

# Soil pH and Its Significance as Ecological Material: Perspectives and Implications



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**Abstract** Soil has been the most widely explored material for construction purpose, since our ancestors stepped out from the cave dwellings and went in search for alternate shelters. As it is the plasticity and consequent mouldability of the soil, that attracted the early humans; it is evident that the clay minerals are the prime contributors for the desired properties. In modern times, the scope of soil as a building material became wider (viz. embankments, landfill liners etc.) and the clay fraction still plays the key role in deciding the material suitability. In this regard, it is necessary to have a thorough understanding of the various elements that influence the behaviour of the clayey fraction within the soil. Among the different factors that influence the clay behaviour, soil pH deserves the prime position, as it can alter the charge distribution of the clay surface and promote mineral dissolution. In view of this, the following chapter address the role of pH in moulding the current personality that we assigned to the clay minerals. In the initial part of the discussion, the different sources and nature of soil acidity/alkalinity, and the role of soil type and genesis in influencing the same has been reviewed. Further, the extent of pH buffering offered by the soil system is discussed, focussing on the various mechanisms involved in the pH-neutralisation. The later section of the chapter discuss the ways with which pH modifies the soil properties such as fabric arrangement and surface charge. Also, the special case of soil-electrokinetic treatment is considered to demonstrate the implications of the property changes in a real life applications.

**Keywords** Buffer capacity · Clay minerals · Soil electro-kinetics · Soil fabric, Soil pH

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## 1 Introduction

Soil has been the most widely explored material for construction purpose, ever since our ancestors stepped out from the cave dwellings and went in search for alternate shelters. Their previous acquaintance with soil as a sticky mouldable nuisance might have helped them to ease their choice. Because, it is the same sticky mouldable personality that made soil, a suitable candidate as building material. Soil is not a single entity, instead an aggregation of a rock particles subjected to different degree of weathering, with the in between space occupied by air, water, or both. In addition, the presence of numerous cations and anions as well as organic matter make the entire soil matrix an interesting chemical recipe. Each component somehow influence the desired quality of the material in one way or another. However, it is the clay fraction of the soil; end product of the chemical weathering of rock, that act as the decisive factor in choosing suitable soil type. This is because of two reasons. Firstly, there are various types of clay minerals, each possessing distinctive character traits. Secondly, unlike the inert sandy or silty fraction, the clay mineral surface is active, hence being influenced by the surrounding pore fluid chemistry.

In the modern times, the scope of soil as a building material doesn't get limited to building bricks or plastering the walls. Instead, soil has been used in the construction of embankments, waste landfill liners, permeable reactive barriers, earthen dam etc. Hence the broad gamut of desirable soil properties includes plasticity, strength, permeability, erodability, chemical attenuation, etc. With the short description hitherto provided, one can presume that the clay fraction of the soil play significant role in all of the above listed engineering attributes. In view of this, a thorough understanding of the various influencing factors on the behaviour of the clay mineral is inevitable for engineering the material to meet the specific requirements. Being a practicing engineer or an academic enthusiast, a proper understanding of the clay behaviour always come for your help as you are dealing with one of the most unpredictable engineering material-soil.

Among the different factors that influence the clay behaviour, soil pH deserves the prime position. This is due to the typical charge distribution on the clay surface. Since the edges of the flaky clay particles act as both acid and base depending on the ambient pH (amphoteric), the charge pattern gets modified with pH. Also, the dissolution of clay minerals under extreme pH exposure can induce physical and surface charge modifications to the material. It has been well established that any kind of the clay response can be approximated as a derived outcome of the surface charge modifications. Hence with the change in pH, the complete spectra of soil properties, significant to each specific application gets altered as function of pH.

In view of this, the following chapter address the various ways by which pH influence the soil properties, with the discussions channelled mainly to the applications in the field of geotechnical engineering. Initially, the idea of soil acidity was introduced by duly mentioning its role in the clay genesis. Also, the pH buffering mechanisms in soil are discussed in detail, as the acid/base neutralization is detrimental in many of the geotechnical and geoenvironmental application areas (Yong

et al. 1990). The later section of the chapter discuss the ways with which pH enhance or retard the desired soil properties. The pH induced modifications in soil properties are viewed in terms of the corresponding alterations in soil fabric and surface charge behavior. Additionally, the specific example of soil electro-kinetics was considered to demonstrate the influence of pH in geotechnical/geoenvironmental scenarios. The discussions are meant to sprout an interest and to provide an initial momentum for the readers to further dig into the broader aspects of clay chemistry and mineralogy. Hence the contents are presented in a lucid way to keep up the interest of the readers.

