ISSN 0255-7193

CLAY RESEARCH

Vol. 36, No.2

December 2017

IOS
Press

Overseas distribution
IOS Press, The Netherlands

THE CLAY MINERALS SOCIETY OF INDIA
Division of Soil Science and
Agricultural Chemistry
Indian Agricultural Research Institute
New Delhi-110 012, India

Overseas subscribers may send
their queries to IOS Press, Nieuwe
Hemweg 6B, 1013 BG Amsterdam,
The Netherlands, orders@iospress.in:
URL: http://www.iospress.nl

THE CLAY MINERALS SOCIETY OF INDIA

(Registered under Act XXI of 1860)
Registration No. S/13028 of 1982

Annual Institutional Subscription Rates Inclusive of Air Mail and Handling Charges :

Subscription Rates (Year 2011)	Indian (INR)	Overseas (USD)
Print + online access	Rs. 1,800.00	$ 350.00
Online access	Rs. 600.00	$ 150.00
Print	Rs. 1,200.00	$ 200.00

All payments should be sent to **"The Clay Minerals Society of India"** Division of Soil Science and Agricultural Chemistry, I.A.R.I., New Delhi-110 012

Clay Research, Vol. 36, No. 2, pp. 47-54 (2017)

Chemical Enrichment and Acid Activation of Bentonite Clay

SERIFE SARIOGLAN* AND HAYRETTIN YÜZER

Institute of Chemical Technology, TUBITAK Marmara Research Center, Gebze 41470, Kocaeli, Turkey.

Abstract–*Bentonite clay with high amorphous SiO_2 content up to 50% has been enriched via the caustic treatment. Caustic concentration varied between 5 to 25%. Operation time and temperature were the other parameters when driving the optimum enrichment conditions. It was found that amorphous silica was successfully removed when the caustic concentration is 15% or above. Operation temperature of 80 C and duration of 90 minutes were the other limitations in order to have an efficient SiO_2 extraction. Recovery of SiO_2 as sodium silicate solution during this enrichment was another concern that might be important affecting the process economy. Acid activation was applied to the enriched clay to obtain a bleaching earth. The so-called bleaching earth showed bleaching efficiencies of 98.3% and 93.3 regarding to the chlorophyll-a and β-carotene, respectively. In agreement with the recorded decreases in chlorophyll-a and β-carotene components, lovibond red and yellow values were also decreased considerably. This study showed that the unpleasant color changes coming from the presence of pigments, such as chlorophyll-a and β-carotene, can be avoided by the use of chemically enriched and acid activated bentonite as the bleaching earth.*

Key words : Enrichment, Acid amorphous silica, Activation, Bentonite, Bleaching, Clay, Soybean oil

Introduction

The color of edible oil is the most important factor in determining its commercial value. The unpleasant color changes comes from the presence of pigments, such as chlorophyll-a and β-carotene, in the raw oil. In refining process, these pigments are selectively removed by adsorption on clays. This was known commercially as bleaching process and it gives intended stable oils with light color in direction to consumers' acceptance (Proctor and Palaniappan, 1989; Boukerroui *et al.,* 2000; Sarioglan *et al.,* 2010).

Bentonite is usually employed in a variety of industrial applications, among them; its usage as bleaching earth has an important place by the virtue of its sorption property. The widely used method is the acid activation to improve its bleaching capacity both for edible and mineral oils (Fahn, R., *et al.,* 1983; Zaki, M.I *et al.,* 1986). Bentonite clay in their raw form does not pose bleaching activity due to its low surface area and impurity content such as calcite and gypsum. Hence, treatment with strong acids is a must. Upon acid activation, calcium ions locating at the external surface of montmorillonite have been primarily exchanged with hydrogen ions. The degree of acidity and duration of activation dictates the level of secondary interaction between cations like calcium in calcite and gypsium and aluminum, magnesium and iron in the clay structure with the treated mineral acids. After acid activation, the clay structure becomes free from these ions (Taylor and Jenkins, 1987). Sulfuric and hydrochloric acids are the most common agents to be used in acid activations. Treatment with strong mineral acids changes the structure, chemical composition, and physical properties of the clay while increasing its adsorption capacity (Mokaya *et al.,* 1993). Acid activation also increases the surface area (Rubert

---

***Corresponding Author Email :** serife.sarioglan@tubitak.gov.tr; hayruddinyuzer@gmail.com

et al., 1987; Srasra *et al.*, 1989; Kaviratna and Pinnavaia, 1994; Christidis *et al.*, 1997) and modifies the structure of smectites (Rubert *et al.*, 1987; Rhodes and Brown, 1992; Tkac *et al.*, 1994). The properties of bentonite treated with acid solutions has been studied in different aspects by several research groups (Volzone at al., 1986; Volzone *et al.*, 1988; Morgado, 1998; Foletto *et al.*, 2000; Foletto *et al.*, 2003, Onal M. *et al.*, 2002, and Alemdaroglu T. *et al.*, 2003). In these studies, the changes in physicochemical properties of bentonites such as chemical composition, cation exchange capacity (CEC), specific surface area and specific micropore/mesopore volumes were evaluated regarding the activation ways of sulphuric acid. The strength of acidity, duration of treatment and operation temperature were the parameters in concern (Christidis *et al.*, 1997).

In some circumstances, an additional enrichment process is needed before acid activation depending on the chemical composition of the clay. In the literature, (Low Philip F, *et al*, 1983; Haihui Zheng; Guanglie LV, 2007) enrichment studies have been conducted by using physical separation like centrifuge, hydrocyclone etc. In those studies, bentonite clay has been enriched in terms of montmorillonite via wet physical methods. By one of these methods, wet or dry enrichment, while the impurities, namely SiO_2 and feldspat have been washed out from the crystal structure, undesired amorphous silica has been left in the structure due to its similar physical properties with montmorillonite.

The importance and innovation of this experimental work lays on its purification step in order to reduce the amorphous SiO_2 content of 50% in low grade bentonites via a chemical method. Although the use of caustic in converting amorphous silica into sodium silicate was extensively experimented, this method has been first applied to the bentonites with high amorphous SiO_2 content. The enriched bentonite after caustic treatment has been exposed to acid activation and tried for bleaching the raw soybean oil. Upon these treatments on low grade bentonite clays, higher bleaching efficiencies have been achieved in comparison to ones directly activated with acid without chemical enrichment, as proved by the measurements of tintometer.

