finally, a calcium hydroxide leaching process through the volcanic-ash soil is simulated in accordance with the proposed variable charge model. A numerical code HP1 (Jacques and Šimůnek, 2005) is used, which couples the water flow and solute transport code HYDRUS-1D (Šimůnek et al., 2005) and the geochemical code PHREEQC.

## 2 VARIABLE-CHARGE MODEL

A hydrogen ion dissociates from the hydroxyl reactive group  $j$  at the edge of clay minerals ( $\text{Soil}_j \cdot \text{OH}$ ) depending on the soil solution pH. Simultaneously, exchangeable cations  $\text{M}^+$  from the solution phase are electrically adsorbed on the surface ( $\text{Soil}_j \cdot \text{O}^- \text{M}^+$ ) because of the electrical neutrality. The dissociated hydrogen forms water with a hydroxyl ion.



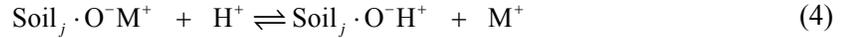
We assume the above reaction does not depend on cation species but simply depends on the total cation concentrations described as

$$[\text{M}^+] = \sum_{i=1}^{N_M} [\text{M}_i^{\nu+}] \quad (2)$$

where  $N_M$  is the number of cation species,  $\nu$  is the valency, and  $[\ ]$  is the ion concentration in terms of moles of charges. We assume higher valency cations such as  $\text{Ca}^{2+}$  also behave similar as a monovalent ion in accordance with the moles of charges. Hence we denote  $\text{Ca}^{2+}$  in Eq. (1) as  $\text{Ca}_{1/2}^+$ . The equilibrium constant for the dissociate reaction  $K_{vc-j}$  is given by

$$K_{vc-j} = \frac{[\text{Soil}_j \cdot \text{O}^- \text{M}^+]}{[\text{Soil}_j \cdot \text{OH}][\text{OH}^-][\text{M}^+]} \quad (3)$$

An ion exchange between  $\text{M}^+$  and  $\text{H}^+$  takes place according to the following exchange reaction:



$$K_{\text{H-M}} = \frac{[\text{Soil}_j \cdot \text{O}^- \text{H}^+][\text{M}^+]}{[\text{Soil}_j \cdot \text{O}^- \text{M}^+][\text{H}^+]} \quad (5)$$

where  $K_{\text{H-M}}$  is the exchange constant between  $\text{M}^+$  and  $\text{H}^+$ . We note that  $\text{O}^- \text{H}^+$  denotes the exchangeable hydrogen whereas  $\text{OH}$  is the hydroxyl group as shown in Eq. (1). It is possible to further determine a specific exchangeable cation concentration for mixed cation solutions if the corresponding exchanges reaction are defined. Since the hydroxyl group may have maximum capacity of dissociation, the parameter  $S_{vc-j}$  (mmol/g soil) is defined for the total amount of the surface reactive group:

$$[\text{Soil}_j \cdot \text{OH}] + [\text{Soil}_j \cdot \text{O}^- \text{M}^+] + [\text{Soil}_j \cdot \text{O}^- \text{H}^+] = S_{vc-j} \quad (6)$$

The sum of exchangeable  $\text{M}^+$  and  $\text{H}^+$  can be regarded as the amount of negative charges, which corresponds to the  $\text{CEC}_v$ , for the reaction group as a result of the hydrogen dissociation.

When the soil consists of  $N_{vc}$  reaction groups, the sum of exchangeable cations for all reaction groups is equal to the variable cation exchange capacity  $\text{CEC}_v$  for the soil. Substituting Eqs. (3) and (5) into Eq. (6) leads to

$$\text{CEC}_v = \sum_{j=1}^{N_{vc}} ([\text{Soil}_j \cdot \text{O}^- \text{M}^+] + [\text{Soil}_j \cdot \text{O}^- \text{H}^+]) = \sum_{j=1}^{N_{vc}} \frac{10^{-14} K_{\text{H-M}} K_{vc-j} S_{vc-j} + K_{vc-j} S_{vc-j} [\text{OH}^-][\text{M}^+]}{1 + 10^{-14} K_{\text{H-M}} K_{vc-j} + K_{vc-j} [\text{OH}^-][\text{M}^+]} \quad (7)$$

Parameters  $K_{\text{H-M}}$ ,  $K_{vc-j}$ , and  $S_{vc-j}$  are strictly specific for any different type of soil. They could be determined from a titration experiment as shown in the next chapter. The variable anion capacity  $\text{AEC}_v$  can be also derived as similar to the  $\text{CEC}_v$ , as described above.