## 2 Origin and Fate of Soil pH

The clay minerals we see today, in its quantity and distribution, is the result of millions of years of chemical weathering. The complex pedogenic process enabled the minerals to hold essential nutrients and supply on demand to facilitate the lush greenery on earth. In this regard, pH played significant role in sustaining life on this planet, as pH was pivotal in the highly complex weathering and transformational pathway underwent by the clay minerals. The major transformational process includes pH specific hydrolysis and acidolysis (Wilson 1999). The topic of clay genesis is highly complex and beyond the scope of the current discourse. However, the breadth of the topic can be appreciated from Fig. 1, which depicts the commonly accepted transformational pathway for the clay minerals. To get a quick glimpse at the extent of property variation that the transformation brings in, consider the case of montmorillonite transformation to kaolinite, by means of total hydrolysis and numerous other favorable physico-chemical conditions. Though the period should be measure in geological time scale, the formation of almost non-swelling kaolinite from montmorillonite, which can swell up to 7 times its dry volume is amazing. The mother nature has been and continues to be a master chef, bringing and modifying the soil flavor throughout the history and this aspect is evident from Fig. 2 that showing the global distribution of soil pH. Due to the dynamic nature of the process involved, I am sure that the readers won't be surprised if I say that the map may look entirely different after several million years from now.

It is now clear that pH not only influences the behaviour of a soil deposit; instead, plays active role in its formation. Fascinated and curious, if you decide to measure the

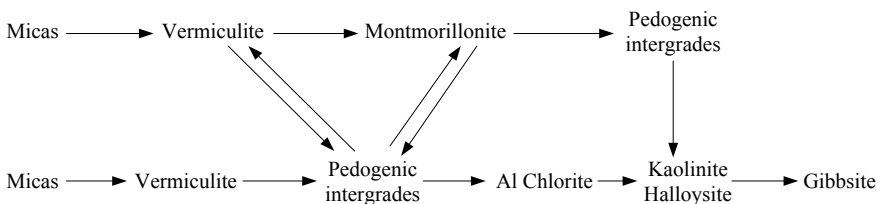
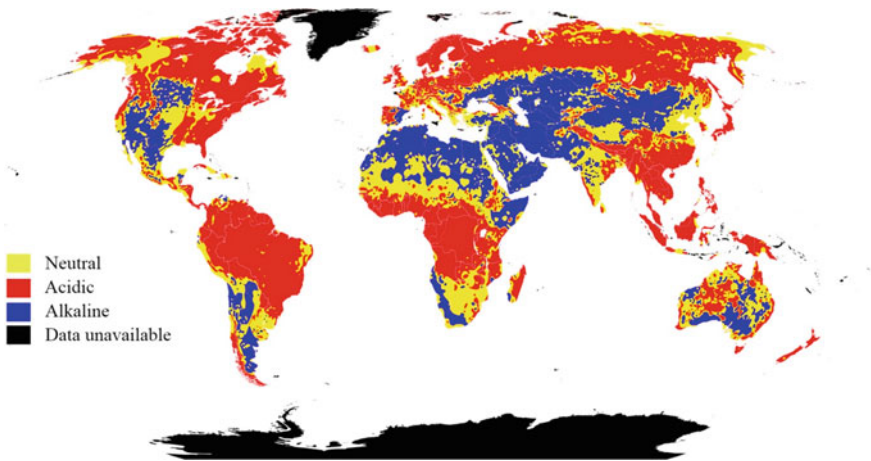


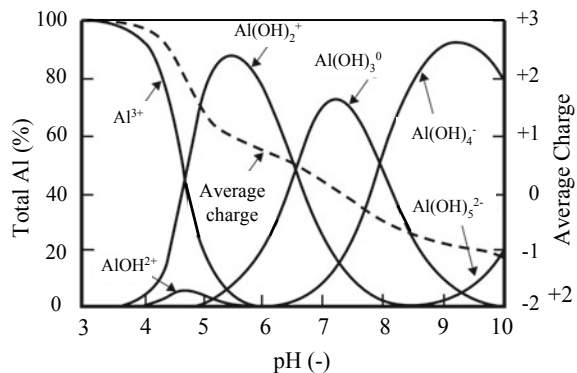
Fig. 1 Pathways for the formation of soil clay minerals (Jackson et al. 1964)



**Fig. 2** Global variation in soil pH (modified from IGBP-DIS 1998; refer the link [https://en.wikipedia.org/wiki/Soil\\_pH#/media/File:World\\_Soil\\_pH.svg](https://en.wikipedia.org/wiki/Soil_pH#/media/File:World_Soil_pH.svg) for the procedure followed in recreating the original map)

pH of your garden soil using a pH electrode, you should be aware of the two major contributors to the observed acidity;  $H^+$  and Al. In the commonly encountered pH range (4–9), Al derived acidity is more significant, whereas  $H^+$  becomes dominant for highly acidic soils (pH < 4) such as mine spoil and acid sulfate soil. Al contributes to the soil acidity by undergoing reversible hydrolysis to form hydroxyl ions. The type of monomeric Al species present depends on the soil pH. Figure 3 shows the relationship between soil pH and the type of monomeric Al species present. Even though polymeric Al species can also undergo hydrolysis, their contribution towards total acidity is insignificant due to the preferential adsorption of the species onto clays and organic matter. Both Al and  $H^+$  are present in exchangeable as well as non-exchangeable forms. The exchangeable Al, normally encountered in highly acidic

**Fig. 3** Relationship between pH and the distribution and average charge of soluble aluminum species (Sparks 2002)



soils, can be quantified by titrating with a neutral salt solution viz. KCl. The non-exchangeable form of Al contributes to the variable charge in the clay minerals (McBride 1994).