Material and Methods

Raw bentonite clay was supplied from Unye region of Turkey. Sodium hydroxide and hydrochloric acid in Merck purity were used in the enrichment and acid activation studies.

The bleaching efficiency of activated clays was measured by determining lovibond red, β-carotene and chlorophyll-a values of the bleached oil with a Tintometer (Lovibond PFX880).

Thermo Jarrell Ash Atomscan-25 model Inductively Coupled Plasma (ICP) Spectrometer was used for the elemental analysis of the filtrate solution. X-ray fluorescence (XRF) spectrometer was applied for determining the chemical compositions of the solid phases. Philips PW 2404 XRF spectrometer was used for these measurements.

As the procedure of the chemical enrichment and acid activation 50 gram of raw calcium bentonite was crushed below 4-5 mm and put into a jacketed reactor of 250 mL. 150 mL of deionized water was poured into the reactor to have clay slurry. Concentrated sodium hydroxide solution was added slightly onto the slurry under stirring to adjust the caustic concentration in prefixed values. Caustic concentrations were changed in between 5 and 25 percentages by weight. Treatment with caustic solution has been carried out for a duration of 60 minutes at 90 °C. After the caustic treatment, the mixture has been filtrated via a filtration funnel under vacuum at 90°C. Determination of sodium hydroxide has been conducted gravimetrically on the received solid.

The results of gravimetric analysis were evaluated in the calculations to determine the amount of strong acid, which will be added in excess during the activation reaction. Acid activation on the enriched bentonite sample was conducted with a solution of HCl (18% volume in concentration) at 90ºC. Acid activation was carried out in a jacketed reactor of 250 mL. The solid phase was slurried with a minimum amount of deionized water. Hydrochloric acid solution in 40 % of raw bentonite on weight basis was added slightly onto the said slurry under stirring. In the beginning of the stirring, additional hydrochloric acid solution was mixed with the slurry in order to neutralize the remaining caustic left after the enrichment. The amount of excess HCl solution was determined based on the above mentioned gravimetric analysis. The reaction temperature was adjusted to 90°C. Temperature has been kept constant throughout the reactor for 5 h under reflux conditions. The mixture received after the acid activation was washed and filtered. Optimum conditions of this acid activation procedure were previously determined and published by the authors of this work (Sarioglan *et al.,* 2010). Figure 1 shows the diagram of chemical enrichment and acid activation process.

The procedure of the bleaching

Acid activated samples were washed until pH of the washing water comes to a point between 2.9 and 3.0. Washed samples were dried at 105˚C, and ground to pass through a 125 µm sieve and used for bleaching the raw soybean oil.

One hundred grams of alkali-refined soybean oil was heated to 120ºC under stirring in an inert atmosphere (nitrogen). The clay material (2 g) was then added to the heated oil, and the mixture was stirred mechanically for 5 min. The oil-clay batch was kept in nitrogen atmosphere throughout the experiment. The hot oil and clay mixture was then separated by filtering at the end of the experiment. The bleaching efficiency of activated clays was determined by measuring lovibond red, β-carotene-a and chlorophyll values of the bleached oil using a Tintometer according to the procedures listed in the American Oil Chemists 'Bleaching Test' (AOCS Offical Method Cc 8a-52).

In the study, the bleaching efficiency is defined by the following expression (Christidis *et al.*, 1997):

Bleaching Efficiency= $100*(C_0 - C)/C_0$

where C_0 is the concentration (ppm) of -

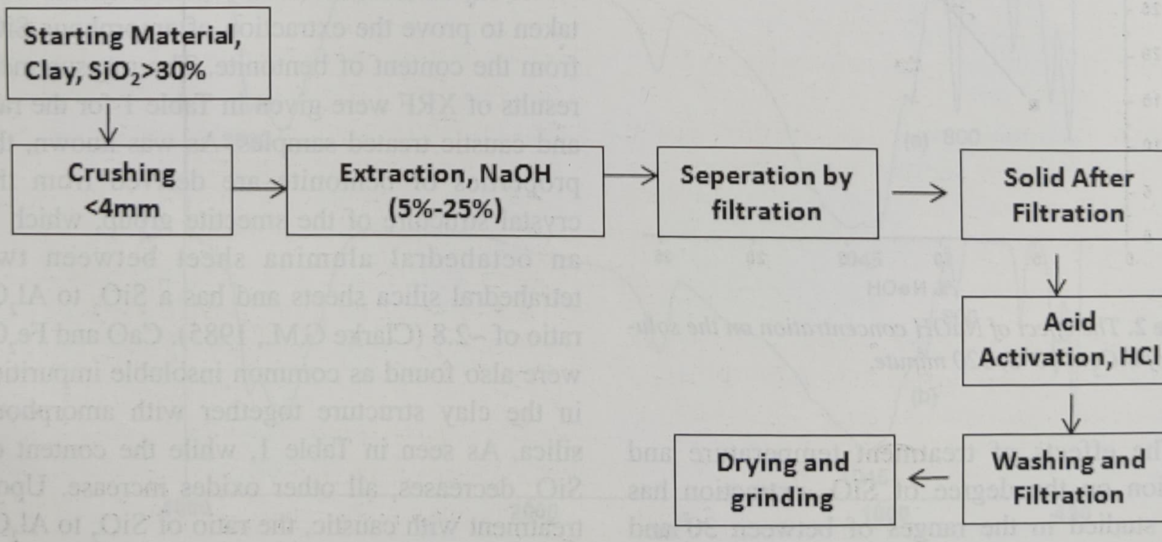


Figure 1. *The diagram of chemical enrichment and acid activation process.*

carotene in the raw oil and *C* is the concentration of β-carotene in the bleached oil.

The soybean oil bleaching performances of the activated samples were compared with those of the bentonite samples directly acid activated without caustic enrichment based on the measurements of tintometer.