## 3 TITRATION EXPERIMENT

A titration experiment was conducted to determine parameters for the variable charge model. A soil sample ( $m_s = 5 \text{ g}$ ) was firstly mixed with distilled water of  $V_0 = 150 \text{ cm}^3$ . After adding  $\Delta V$

$\text{cm}^3$  of a NaOH solution ( $c_0 \text{ mmol}_c/\text{cm}^3$ ), pH of the supernatant solution was measured. The mass conservation for  $\text{Na}^+$  leads to:

$$c_0 \Delta V = (V_0 + \Delta V) [\text{Na}^+] + m_s \sum_{j=1}^{N_{vc}} [\text{Soil}_j \cdot \text{O}^- \text{Na}^+] \quad (8)$$

Substituting (7) into (8) and assuming  $[\text{Na}^+]$  is equal to  $[\text{OH}^-]$  results in

$$\Delta \text{OH}^- (c_0 - [\text{OH}^-]) = \frac{V_0}{m_s} c_0 [\text{OH}^-] + \sum_{j=1}^{N_{vc}} \frac{K_{vc-j} S_{vc-j} c_0 [\text{OH}^-]^2}{1 + 10^{-14} K_{\text{H-M}} K_{vc-j} + K_{vc-j} [\text{OH}^-]^2} \quad (9)$$

where  $\Delta \text{OH}^- (= \Delta \text{Na}^+)$  is the amount of added NaOH per unit weight of soil. The pH of the supernatant solution can be determined as a function of  $\Delta \text{OH}^-$  according to Eq. (9).

The parameters  $K_{vc-j}$  and  $S_{vc-j}$  for the variable charge model as well as  $K_{\text{HM}}$  for the cation exchange were determined based on the observed titration data (Fig. 1). When the soil consists of two types of reaction groups ( $N_{vc} = 2$ ), the fitted curve could reasonably agree well with the observed data. The corresponding variable cation exchange capacity  $\text{CEC}_v$  as function of solution pH for three ionic concentrations is calculated with Eq. 7 for the optimized parameter values (Fig. 2).

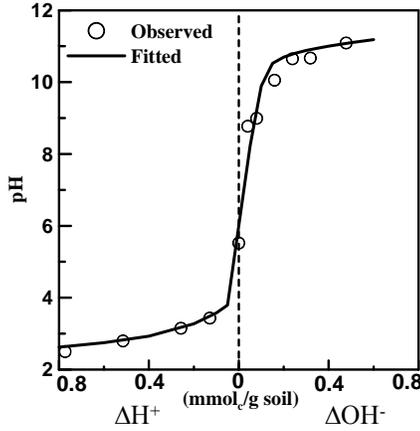


Figure 1. A titration curve for a volcanic-ash soil. Solid line is fitted with Eq. (9).

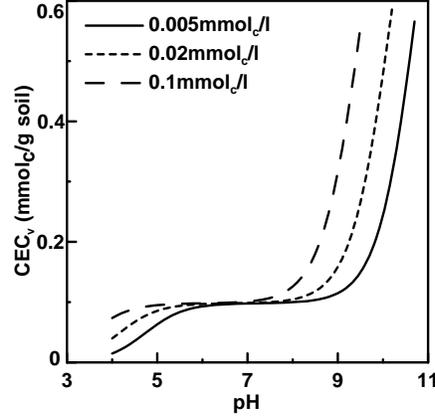


Figure 2. Calculated cation exchange capacity  $\text{CEC}_v$  based on optimized fitted parameters to an observed titration curve.

#### 4 CALCIUM HYDROXIDE LEACHING

Calcium hydroxide leaching transport through a volcanic ash soil is numerically evaluated. The soil is uniformly packed at a bulk density of  $0.53 \text{ g/cm}^3$  in a 20 cm length column (Fig. 3). A calcium hydroxide solution of  $10 \text{ mmol}_c/\text{cm}^3$  is applied to the saturated solute-free soil with steady-state water flux of  $30 \text{ cm/h}$ . The volcanic-ash soil has a charge property as described in Fig. 1.

Transport of  $\text{Ca}^{2+}$  is described with the convection dispersion equation:

$$\frac{\partial}{\partial t} (\rho_b Q_{Ca} + \theta C_{Ca}) = \frac{\partial}{\partial x} \left( D \frac{\partial C_{Ca}}{\partial x} \right) - \frac{\partial}{\partial x} (J_w C_{Ca}) \quad (10)$$

where  $C_{Ca}$  is the  $\text{Ca}^{2+}$  aqueous concentration ( $\text{mmol}_c/\text{cm}^3$ ),  $\rho_b$  is the soil bulk density ( $\text{g/cm}^3$ ),  $\theta$  is the volumetric water content (-),  $D$  is the hydrodynamic dispersion coefficient ( $\text{cm}^2/\text{h}$ ),  $J_w$  is the volumetric flux ( $\text{cm/h}$ ), and  $Q_{Ca}$  is the  $\text{Ca}^{2+}$  adsorbed concentration ( $\text{mmol}_c/\text{g soil}$ ) described with the variable charge model:

$$Q_{Ca} = \sum_{j=1}^{N_{vc}} [\text{Soil}_j \cdot \text{O}^- \text{Ca}_{1/2}^+] = \sum_{j=1}^{N_{vc}} \frac{K_{vc-j} S_{vc-j} [\text{OH}^-] [\text{Ca}_{1/2}^+]}{1 + 10^{-14} K_{H-M} K_{vc-j} + K_{vc-j} [\text{OH}^-] [\text{Ca}_{1/2}^+]} \quad (11)$$

Because of the electrical neutrality of the soil solution,  $[\text{OH}^-]$  is assumed to be equal to  $[\text{Ca}_{1/2}^+] + [\text{H}^+]$ . Furthermore, for an alkaline condition, neglecting  $[\text{H}^+]$  leads to  $[\text{OH}^-] \approx [\text{Ca}_{1/2}^+]$ , which means the solution pH ( $[\text{OH}^-]$ ) can be solely determined from  $[\text{Ca}_{1/2}^+]$ .