## 2.1 Soil pH Buffering

In simplest form of definition, pH buffering refers to the resistance to change in pH. In the case of a soil system, the buffering mechanisms involved are quite complex, owing to the various contributory factors as well as the inherent dynamic nature of the system. The following section makes an attempt to comprehend the various ways with which the soil tries to resist a change in its pH. The understanding may aid in various geotechnical applications, as will be discussing in the later sections.

Generally encountered buffers are the combinations of weak acids/bases and their salts derived from strong bases/acids (e.g.,  $\text{CH}_3\text{-COOH}$  &  $\text{CH}_3\text{-COONa}$ ,  $\text{NH}_4\text{OH}$  &  $\text{NH}_4\text{Cl}$ ), provided the pH of the buffer is in the range of the acid/base equilibrium constant of the system. A second possibility is the presence of salts of multi proton donating acids (e.g.,  $\text{H}_3\text{PO}_4$ ). When the acid donates a proton, its conjugate base is formed, and the mixture of the acid and its conjugate base can effectively buffer the pH change (Chesworth 2008).

Well documented literature is available pertaining to the acidic/basic nature of clay minerals, and it is reported that most of the mineral groups act either as a partially ionized weak acid or partially ionized salt of a weak acid (van Breemen and Wielemaker 1974a; Ritchie 1989). This behavior associated with the minerals provides an inherent pH buffering capacity to the soil, though the extent of buffering depends mostly on the acid/base equilibrium constant of the system (van Breemen and Wielemaker 1974b; Bloom and Skyllberg 2012). Moreover, it has been noticed that almost all the chemical components and reactions involved within the clay matrix; ranging from the soil solution chemistry to the pH-dependent mineral dissolution can potentially affect the pH buffering response of the soil system. This corroborates the fact that protonation/deprotonation reactions are the predominant processes that occur when the chemical equilibrium within the soil matrix is disturbed.

Buffering with regard to bases occurs through the neutralization by residual acid fractions, whereas acidic buffering is mostly due to the re-adsorption of the excess  $\text{H}^+$  into the colloidal soil fraction. The different components that offer buffering within a soil-electrolyte system can be grouped under two broad headings of buffering by soil solution and buffering by the solid phase. In soil solution,  $\text{CO}_2$  and organic acids are the major contributors towards buffering. Also, a variety of organic colloidal fraction is present in the soil solution, having acid/base neutralizing potential over a wide range of pH. Carbonic acid is having an acid dissociation constant,  $\text{pK}_a$  of 6.3, and hence  $\text{CO}_2$  usually exhibits appreciable buffering ability at a pH of above 5.5. There can be a variety of organic acids present in the soil, such as formic acid and acetic acid, all showing a  $\text{pK}_a$  value of less than 4, and hence their presence can offer buffering to the soil system in the acidic range. It has been observed that the

partial neutralization of acidic groups with the formation of a stable metal complex can significantly alter/reduce the buffer capacity of the system (Sposito 2008).

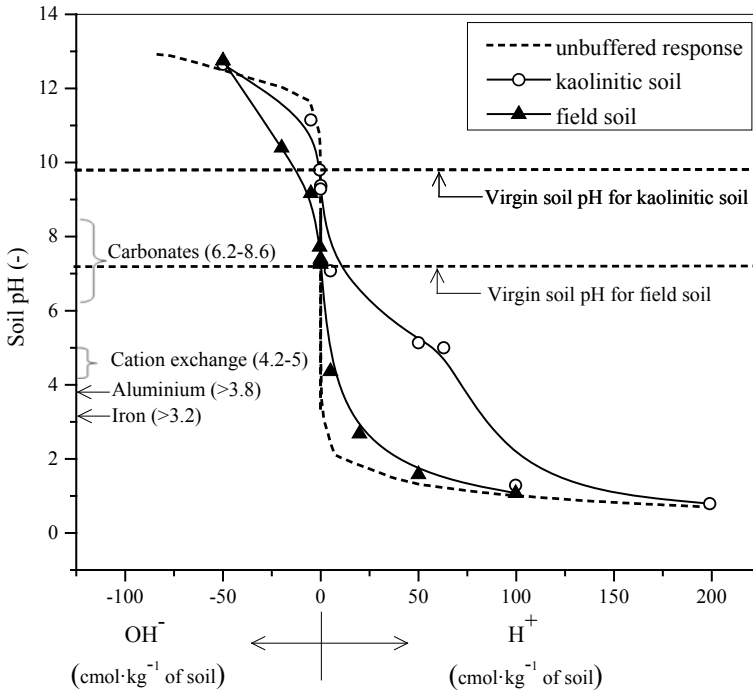
In the case of the soil solids, the inputs towards the acid/base neutralization capacity are mainly from the permanent and pH-dependent charge surfaces of the clay minerals. In addition, the process of dissolution of clay minerals at specific pH-includes protonation/deprotonation reactions. Hence it can be deduced that pH buffering increases with increase in clay mineral dissolution. Permanently charged surfaces participate in buffering mainly by means of its cation exchange capacity. A decrease in ionic adsorption is reported at low ionic strength, maybe because of the overlap of diffused double layer (DDL) from edges and faces, and thereby decreasing the net attractive forces (Aitken and Moody 1994). The concept of clay DDL has been elaborated in following sections. In the case of variable charged edge surface, the extent of adsorption depends on several factors such as the soil pH, ionic type and concentration and the surface affinity towards  $H^+$  or  $OH^-$ . Studies reported a minimum contribution from the variable charges, towards the total buffering at the point of zero charge (refer Sect. 2.2.2 for PZC). The soil pH shift to either side of the PZC increases the buffer capacity. An increased buffering is observed with mineral solubility, because of the consumption of proton by the dissolution of minerals. Clay minerals with weak acid cations (Ca, Mg, Na, K, etc.) such as smectites and illites show higher buffering with dissolution, compared to minerals with strong acid cations, viz. kaolinite and gibbsite (Table 1).