Results and Discussions

The effect of sodium hydroxide concentration on the removal of silisium dioxide from the content of raw bentonite was studied by stepwise increasing of caustic concentration from 5 to 25%. Extracted SiO_2 in the form of sodium silicate has been calculated per 100 gram of raw bentonite. The degree of SiO_2 removal was plotted against the concentration of NaOH in Fig. 2. Extracted SiO_2 was observed to increase by caustic concentration up to a certain level and then reached a stable plateau. Maximum SiO_2 removal of 35.8% in weight was achieved at a caustic concentration of 15%. Then excess caustic more than 15% was seen to have no effect on removing SiO

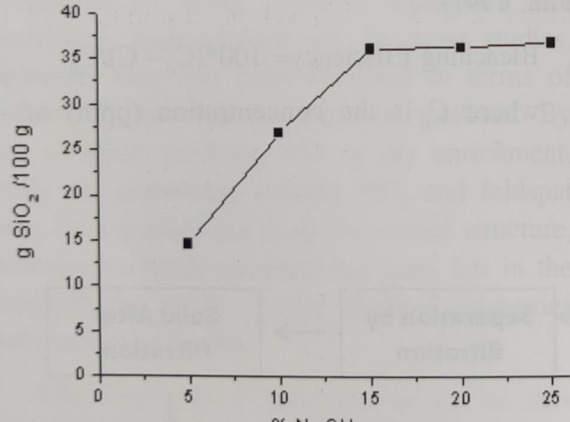


Figure 2. *The effect of NaOH concentration on the solubility of SiO_2 at 90°C, 120 minute.*

The effects of treatment temperature and duration on the degree of SiO_2 extraction has been studied in the ranges of between 30 and 100°C and 30 and 120 minutes, respectively. During these experiments, caustic concentration was kept constant at 15% in weight. As seen in Fig. 3. The degree of SiO_2 extraction has been increased steadily with operation temperature. Duration of caustic treatment has the same effect as operation temperature. On the other hand, for caustic treatments of 90 and 120 minutes, extracted SiO_2 values were nearly the same after the operation temperature of 80°C. This means that equilibrium of SiO_2 dissolution has been attained at operation temperatures above 80°C provided that sufficient treatment time was applied.

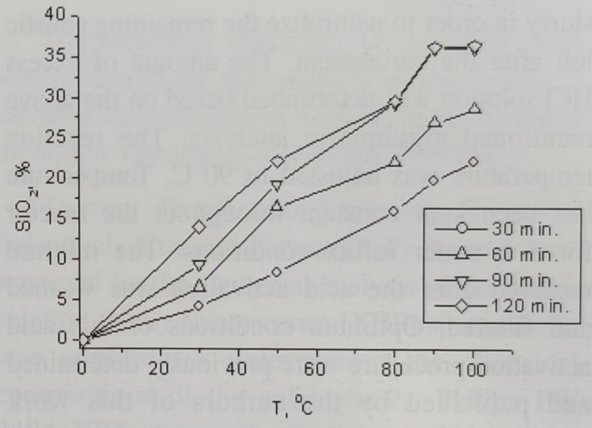


Figure 3. *The effect of leaching time and temperature in the presence of 15% NaOH*

X-ray fluorescent (XRF) measurements were taken to prove the extraction of amorphous SiO_2 from the content of bentonite. The measurement results of XRF were given in Table 1 for the raw and caustic treated samples. As was known, the properties of bentonite are derived from the crystal structure of the smectite group, which is an octahedral alumina sheet between two tetrahedral silica sheets and has a SiO_2 to Al_2O_3 ratio of ~2.8 (Clarke G.M., 1985). CaO and Fe_2O_3 were also found as common insoluble impurities in the clay structure together with amorphous silica. As seen in Table 1, while the content of SiO_2 decreases, all other oxides increase. Upon treatment with caustic, the ratio of SiO_2 to Al_2O_3 became closer to pure smectite type bentonite.

Table 1. The results of x-ray fluorescent measurements of Unye Bentonites before and after reaction with NaOH

Sample	Na_2O%	K_2O%	CaO%	MgO%	SiO_2%	Al_2O_3%	Fe_2O_3%
Raw Unye Bentonite	-	0.16	2.25	2.84	78.62	14.63	1.16
Bentonite after reaction with NaOH at 90°C	2.64	0.33	4.05	5.53	59.40	22.80	4.73

This shows that only the SiO_2 species in the form of amorphous silica has been removed via caustic treatment. By combining the gravimetric analysis results of Si in the solution by inductively coupled plasma and determination of chemical composition by XRF, it was proposed here that caustic treatment was successful in removing the amorphous silica from the structure of raw bentonite.

FTIR spectra of the natural and treated bentonite samples were given in Figure 4 showing the change of Si-O stretching and bending bonds upon caustic leaching process. Si-O stretching band at ~1045cm^{-1} and Si–O bending bonds at ~800cm^{-1} decreased after the treatment of the raw bentonite with NaOH. FTIR measurement on raw and leached samples supported the above mentioned finding of selective amorphous SiO_2 removal via caustic leaching. The remaining bands at 3630 cm^{-1} and 3434 cm^{-1} were known to be hydroxyl groups of Al-Al-OH and Mg–OH–Al and water captured by the interlayers, respectively (Christidis *et al.*, 1997).

Upon enrichment of the raw clay in order to remove its amorphous SiO_2 content, it was acid activated to gain a bleaching property as described before (Sarioglan, *et al.*, 2010). Then acid activated clay was tested in terms of its bleaching activity. To do this, raw soybean oil was treated with the acid activated clay. Chlorophyll-a content of soybean oil is the most important quality parameter for the bleaching process. It has been found that adequate bleaching has occurred if this constituent can be reduced to the 0-19 ppb range (Taylor Dennis *et al.*, 1990). When this level of reduction has been attained, other undesired constituent, β-Carotene was usually found to be well below the determined limits. Otherwise, the presence of chlorophyll-a and β-Carotene in certain amounts lead to