The numerical calculation for the  $\text{Ca}^{2+}$  transport through the profile is carried out using the HP1 code (Fig. 4): *i.e.*, water flow and nonreactive solute transport parts in Eq. (10) are evaluated in HYDRUS-1D, and chemically reactive part  $Q_{Ca}$  in Eq. (10) is evaluated in PHREEQC based on the variable charge model with the optimized  $K_{vc-j-M}$ ,  $S_{vc-j-M}$  and  $K_{H-M}$  for Eq. (11). Then, using the assumption of  $[\text{OH}^-] \approx [\text{Ca}_{1/2}^+]$  and the general equation of pH, the pH distribution through the profile is also evaluated (Fig. 5). Finally, the  $\text{CEC}_v$  in the soil profile as a function of  $\text{Ca}^{2+}$  according to Eq. (7) is calculated (Fig. 6).

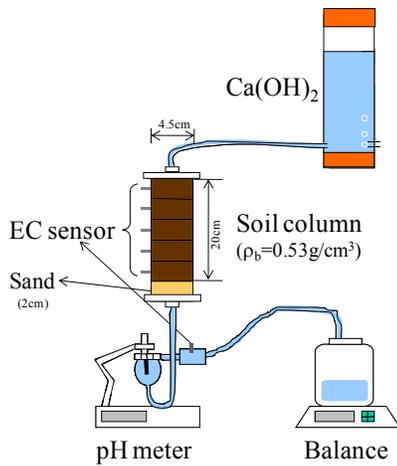


Figure 3. Principle scheme of calcium hydroxide leaching experiment.

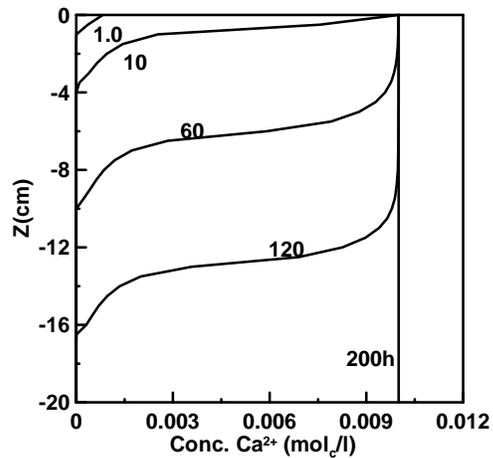


Figure 4. Calculated  $\text{Ca}^{2+}$  concentration profiles.

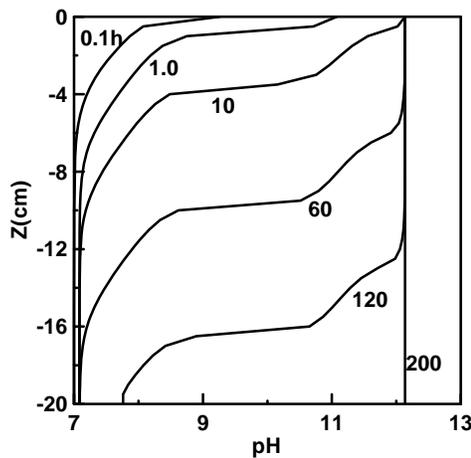


Figure 5. Calculated pH profiles during leaching through the soil profile.

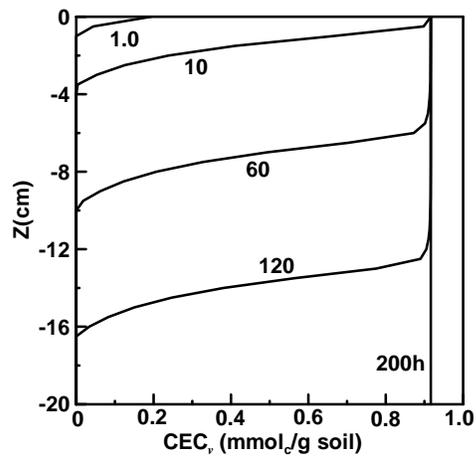


Figure 6. Calculated variable cation exchange capacity through the soil profile.

It takes 160 hours (300 pore volume)  $\text{Ca}^{2+}$  reaches at the bottom of the column because of high buffering capacity of the volcanic-ash soil (Fig. 4). The calculated pH in the soil column (Fig. 5) is in correspondence with the experimental observations. As the  $\text{CEC}_v$  is a function of pH and the cation concentration according to Eq. (7), increases in the  $\text{Ca}^{2+}$  concentration and pH results in the increase in the  $\text{CEC}_v$  as shown in Fig. 6. With taking into account a suitable buffering capacity based on the variable charge model, HP 1 is a promising tool for quantitative evaluation of the acid or alkaline contaminant transport through well-buffered soils.

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