Normally, the pH buffering response of a soil solution can be delineated by titrating with known concentrations of acids/bases. Figure 4 shows the potentiometric titration curves of a kaolinitic clay and a field soil (from IIT Madras, Chennai). The detailed soil characterization and the methodology adopted for the study can be found in Kollannur and Arnepalli (2019b). The carbonate content in the kaolinitic clay explains the unusual buffering observed in the neutral zone. Further, the two soils significantly differ in their base neutralization capacity, with the field soil exhibiting higher base buffering compared to kaolin. This was due to an increased percentage of sulfate in lake clay, forming hydrogen sulfide that possesses high values of acid dissociation constant. Also, the silicic acid formed by the dissolution of silica in water can

**Table 1** Buffering mechanisms for different soil pH ranges<sup>a</sup>

pH range	Soil classification	Buffering mechanism
<4.5	Extremely acid	Iron range (pH 2.4–3.8)
4.5–5	Very strongly acid	Aluminum/iron range (pH 3.0–4.8)
5.1–5.5	Strongly acid	Aluminum range (pH 3.0–4.8)
5.6–6	Moderately acid	Cation exchange (Ph 4.2–5.0)
6.1–7.3	Slightly acid to neutral	Silicate buffers (all pH values typically > 5)
7.4–7.8	Slightly alkaline	Carbonates (pH 6.5–8.3)
7.9–14	Moderate to extreme alkaline	Mineral weathering, OH-from water and oxides of Ca, Mg, Na, K

<sup>a</sup>Schwertmann et al. (1987), Ulrich (1991), Reuss and Walthall (1990)



**Fig. 4** pH buffering response in two soils exhibiting diverse chemical and mineralogical composition (modified from Kollannur and Arnepalli 2019b)

offer buffering in the alkaline region. Since the dissolution is mineral dependent and the selected soils differ in their mineralogical particularities, the varying proportion of silicic acid can also add to the difference in buffer response.

## 2.2 Effect of Soil pH in Geotechnical and Geoenvironmental Applications

So far we have seen that the clay genesis is the prime reason for the wide range of pH in soils. At the same time, there are instances which disturbs the  $H^+/OH^-$  balance and in-turn modifying the soil pH in short time durations, viz. acid rain, contamination/spill from industries etc. In the context of geotechnical engineering, the inherent soil pH or the incidental modifications may interfere as a hindering or an enhancing factor during our attempts to treat the soil. This can be either due to the direct modifications in soil fabric and surface charge, or because of the resultant changes in chemical diffusivity. The second aspect comes into play when we are deploying any chemicals to stabilize the soil. Further in the context of geoenvironmental engineering, the pH induced alterations in chemical diffusivity can influence contaminant plume spread

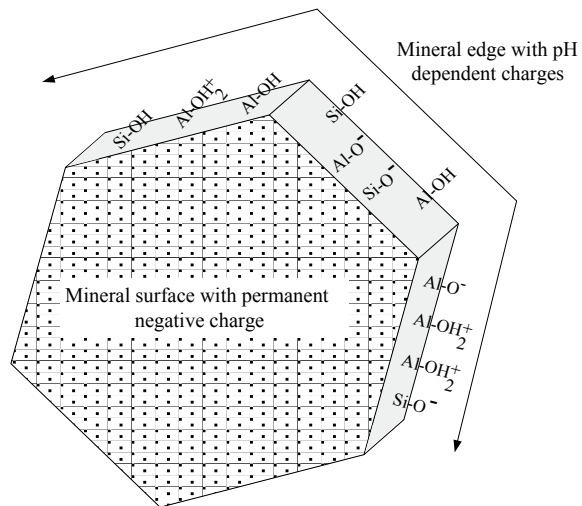
as well as soil remediation efficiency. These aspects are discussed in the following section, and their practical manifestation are elaborated by considering the example of soil electro-kinetic treatment.