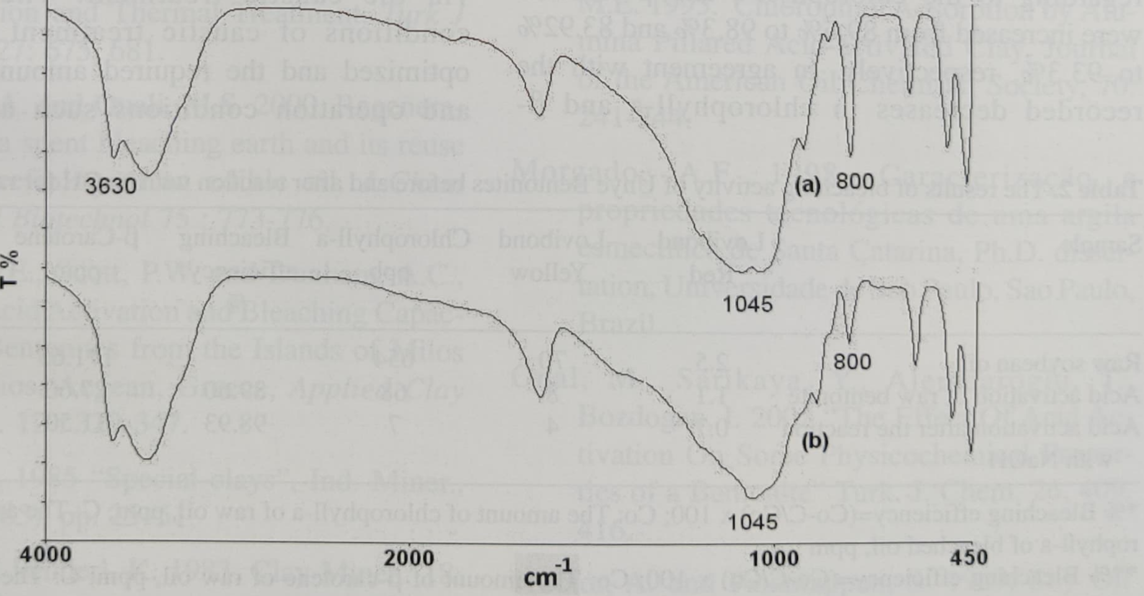


Figure 4. FT-IR results of the natural (a) and treated bentonite (b).

unpleasant discoloring of oil and deteriorates its end use quality.

Table 2 shows the results of bleaching tests. Bleaching activities of three clay samples, namely the raw sample, the sample after acid activation and the sample after caustic treatment plus acid activation were compared in terms of their bleaching efficiencies according to chlorophyll-a and β-carotene constituents. As seen in Table 2, raw soybean oil has a chlorophyll-a content of 654 ppb, β-carotene content of 171.65 ppm and lovibond red and yellow values of 2.5 and 70. When acid activated clay was used without removing its amorphous SiO_2 content, the quality of oil has been improved by 89.6% according to its chlorophyll-a content and 83.92% according to its β-carotene. In parallel to a decrease in chlorophyll-a and β-carotene content of oil, Lovibond Red and Yellow decreased from 2.5 to 1.1 and 70 to 8, respectively. For the bleaching clay as prepared by the proposed method in this study, highest bleaching efficiencies have been achieved. Upon SiO_2 removal and acid activation, chlorophyll-a content of bleached oil falls into the desired range of 0-19 ppb. A chlorophyll-a content of 7 ppb after bleaching was reached with the last sample. The Bleaching efficiencies regarding to the chlorophyll-a and β-carotene were increased from 89.6% to 98.3% and 83.92% to 93.3%, respectively. In agreement with the recorded decreases in chlorophyll-a and β-carotene components, Lovibond red and yellow values were also decreased considerably as seen in Table 2. Bleaching activity results showed that removal of amorphous SiO_2 from the content of clay before acid activation was very effective in improving the bleaching activities of smectite type clays.

Although removal of silica contaminants by solubilizing the silica at high pH and separating the solid montmorillonite clay in a more pure form was known in general, the novelty of the proposed method in this study comes from the enrichment of the raw bentonite clay with high amorphous SiO_2 and subsequent acid activation of it to obtain an efficient bleaching earth. The chemical enrichment process has been optimized to determine the required amount of caustic and operation conditions such as time and temperature. Finally, another advantage of the proposed method is the recovery of SiO_2 as sodium silicate solution when accordingly after-treated.

Conclusion

Bentonite clay with high amorphous SiO_2 content up to 50% has been enriched successfully via the caustic treatment. The operating conditions of caustic treatment have been optimized and the required amount of caustic and operation conditions such as time and

Table 2. The results of bleaching activity of Ünye Bentonites before and after reaction with NaOH for raw soybean oil

Sample	Lovibond Red	Lovibond Yellow	Chlorophyll-a ppb	Bleaching efficiency*. %	β-Carotene ppm	Bleaching efficiency**. %
Raw soybean oil	2.5	70	654		171.65	-
Acid activation of raw bentonite	1.1	8	68	89.60	27.60	83.92
Acid activation after the reaction with NaOH	0.7	4	7	98.93	11.50	93.30

*% Bleaching efficiency=(Co-C/Co) x 100; Co: The amount of chlorophyll-a of raw oil, ppm; C: The amount of chlorophyll-a of bleached oil, ppm

**% Bleaching efficiency=(Co-C/Co) x 100; Co: The amount of β-carotene of raw oil, ppm; C: The amount of β-carotene of bleached oil, ppm temperature were determined. It was found that 15% of caustic concentration was sufficient to remove most of the amorphous SiO_2 content of the clay at 80 °C with the treatment durations of more than 90 minutes. After the caustic treatment, the ratio of SiO_2 to Al_2O_3 of raw clay became closer to that of pure smectite type bentonite showing the success of the experimented enrichment method. As measured by a tintometer, highest bleaching efficiency has been achieved with the modified clay as prepared by the proposed method in comparison to that of the bentonite directly activated with acid. Upon SiO_2 removal and acid activation, chlorophyll-a content of bleached oil falled into the desired range of 0-19 ppb. In the study, removal of amorphous SiO_2 from the content of clay before acid activation was seen to improve the bleaching activity of smectite type clays considerably. Moreover, the recovery of SiO_2 as sodium silicate solution was another concern that might be important in the developed method affecting the process economy.

References

Alemdaroglu, T.,Akkus, G., Onal, M., and Sarikaya, Y.,2003. Investigation of the Surface Acidity of a Bentonite Modified by Acid Activation and Thermal Treatment. *Turk J Chem.* 27: 675, 681.

Boukerroui, A. and Ouali, M.S. 2000. Regeneration of a spent bleaching earth and its reuse in the refining of an edible oil. *J Chem Technol Biotechnol* 75 : 773-776.

