

# Variable Charge Surface and Chemical Processes in Highly Weathered Soils with Emphasis on Fertility and Environment Implications in the Tropics

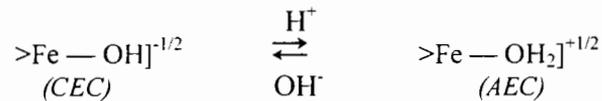
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## Abstract

Most of soils in humid and wet-dry tropics are highly weathered soils (HWS), which also occur in humid subtropical areas. HWS are the result of intense and long weathering, in well-drained soil conditions where rainfall exceeds evapotranspiration. Consequently, they are characterized by very few if any weatherable primary minerals, and by low-activity clay minerals: 1:1 kaolinite-group clays and Fe and Al oxides. Such clays are variable charge colloids and determine very specific properties at the solid-solution interfaces in HWS. A brief review of these properties and related processes is made in the paper, with emphasis placed on surface reactions with bases, metals and phosphorus, and implications in fertility and environment quality management.

Unlike permanent negative surface charge that is generated by isomorphic substitution in high activity 2:1 layer clays, which predominate in other soils, variable charge is due to the amphoteric properties of OH groups mainly exposed on 1:1 layer and oxide clay surfaces in HWS. In that case, the surface charge is created by the adsorption of H<sup>+</sup> and OH<sup>-</sup> ions onto the colloid surface, with the net charge being determined by that ion sorbed in excess. The reactions on pH-dependant charge surfaces can be summarized as follows:



CEC increases as pH increases, and conversely for AEC (anion exchange capacity). The noteworthy Point of Zero Net Charge (PZNC) is the pH value at which the negative and the positive charges are equal. Variation curves of CEC and AEC in different soil samples show that organic matter (OM) is a major CEC contributor in topsoil, and that oxides promote AEC where they are predominantly present. As a result, net AEC preferentially occurs in subsoil horizons. As a general rule, base cation exchange capacity (CECb) dramatically decreases at pH values over and lower than 5, due the increasing content in exchangeable Al.

Moreover, variable charge clays are able to develop more selective and less reversible bonding than electrostatic adsorption. The process referred to as specific adsorption or chemisorption occurs through the unsaturated OH (or OH<sub>2</sub><sup>+</sup>) groups exposed on mineral surfaces, involving covalent bonding with cation metals, as well as with anions such as phosphate and other oxyanions. Beside pH, other factors controlling surface reactivity in HWS are also recalled in the paper.

HWS are naturally prone to base depletion and acidification, for several converging reasons such as: low native nutrient reserve, high drainage and leaching capacity, low CEC and exchangeable base content, with frequently low pH (≈ 4.5). Even in the less desaturated and acid soils, nutrient impoverishment and acidification may occur rapidly after clearing of the original vegetation and continuous cultivation. Surface reactions also facilitate the acidification process, in the way that the increase in soil acidity with any excess of H<sup>+</sup> generates lower CEC and greater cation mobility, so making easier the processes of base leaching and acidification. Nitrification process is a major source of protons, all the more since N fertilizer dressings are higher. It is

noteworthy that adsorption of exchangeable  $\text{NO}_3^-$  can occur on positive charge surface, mainly in subhorizons. The process is able to retard nitrate movement downward, but cannot avoid leaching and pollution risks.

Metal cations, such as trace metals that may be found as toxic elements or pollutants, can be retained in soil by both surface bonding and precipitation reactions. HWS have a rather low metal retention capacity at field pH, compared with soils having permanent negative charge, and this can be a matter of environmental concern in the tropical and subtropical regions. Neither purely electrostatic nor covalent models of surface bonding are adequate explaining metal adsorption. The soil pH that controls both the surface charge and the formation of hydroxyl metal species is the most important soil property affecting metal adsorption and hence transport in soils. The total adsorption and the fraction of specifically adsorbed metal increases with the increasing pH, and high pH favours sorption and precipitation of metal cations as oxides, hydroxides and carbonates. Consequently, the proportion of easily desorbable metal is low at higher pH. Addition of inorganic and organic ligands generally enhances metal sorption at low and medium pH. Other metal cations, especially Al, Fe and Mn cations that may be present in relatively high content in acid HWS, can also compete with metals for access on adsorbing sites, resulting in higher leaching of non-specifically adsorbed metals.

HWS are often deficient in phosphorus, due to low P reserves and high P sorption capacity. P sorption involves several rapid and slow reactions, including electrostatic adsorption, chemisorption on variable charge sites and precipitation as metal-phosphate compound. High P sorption capacity of HWS has often been related to high contents of oxides and/or clay fraction. Inorganic colloids have quite different sorption capacities, in the ordered sequence: amorphous hydrous oxides > crystalline oxides > 1:1 clays > 2:2 clays. The degree of crystallinity affects the specific surface and the magnitude of P sorption. P sorption is also controlled by soil pH and increases as pH decreases. OM anions compete with  $\text{PO}_4^{3-}$  on similar sorbing sites, which explains that P sorption capacity generally increases with increased depth in the soil profile.  $^{32}\text{P}$  exchange in soil showed that available P desorption is a function of time, that can be seen as the result of several connected P compartment working at different exchange rates of P. P desorption is also controlled by diffusion process, and can be negatively affected when soil water content decreases.

As a result of high P sorption capacity, P fertilizer efficiency may be very low in HWS. Conversely, the risks of ground water pollution through P leaching are very low. Economically sounded fertilization requires appropriate strategies, with P fertilizers better suited for HWS, using lower cost local resources and phosphate rocks.

The control and optimization of surface properties with appropriate agricultural practices are essential in the rational management of HWS, aiming at sustainable qualities of soil and environment. A major point is that factors that influence the surface reactions with cations influence in the same time those with anions. Well-balanced agricultural practices are needed for the amelioration and maintenance of soil fertility, without overlooking suitable management of OM and base status, which are particularly important in these soils. Increases in OM content and in pH value as well have favourable effects on soil fertility properties, concerning both cations and anions availability for plants, within reasonable pH values. On the other hand, the results may be rather divergent for purification purpose of waste materials by soil, as cation and anion immobilization occur at opposite values of the variations in OM and pH.



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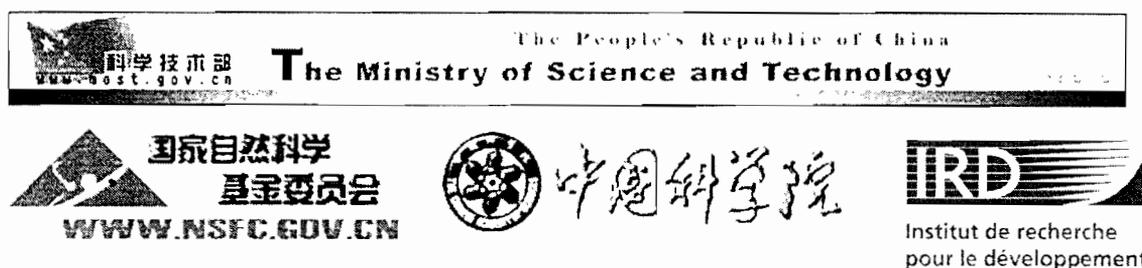
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