### 2.2.1 Soil pH and Charge Distribution on Clay Minerals

To understand the influence of pH on the surface charge and soil fabric, it is essential to apprehend the origin and distribution of charges on the clay surface. Clay mineral surface carry negative charges due to isomorphous substitutions and bond breakages within the clay lattice. But the mineral edges are amphoteric, and the nature of charge is determined by the electrolyte pH (Tombác and Szekeres 2004). Figure 5 shows the schematic of the typical charge distribution on clay surface. These charges will get satisfied by cations/anions attached on the mineral surface. However, when the mineral is dissolved in a solution, the surface attached ions gets higher kinetic energy and they try to diffuse out into the solution. At the same time, we know that they are electrically attached to the clay surface. These two counteracting mechanisms causes the charges to arrange in a specific pattern from the clay surface.

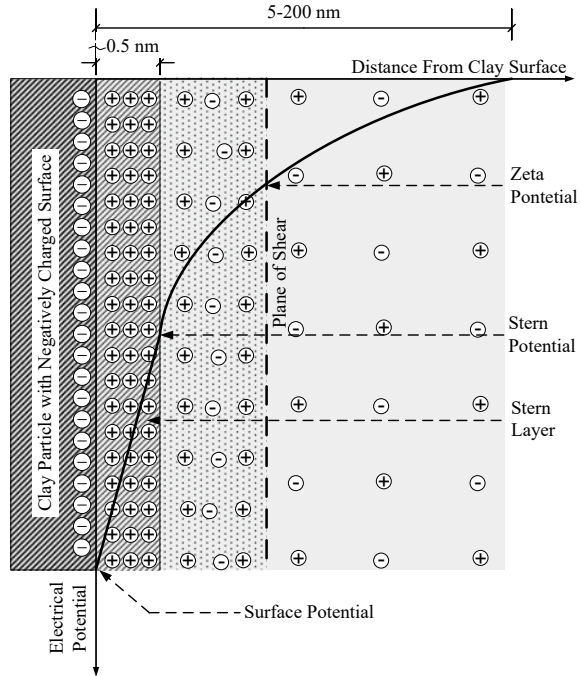
The distribution of the ions at the interface boundary can be explained in terms of Gouy-Chapman double layer theory (Fig. 6). According to this model, the counter ions as well as polarized water will attach strongly over a short distance from the clay surface. This layer is known as the stern layer, which experience a linear decay of the surface potential. After the stern layer, the ions are now loosely held, creating the diffused layer and the potential decay is exponential in nature. The stern layer and diffused layer constitutes the diffused double layer (DDL) of charges on the clay surface. Now, if we attempt to drain out water from a clay matrix, it is intuitive that some quantity will stick to the clay surface due to the electrostatic attraction. To

**Fig. 5** Schematic of a typical clay mineral with surface charge heterogeneity (Kollannur and Arnepalli 2019b)





**Fig. 6** Schematic view of electrical diffused double layer on clay surface in an aqueous solution (Nikhil John and Arnepalli 2019)



be precise, the whole of the stern layer and a portion within the diffused layer will not take part in the flow. The notional boundary within the diffused layer, beyond which the adsorbed water participate in the bulk flow is called the plane of shear and potential at the plane is knows as zeta potential ( $\zeta$ ). As zeta potential connotes every variation in the thickness of the DDL, it is very much useful in understanding the variation in surface charge distribution of the clay mineral surface.

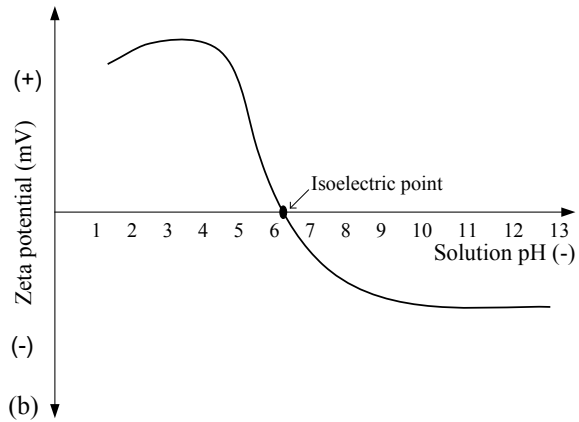
Now to understand how pH plays a role in modifying the charge distribution, we should know the factors influencing the thickness of the DDL. The DDL thickness  $1/k$ , which is measured form the clay surface to the centroid of the charge distribution is given by the formula

$$\frac{1}{k} = \left( \frac{\epsilon k T}{8\pi n_0 e^2 v^2} \right)^{\frac{1}{2}} \tag{1}$$

where  $\epsilon$  is the dielectric constant of the medium,  $T$  is the absolute temperature in Kelvin,  $e$  is unit electric charge,  $n_0$  is the electrolyte concentration, and  $v$  is the ionic valency.