Christidis, G.E., Scott, P.W. and Dunham, A.C., 1997. Acid Activation and Bleaching Capacity of Bentonites from the Islands of Milos and Chios, Aegean, Greece, *Applied Clay Science.* 12 : 329-347.

Clarke G.M., 1985 “Special clays”, Ind. Miner., 216 (1985), pp. 25–51.

Fahn, R. and Fenderl, K. 1983. Clay Miner., 18: 447-458.

Foletto, E.L., Volzone, C., Morgado, A.F. and Porto, L.M. 2000, Análise comparativa da ativação ácida de dois materiais argilosos com diferentes composições mineralógicas, VI Jornadas Argentinas de Tratamiento de Minerales, Salta, Argentina, 43-48.

Foletto, E.L., Volzone, C. and Porto, L.M. 2003, Performance of an Argentinian acid-activated bentonite in the bleaching of soybean oil. *Braz. J. Chem. Eng.* vol.20, 2.

Haihui Zheng; Guanglie LV, Patent WO2007090355 (A1), “A Method for Purification of Montmorillonit, Purified Montmorillonite and Composition Thereof”, (2007).

Kaviratna, H. Pinnavai, T., 1994. Acid hydrolysis of octahedral Mg2+ sites in 2:1 layered silicates: An assessment of edge attack and gallery access mechanisms. *Clays and Clay Miner.* 42: 717-723.

Low Philip, F., Roth Charles, B., Stucki Joseph W., Patent US 4411530(A), “System and method for rapid beneficiation of Bentonite clay”, (1983). mineralogico, *Anales de la Asociación Química Argentina*, 76 : 57-68.

Mokaya, R., Jones, W., Davies, M.E. and Whittle, M.E. 1993. Chlorophyll Adsorption by Alumina Pillared Acid-activated Clay, Journal of the American Oil Chemists’ Society, 70: 241-244.

Morgado, A.F. 1998. Caracterização e propriedades tecnológicas de uma argila esmectítica de Santa Catarina, Ph.D. dissertation, Universidade de Sao Paulo, Sao Paulo, Brazil.

Onal, M., Sarikaya, Y., Alemdaroglu, T., Bozdogan, I. 2002 “The Effect Of Acid Activation On Some Physicochemical Properties of a Bentonite” Turk. J. Chem. 26, 409, 416.

Proctor, A. and Palaniappan, S. 1989. Soy Oil Lutein Adsorption by Rice Hull Ash, Journal of the American Oil Chemists' Society, 66 (11) : 1618-1621.

Rhodes, C.N., Brown, D.R., 1992. Structural characterization and optimation of acid-treated montmorillonite and high-porosity silica support for ZnCl2 alkylation catalysts. *J. Chem. Faraday Trans.* 88 (15) : 2269-2274.

Rupert, J.P., Granquist, W.T., Pinnavai, T.J., 1987. Catalytic properties of clay minerals. In: Newman, A.C.D. (Ed.), Chemistry of Clays and Clay Minerals. Mineralogy Society, London, pp. 275-318.

Sarioglan S, Yüzer H., and Koral M., 2010 "Acid Activation And Bleaching Performance Of Turkish (Somas) Bentonite In The Crude Soybean Oil", *Particulate Sci. Tech.* 28, 4, 298.

Some Physicochemical Properties of a Bentonite" *Turk. J. Chem.* 26, 409, 416.

Srasra, E., Bergaya, F., van Damme, H. Arguib, N.K., 1989, Surface properties of an activated bentonite. Decolorization of rape-seed oil. *App. Clay Sci.* 4 : 411-421.

Taylor, D.R. and Jenkins, D.B. 1987. Acid-activated Clays, Society of Mining Engineering of the American Institute of Mechanical Engineers. *Transactions*. 282 : 1901-1910.

Taylor, D. R. and Ungermann, C. B. 1990. A process for making acid activated bleaching 260 earth. European patent EP0398636.

Tkac, I., Komadel, P. and Müller, D. 1994. Acid treated montmorillonites: A study by 29Si and 27Al MAS-NMR. *Clay Miner*. 29 : 11-19.

Volzone, C., López, J.M. and Pereira, E. 1986. Activación ácida de un material esmectítico, Revista Latinoamericana de Ingeniería Química y Química Aplicada. 16 : 205-215.

Volzone, C., Zalba, P.E. and Pereira, E. 1988. Activación ácida de esmectitas. II - Estudo mineralogico, Anales de la Asociación Química Argentina. 76 : 57-68.

Zaki, M.I., abdel-Khalik, M. and Habashy, G.M. 1986. Acid-Leaching and consequent pore structure and bleaching capacity modifications of Egyptian clays. *Colloids and Surfaces.* 17: 241-249.

(Received December 2017; Accepted March 2018)

Clay Research, Vol. 36, No. 2, pp. 55-63 (2017)

Characterization of some cracking clay soils of Rajmahal Trap in Sahibganj District, Jharkhand

***D. C. NAYAK, SILADITYA BANDYOPADHYAY, A.K. SAHOO, S.K. REZA AND S.K. SINGH[1]**

ICAR-National Bureau of Soil Survey and Land Use Planning, Regional Centre, Kolkata 700 091
[1]ICAR-National Bureau of Soil Survey and Land Use Planning, Nagpur 440 033

Abstract: *Two cracking clay soils of Rajmahal Trap viz., Jetkumarjari and Jirul Series were studied for their morphological, physical, chemical and mineralogical characteristics. The soils are very deep, somewhat poor to moderately well drained, silty clay in texture with cracking characteristics indicated by occurrence of pressure faces at sub surface horizons. They are weakly acidic (pH 6.0) to slightly alkaline (pH 7.6) in reaction, medium to high CEC (25.8-33.3 $(p^+)kg^{-1}$), high base saturation (74-86%) and low EC (0.07-0.36 dSm^{-1}). Clay mineralogical studies indicated the dominant presence of low charge di-octahedral smectitic minerals, followed by small amount mica and kaolinite and very small amount of vermiculite. Similarities in mineral assemblage indicated that both the soils are developed mainly from common source i.e., Rajmahal Trap. The presence of mica indicates their inheritance from granite-gneiss whereas vermiculite is the weathering product of biotite. Clay minerals other than vermiculite formed in humid climate of earlier geological period and are preserved in the present day dry climate along with vermiculite. Land resource managers need to take note of the unique mineralogical make up of the soils for advising the agricultural land use planning to maintain soil health. Cracking clay soils developed in smectite rich alluvium of the Rajmahal Trap are of both young and matured in nature as evidenced by their classification. The soils were classified under the fine, smectitic hyperthermic family of Vertic Endoaquepts and Typic Haplusterts.*

Key words : Chhotanagpur plateau, Rajmahal trap, Cracking clay soils, Mineral assemblages, Smectite, Vertisols.

Rajmahal Trap is one of the oldest geomorphic units of Eastern India, covering 10360 sq. km. area. Its formation is critically important in terms of stratiography, petrography and topographic configurations (Mandal, 2018). Rajmahal trap consists of basaltic parent rock of Lower Jurassic Age (Ball, 1877). Considering the study area as physiographic and geological hotspot of Eastern India (Roy Chowdhury, 1965), a research attempt was made to identify and characterize some cracking clay soils in the region. The Rajmahal trap occupying a significant part of Sahibganj district of Jharkhand comprises substantial amount of basaltic parent materials. Henceforth, formation of cracking clay soils is highly expected in this zone. Systematic information on the formation of black soils in Chhotanagpur plateau regions is scattered (Pal *et al.*, 2012a; Pal, 2017). Distribution of cracking clay soils in Jharkhand was reported in 34000 ha (0.11% of total geographical area of the state) only under sub-humid (dry and/ or moist) climate (Bhattacharyya *et al.*, 2009). Cracking clay soils have attracted global attention in research on their properties and management (Coulombe *et al.*, 1996; Mermut *et al.*, 1996). Although substantial information is available on Vertisols, it remains challenging to optimize their use and management (Coulombe *et al.*, 1996; Myers and Pathak, 2001). With the anticipation of existence of cracking clay soils in vast areas of the Rajmahal trap sub region of Chhotanagpur

---

***Corresponding Author Email:** dulalnayak@yahoo.co.in

Plateau, it is strongly felt to re-inventorize the soil resources for their detailed characterization and classification. Hence, the objectives of the present investigation are: (i) to characterize and classify some cracking clay soils of Rajmahal Trap and (ii) to study their mineralogical assemblage.

Materials and Methods

Study area

Borio block, located in Sahibganj district, representing a significant part of Rajmahal Trap landscape was selected as the study area, situated in the geographic extent between $24^0$57'18" to $25^0$16' 48" N latitude and $87^0$27'46" to $87^0$42' 27"E longitude, covering an area of 38590 ha. The Rajmahal trap occupying a significant part of the block represents basalt formations (Chatterjee, 1946; Prasad, 1965). The other parts comprise granite-gneissic complex with intrusion of alluviums of Quaternary deposits of both Holocene and Pleistocene periods (Prasad, 1971). The climate of the study area is hot, dry, sub humid under the agro-ecological sub region of 13.1 (Velayutham *et al.,* 1999). The annual rainfall is 1500 mm. The mean annual summer soil temperature is 32ºC and means annual winter soil temperature is 20ºC. The difference between the mean summer and mean winter soil temperature is more than 6°C. The soil temperature regime is "*hyperthermic*". The soil moisture regimes are "*aquic*" and "*ustic*" (Velayutham *et al.,* 1999).

Methodology

Two representative soil series *viz.,* Jirul and Jetkumarjari, occurring on older alluvial plains of the Rajmahal Trap were selected for the study. Morphological characteristics of soils were examined during the soil survey on 1: 10,000 scale (Soil Survey staff, 1975). The soils were analyzed for important physical and chemical parameters *viz.,* particle size distribution by international pipette method (Piper, 1966), pH (1: 2.5 water and 1N KCl) (Jackson, 1979), organic carbon (Walkley and Black, 1934) and cation exchange capacity by 1 N ammonium acetate at pH 7.0 (Sparks, 1996). Soils were classified in USDA taxonomy (Soil Survey Staff, 2014) by interpretation of morphological data in the field and analytical data in laboratory.

The clay fractions (2.0-0.2μm) were separated from soil samples after dispersion according to size segregation procedure of Jackson (1956). The clay samples were flocculated with KCl and $CaCl_2$. Ca saturated samples were further glycolated using ethylene glycol (EG). Potassium saturated clay samples were heated to 400ºC for 1 hour and again up to 500°C for 1 hour. Fine clay fraction (< 0.2 μm) was separated from the < 2 μm clay fractions by agitating a volume of water suspension of clay fraction upto 10 cm depth in Robinson pipette at a speed of 3000 rotation per minute (RPM) for 23 minutes and 4 seconds at a recorded room temperature of 30ºC using REMI heavy duty Centrifuge. The supernatant was separated as fine clay, which was dried and placed in slides. The powdered and Ca/ K saturated samples were put to X-ray diffractometry using Philips X-ray diffractometer with Cu-Kα radiation at a scanning speed of 1 °2θ/min. Clay minerals were identified according to the procedure outlined by Jackson (1956). Semi-quantitative estimation of minerals was made as per the procedure of Brown (1961).

Results and Discussions

Morphological characteristics of soils

The soils of Jetkumarjari series were very deep, somewhat poorly drained, dark yellowish brown (10YR3/4 M) in surface and dark brown (10 YR 3/3) to very dark brown (10 YR 3/3) in sub surface, silty clay in texture with sticky and plastic in consistence throughout the depth. The structure is sub angular blocky at sub surface (Table 1 and 2). The stress features in surface peds are often obscured, though they are visible at a depth below 75 cm from surface with irregular increase in clay content with depth. The sub surface horizons are designated as cambic (Bw), as there is no strong evidence of formation of slickensides. However, coefficient of linear extensibility (COLE) varying from 0.09 to 0.11 was enough to confirm the existence of Vertic intergrades of Inceptisols (Table 3). These soils are possibly in the verge of transition between Inceptisols to Vertisols. On the contrary, the soils of Jirul series have a completely varying sets of morphological characteristics with moderately well drained situation, dark brown (10 YR 3/3) in surface to very dark gray (10 YR 3/1) in sub surface, silty clay in texture throughout the depth, firm, very sticky and very plastic consistence with angular blocky structure in sub surface. The COLE values ranged from 0.09 to 0.13. Slickensides are clearly observed at sub surface horizons started below 45 cm and extended upto 150 cm. The sub surface horizons are designated as the Bss with clear evidence of the occurrence of pressure faces.