When the solution becomes more acidic/alkaline, the dielectric constant reduces, resulting in a thinner DDL for the colloidal particles. However, the higher incorporation of  $\text{OH}^-$  into the DDL as a result of increase in alkalinity makes the DDL thicker. This is due to the larger hydrated ionic radius of  $\text{OH}^-$  and the vice versa is

**Fig. 7** Typical zeta potential variation with solution pH



applicable in the case of acidic pH conditions. This is evident from Fig. 7, which shows the typical variation in zeta potential with solution pH, where we can observe an increase in zeta negativity with the pH value. The cross over point corresponds to a specific pH value where the net charge on the colloidal particle is zero, and is termed as isoelectric point (IEP). The IEP bears great significance in many of the application areas of colloids (including clay minerals). Since the discussions are beyond the scope of this book, it is suggested to refer the detailed reviews by authors such as Sposito (1998) and Kollannur and Arnepalli (2019b) for better comprehension.

In the case of soils, the influence of pH doesn't get limited to the above mentioned ways. The minerals can undergo dissolution, which is a pH specific process. The dissolution can not only alter the surface charge but modifies the structure by means of precipitation of the dissolved minerals.

## 2.2.2 Soil PH: Influence on Fabric and Surface Charge Properties

In the previous section, we have seen how the pH can take active role in the modifying the surface charge of clay minerals. The state of pH in a soil-system can be defined with respect to its point of zero charge (PZC). PZC corresponds to the pH value at which one or more categories of charges on the clay mineral surface approach zero (Sposito 1998). Just like there are many categories of soil surface charges, PZC also includes many sub divisions and note that the IEP; the cross over point of the zeta plot, is closely related to PZC. The details regarding the same can be found in Kollannur and Arnepalli (2019b). For the brevity of the present discussion, let's consider only the case of zero point of charge (ZPC); a subset of PZC, defined as the pH that brings true electro-neutrality to the clay particle.

At ZPC, the reduced DDL causes particle to flocculate. Towards the acidic side of ZPC, the clay edges undergoes higher protonation, thereby resulting in edge-surface interaction. As we move towards the alkaline side of ZPC, the degree of flocculation

decreases, and with increase in the inter-particle separation, the structure becomes increasingly oriented (Goldberg and Glaubig 1987). Additionally, the exposure to acidic/basic solutions can cause dissolution of primary minerals such as kaolinite and montmorillonite (Nakayama et al. 2004; Cherian et al. 2018). Also, it can pave way for the formation of secondary minerals. The entire process can re-organize the soil fabric by filling or opening of the matrix voids. Also, the process can significantly alter the active surface area of the clay minerals as well as the porosity of the clay matrix, by either removing the oxide coating from the clay surface, or by the precipitation of the dissolved products (Bhattacharyya and Gupta 2008). We are concerned about the particle structure, as most of the soil engineering properties (viz. compressibility, permeability and shear strength) are influenced by the clay fabric (Mesri and Olson 1971). For instance, flocculated structure offers isotropic flow patterns whereas in the case of dispersed structure, the flow will be higher in the in-plane direction and lower in the cross-plane direction.

Apart from the impact on the engineering properties, the modification in fabric and the corresponding alteration in the matrix tortuosity can affect the chemical diffusion through soil and this part will be discussed in later sections.

Also, the modification in surface charge can severely impact the chemical attenuation. For example, at acidic pH, the cationic attenuation will be low due to the competition from  $H^+$  ions. On the other side, with increase in solution alkalinity, higher amount of  $OH^-$  gets sorbed onto the clay surface. This is due to the increase in the negativity of the mineral edges. In effect, as the combined outcome of fabric and surface charge modifications, the chemical diffusivity can get affected, which have implications in many areas of soil improvement and remediation. In this context, the following section address the specific case of soil electro-kinetic treatment to see how the aforementioned factors are influencing real world problems. There are two reasons for considering the electro-kinetic method to demonstrate the manifestations of soil pH variations. Firstly, the temporal and spatial variation in soil pH is inherent in the treatment process. Secondly, the technique has been used widely for both soil stabilization and remediation aspects, thereby fitting well within the scope of the affected category.

### 2.2.3 Soil Electro-Kinetics—An Overview

Soil electro-kinetics refers to the application of electrical potential across the soil mass, either to facilitate chemical movement or to cause water flow. Chemical movement is demanded at two situations; (1) for chemical grouting of weak soils (Electro-chemical Stabilization) and (2) for remediating contaminated soils (Electro-kinetic Remediation). The current facilitated water flow takes advantage of electro-osmotic phenomenon to accelerate the dewatering of highly impermeable soils. Electro-osmosis corresponds to the water flow within a colloidal system under the application of an electrical potential. Under the potential head, the hydrated cations and anions within the DDL moves towards their respective polarities. The moving ions exerts a drag force on the bulk liquid, which eventually results in electroosmotic flow

(normally from anode to cathode in a soil-electrolyte system). The flow is partially responsible for the migration of chemicals in the form of advective flux. However, the major contributor in this regard is the electro-migration, which is the direct migration of chemical ions under the electrical potential. A detailed description of the various mechanisms involved in the electro-kinetic phenomena can be found the review by Kollannur and Arnepalli (2019a).