Physical and chemical characteristics of soils

The high clay content in the two soils (47-53%) is indicative of cracking characteristics, which could be due to the dominance of smectitic minerals in clay fraction of soils. The soils are slightly acidic (pH 6.0-6.5) in surface and neutral (pH 7.0) to slightly alkaline (pH 7.6) in sub surface. Both the soils have an electrical conductivity of less than 1.0 dSm^{-1} (ranging from 0.05-0.36 dSm^{-1}), indicating their non-saline character (Table 3). Organic carbon was high (0.78-1.22%) in surface with an irregular decrease with depth, which may be due to depositional history of the basaltic alluvium from the basalt rock. CEC of soils is generally high ranging from 25.8 to 34.1 cmol (p^{+}) kg^{-1} with high CEC/ Clay ratio (0.48-0.68), further indicating the dominance of smectitic minerals in clay fraction of soils (Smith, 1986). Similar findings were also been reported in cracking clay soils of USA (Hajek, 1985) and El Salvador (Yerima *et al.*, 1985). The high base saturation status (74-86%) of the soils may be attributed to the dominance of divalent bases in soil exchange complex,

Table 1. Site characteristics of the study area

Land form	Soil series	Lat. & Long.	Slope	Drainage	Micro features
Old alluvial plains of Rajmahal trap	Jetkumarjari	24° 59′ 5″ N 87° 31′ 21″ E	1-3%	Moderately well below 75 cm	Small cracks
	Jirul	25° 1′ 4.3″ N 87° 35′ 40.9″ E	0-1%	Somewhat poor	Pressure face below 45 cm

Table 2. Morphological characteristics of the soils

Soil series	Depth (cm)	Horizon	Colour	Texture	Structure	Consistence
Jetkumarjari	0-20	Ap	10YR 3/4 M	silty clay	Massive	Firm, sticky and plastic
	20-53	Bw1	10YR 2/1 M	silty clay	Sub angular blocky	Firm, sticky and plastic
	53-82	Bw2	10YR 2/2 M	silty clay	Sub angular blocky	Firm, sticky and plastic
	82-108	Bw3	10YR 3/3 M	silty clay	Sub angular blocky	Firm, sticky and plastic
	108-150	Bw4	10YR 4/4 M	silty clay	Sub angular blocky	Firm, sticky and plastic
Jirul	0-19	Ap	10YR 3/3 M	silty clay	Angular blocky	Firm, very sticky and very plastic
	19-45	BA	10YR 3/2 M	silty clay	Angular blocky	Firm, very sticky and very plastic
	45-89	Bss1	10YR 3/2 M	silty clay	Angular blocky	Firm, very sticky and very plastic
	89-120	Bss2	10YR 3/1 M	silty clay	Angular blocky	Firm, very sticky and very plastic
	120-150	Bss3	10YR 3/1 M	silty clay	Angular blocky	Firm, very sticky and very plastic

especially calcium ranging from 13.9 to 19.5 cmol (p$^+$) kg^{-1}. The $CaCO_3$ equivalence was low ranging from 2.3 to 2.5% in both the profiles. This indicates that these cracking clay soils comprise non-pedogenic calcium carbonates which occurred as alluvium materials in the soils.

Mineralogical studies of soils

The existence of Vertisols in the study area can be better clarified with the help of detailed mineralogical studies. The basic parent materials of the Rajmahal trap are essential for the formation of Vertisols. The parent materials from inheritance or weathering provide a large quantity of smectites (Murthy *et al.,* 1982). Soil Survey Staff (1999) stipulated the smectitic mineralogy of soils is associated with vertic properties when smectite exceeds 50% of the total mineral content in the less than 2 μm clay fraction. Later on, a qualitative smectite mineralogy class was proposed by the Soil Survey Staff (1999) for the soils that contain more smectite by weight than any other single clay mineral. X-ray diffractograms of Ca-saturated and Ca-EG treated fine clay (< 0.2 μm) samples of both Jetkumarjari and Jirul series showed strong reflections at 1.5 and 1.7 nm, respectively, indicating clear evidence of presence of smectitic minerals (Fig. 1-2). The fine clay smectite on K-saturation at 25^{0}C shifts to 1.1-1.2 nm peak area, indicating its low charge density (Pal *et al.* 2012a) and it is of di-octahedral nature as confirmed by Ray *et al.* (2006) for similar cracking clay soils (Vertisols) developed in West Bengal in the smectitic parent alluvium of the Rajmahal Trap. These smectites are fairly well crystalline and show higher order reflections but are little hydroxy-interlayered as evidenced from the tailing in the low angle side of 1.0 nm peak when K-saturated samples are heated to 550^{o}C (Fig. 1-2). Such hydroxy-interlayered smectites are formed at pH much below 7 maintained during their formation in humid climatic condition (Pal *et al.* 2012b). Thus their presence

Table 3. Physical and chemical characteristics of soils

Soil series	Depth (cm)	Sand	Silt	Clay	Fine clay/ total clay	pH (1: 2.5 H_2O)	E.C. (dSm^{-1})	O.C. (%)	CEC	Sum of bases	PBS (%)	CEC/ clay	$CaCO_3$ (%)	COLE
		———	%	———					—Cmol(p$^+$)kg^{-1}	—				
Jetkumarjari	0-20	2.6	43.9	53.5	0.52	6.0	0.09	1.22	25.8	19.1	74	0.48	2.5	0.11
	20-53	5.2	44.9	49.9	0.49	7.6	0.10	0.60	27.9	24.0	86	0.60	2.5	0.09
	53-82	5.6	44.2	50.2	0.49	7.5	0.07	0.58	28.7	24.7	86	0.57	2.3	0.11
	82-108	5.7	40.8	53.5	0.52	7.0	0.18	0.45	30.8	25.3	82	0.58	2.3	0.11
	108-150	5.1	47.6	47.3	0.46	7.0	0.36	0.43	31.8	26.1	82	0.67	2.3	0.09
Jirul	0-19	0.4	52.0	47.6	0.47	6.5	0.05	0.78	28.8	21.9	76	0.60	2.5	0.09
	19-45	0.8	50.6	48.6	0.48	7.2	0.09	0.55	31.8	26.7	84	0.65	2.3	0.13
	45-89	1.0	48.5	50.5	0.50	7.3	0.06	0.53	33.2	28.5	86	0.66	2.3	0.13
	89-120	1.3	48.1	50.6	0.50	7.2	0.07	0.49	33.3	28.3	85	0.66	2.5	0.13
	120-150	1.4	48.5	50.1	0.49	7.3	0.17	0.52	34.1	29.3	86	0.68	2.5	0.11