During the application of potential, along with the species migration, the current flow causes electrolysis of pore water and results in the generation of  $H^+$  and  $OH^-$  ions at the anode and cathode sides respectively. The generated ions eventually migrate into the soil mass, thereby altering the pH of the soil system. The following section describes how the change in pH influence the electro-kinetic phenomena (viz. electro-osmosis and electro-migration) and in-turn the complete treatment efficiency.

### Effect of pH on electro-osmosis

We have already stated that the electroosmotic flow is due to the viscous drag exerted on the pore fluid by the moving cations and anions within the soil system. The expression for electro-osmotic permeability is given by

$$k_e = \left( \frac{\zeta \varepsilon}{\eta} \right) n i_e \quad (2)$$

where  $i_e$  is the electrical potential gradient in  $v\text{-cm}^{-1}$ ,  $\eta$  is the viscosity of the pore fluid and  $n$  is the porosity.

The influence of pH on the dielectric constant of the pore fluid as well as the zeta potential of the colloid has been previously discussed (Fig. 7). Since the electroosmotic flow depends on the same parameters (Eq. 2), the change in pH can bring a profound influence on the electroosmotic flow efficiency. With increase in acidity (observed in the anodic zone), there will be a reduction in zeta potential (DDL contraction), resulting in lesser flow rate. The opposite is applicable in the case of alkaline flow. As the dielectric constant always reports a reduction with increase in ionic concentration (Mitchell and Soga 2005), any deviation from the neutral pH can reduce the flow rate. Also we have seen that the porosity plays an important part. Since fabric modification is very much likely in a system of varying pH (Sect. 2.2.2), it can bring noticeable changes in the soil porosity and the resultant electroosmotic flow will be a combined outcome of the DDL/zeta potential modification, change in dielectric constant as well as the soil fabric.

### Effect of pH on electro-migration

Electro-migration is a function of the diffusivity of the chemical species under consideration. The transport of reactive chemicals through soil is derived from Fick's second law and is given by the equation

$$\frac{\partial c_i}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 c_i}{\partial x^2} \quad (3)$$

where  $R_d = 1 + \left(\frac{\rho_d}{\eta}\right)k$  is the retardation factor,  $k = \frac{ds}{dc}$  is the sorption coefficient, expressed as the ratio of sorbed to equilibrium solute concentration and  $\rho_d$  is the dry density of the soil.  $D^*$ , the effective diffusion coefficient, is a function of soil geometry, fluidity and anion exclusion. This shows that the diffusion characteristics are dependent on the soil fabric. Further, the retardation factor ( $R_d$ ) is a function of the sorption characteristics of soil, emphasizing the importance of surface charge properties of the soil. As pH influence the fabric and soil surface charge, the chemical diffusivity gets altered as function of pH, which in turn modifies the electro-migration.

### Implications of pH induced changes in soil electro-kinetics

During electro-kinetic treatment, the modifications in soil pH may bring positive or negative effects based on the treatment purpose. For instance, electrochemical treatment requires alkaline pH to facilitate the precipitation of the injected chemicals. At the same time, high alkaline pH generated during the initial treatment hours can clog the pathways and thereby preventing further chemical movement. Whereas for electro-kinetic remediation, the soil matrix should be acidic, in order that the contaminants will remain in the dissolved state without precipitation for easy recovery. In most of the electro-kinetic applications,  $\frac{3}{4}$ th of the soil becomes acidic, and this is due to the higher diffusivity of  $H^+$  as well as the favourable electro-osmotic flow direction (Kollannur and Arnepalli 2019a). It is obvious that such soil pH profile can facilitate the remediation attempts. However, if we aim to stabilize the soil, then the system need to be buffered to an alkaline pH value to derive the maximum benefit out of it. Hence the inherent buffering of response of the soil-system need to be thoroughly comprehended in order to estimate the extent of treatment needed to bring the pH to desired range.

## 3 Summary

The discourse attempted to emphasize the paramount role of pH in modifying the properties of soil. A comprehensive detailing is provided with regard to the origin and fate of soil pH, with due regard given on the various pH buffering mechanisms involved within the soil-system. Further, the soil property modification, which are direct and derived outcomes of the system pH was elaborated and in light of the understandings, the specific case of soil electro-kinetics was considered to inspect the influence of pH change.

With the fundamental understanding about the behaviour of a soil system to acidic/alkaline environments, we hope that the readers can further explore other application areas of soils (viz. building materials, landfill liners etc.) and channel their though process for engineering the material to meet their specific needs.

## References

- Aitken, R. L. & Moody, P. W. (1994). The effect of valence and ionic strength on the measurement of pH buffer capacity. *Australian Journal of Soil Research*, 32(5), 975–984.
- Bhattacharyya, K. G., & Gupta, S. S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science*, 140(2), 114–131.
- Bloom, P. R., & Skyllberg, U. (2012). Soil pH and pH buffering. In P. M. Huang, Y. Li & M. E. Summer (Eds.), *Handbook of soil sciences: Properties and processes*, vol. 19, 2nd edn. (CRC Press, Florida, USA), pp. 1–14.
- Cherian, C., Kollannur, N. J., Bandipally, S., & Arnepalli, D. N. (2018). Calcium adsorption on clays: Effect of mineralogy, pore fluid chemistry and temperature. *Applied Clay Science*, 160, 282–289.
- Chesworth, W. (2008). *Encyclopedia of soil science*. Netherlands: Springer.
- Goldberg, S., & Glaubig, R. A. (1987). Effect of saturating cation, pH, and aluminum and iron oxide on the flocculation of kaolinite and montmorillonite. *Clays and Clay Minerals*, 35(3), 220–227.
- IGBP-DIS. (1998). Soil Data (V.0) A program for creating global soil-property databases, IGBP Global Soils Data Task, France.
- Jackson, M. L. (1964). Chemical composition of soils. In F. E. Bear (Ed.), *Chemistry of the soil* (pp. 71–141). New York: Reinhold Publishing Corp.
- Kollannur, N. J., & Arnepalli, D. N. (2019a). Electrochemical treatment and associated chemical modifications of clayey soils: A review. *International Journal of Geotechnical Engineering*. <https://doi.org/10.1080/19386362.2019.1653513>.
- Kollannur, N. J., & Arnepalli, D. N. (2019b). Methodology for determining point of zero salt effect of clays in terms of surface charge properties. *Journal of Materials in Civil Engineering*, 31(12), 1–9.
- McBride, M. B. (1994). *Environmental chemistry of soils*. New York, USA: Oxford University Press.
- Mesri, G., & Olson, R. E. (1971). Mechanisms controlling the permeability of clays. *Clays and Clay Minerals*, 19, 151–158.
- Mitchell, J. K., & Soga, K. (2005). *Fundamentals of soil behaviour*. New Jersey, USA: John Wiley and Sons.
- Nakayama, S., Sakamoto, Y., Yamaguchi, T., Akai, M., Tanaka, T., Sato, T., et al. (2004). Dissolution of montmorillonite in compacted bentonite by highly alkaline aqueous solutions and diffusivity of hydroxide ions. *Applied Clay Science*, 27(1), 53–65.
- Nikhil John, K., & Arnepalli, D. N. (2019). Factors influencing zeta potential of clayey soils. In V. Stalin & M. Muttharam (Eds.), *Geotechnical characterisation and geoenvironmental engineering—lecture notes in civil engineering*, vol. 16 (pp. 171–178). Singapore: Springer.
- Reuss, J. O., & Walthall, P. M. (1990). Soil reaction and acidic deposition. In S. A. Norton, S. E. Lindberg & A. L. Page (Eds.), *Advances in environmental science—4. Acidic precipitation*, vol. 1 (pp. 1–33). New York, USA: Springer-Verlag.
- Ritchie, G. S. P. (1989). The chemical behaviour of aluminium, hydrogen and manganese in acid soils. In A. D. Robson (Ed.), *Soil acidity and plant growth*, vol. 1 (pp. 1–60). Australia: Academic Press.
- Schwertmann, U., Susser, P., & Natscher, L. (1987). Proton buffer systems in soils. *Journal of Plant Nutrition and Soil Science*, 150, 174–178.
- Sparks, D. L. (2002). *Environmental soil chemistry* (2nd ed.). New York, USA: Academic Press.
- Sposito, G. (1998). On points of zero charge. *Environmental Science and Technology*, 32(19), 2815–2819.
- Sposito, G. (2008). *The Chemistry of Soils*. New York, USA: Oxford University Press.
- Tombácz, E., & Szekeres, M. (2004). Colloidal behavior of aqueous montmorillonite suspensions : the specific role of pH in the presence of indifferent electrolytes. *Applied Clay Science*, 27(1–2), 75–94.

- Ulrich, B. (1991). An ecosystem approach to soil acidification. In B. Ulrich & M. E. Sumer (Eds.), *Soil acidity* (pp. 28–79). Berlin, Germany: Springer-Verlag.
- van Breemen, N., & Wielemaker, W. G. (1974a). Buffer intensities and equilibrium pH of minerals and soils: I. The contribution of minerals and aqueous carbonate to pH buffering. *Soil Science Society of America Journal*, 38(1), 55–60.
- van Breemen, N., & Wielemaker, W. G. (1974b). Buffer intensities and equilibrium pH of minerals and soils: II. Theoretical and actual pH of minerals and soils. *Soil Science Society of America Journal*, 38(1), 61–66.
- Wilson, M. J. (1999). The origin and formation of clay minerals in soils: past, present and future perspectives. *Clay Minerals*, 34, 7–25.
- Yong, R. N., Warkentin, B. P., Phadungchewit, Y., & Galvez, R. (1990). Buffer capacity and lead retention in some clay materials. *Water, Air, and Soil pollution*, 53, 53–67.