in soils of Jharkhand in dry sub-humid climate indicates their inheritance from alluvium of the Rajmahal Trap basalt. The reflection at 1.0 nm which resisted collapse even after heating up to 550°C indicates the presence of mica which is consisted of both muscovite and biotitic micas, confirmed by the more than unity of the 001/002 peak height of the basal reflections of mica at 1.0 nm for Jirul (ranging from of 2.5 to 2.7) and for Jetkumarjari series (ranging from 0.7 to 2.6) (Pal *et al.*, 2012a). The 1.0 nm peak of mica is broader and more asymmetrical towards low angles in the clay fractions. These characters indicate the replacement of interlayer K of mica and concomitant formation of vermiculite. The presence of small amount of vermiculite is not perceptible from the glycolated fine clay saturated with Ca-ions at 1.4nm peak area. But it is detected by the reinforcement of the 1.0 nm peak of mica when K-saturated samples are heated to 100°C and 300°C. Presence of small amount of vermiculite is very common in Vertisols of Peninsular India as the weathering product of biotite mica during dry period of Vertisol formation (Pal *et al.*, 2012a). The observed 0.7 nm peak is not of pure kaolinite but is of kaolin as evidenced by its broad peak which does not collapse upon heating to 550°C but reinforced 1.0 nm mica peak. This suggests that the 0.7 nm peak is an interstratified 0.7-1.4 nm minerals. The 1.4 nm mineral is smectite which is hydroxy-interlayered because 1.0 nm peak after heating to 550°C shows tailing towards the low angle side of 1.0 nm peak (Fig.1-2). Semi-quantitative estimates of the clay minerals in the fine clay fractions show very little variations among the two soils. Comparing mineral assemblage of the two soil series, it is clear that smectite is the most abundant mineral (66.4-76.8%) followed by mica (13.1-17.8%) and kaolin (9.8-15.8%) and traces of vermiculite (Table 4). It was noted that relative abundance of smectite is little more in soils of Jirul series as compared to Jetkumarjari series. However, relative abundance of kaolinite

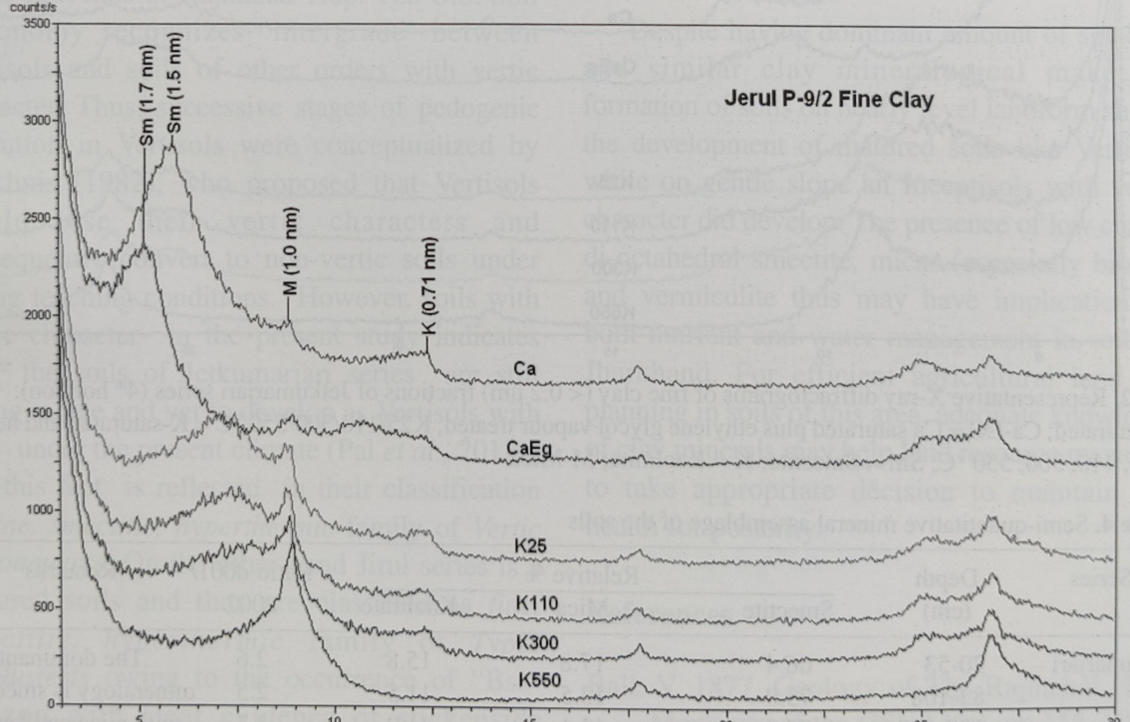


Fig. 1. Representative X-ray diffractograms of fine clay (< 0.2 μm) fractions of Jirul series (4th horizon): Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K25/110/300/550 °C = K-saturated and heated to 25, 110, 300, 550 °C; Sm = Smectite; K = Kaolinite; M-Mica.

is also little more in Jetkumarjari series as compared to Jirul series. Huge amount of fine clay smectites in both the soils clearly indicates that clays are developed from smectite rich alluvial parent material derived from the Rajmahal traps. Presence of kaolin indicates the formation of smectite originated at the source of the Rajmahal trap during previous humid climate when smectite transformed to 0.7-1.4 nm (K-Sm) minerals and this climate did not persists for long as evidenced from the preservation of huge amount of smectite in the soils during the present dry sub-humid climate. Basalt does not contain mica and thus its presence is due to the addition from granite gneiss system of the complex geological formation of the Chhotanagpur plateau region. The presence of hydroxy-interlayered smectite, mica, vermiculite, and kaolin (K-Sm) in cracking clay soils of Jharkhand is almost similar to Vertisols developed in the alluvium of the Deccan basalt areas of peninsular (Bhattacharyya *et al.*, 1993, 1997; Pal

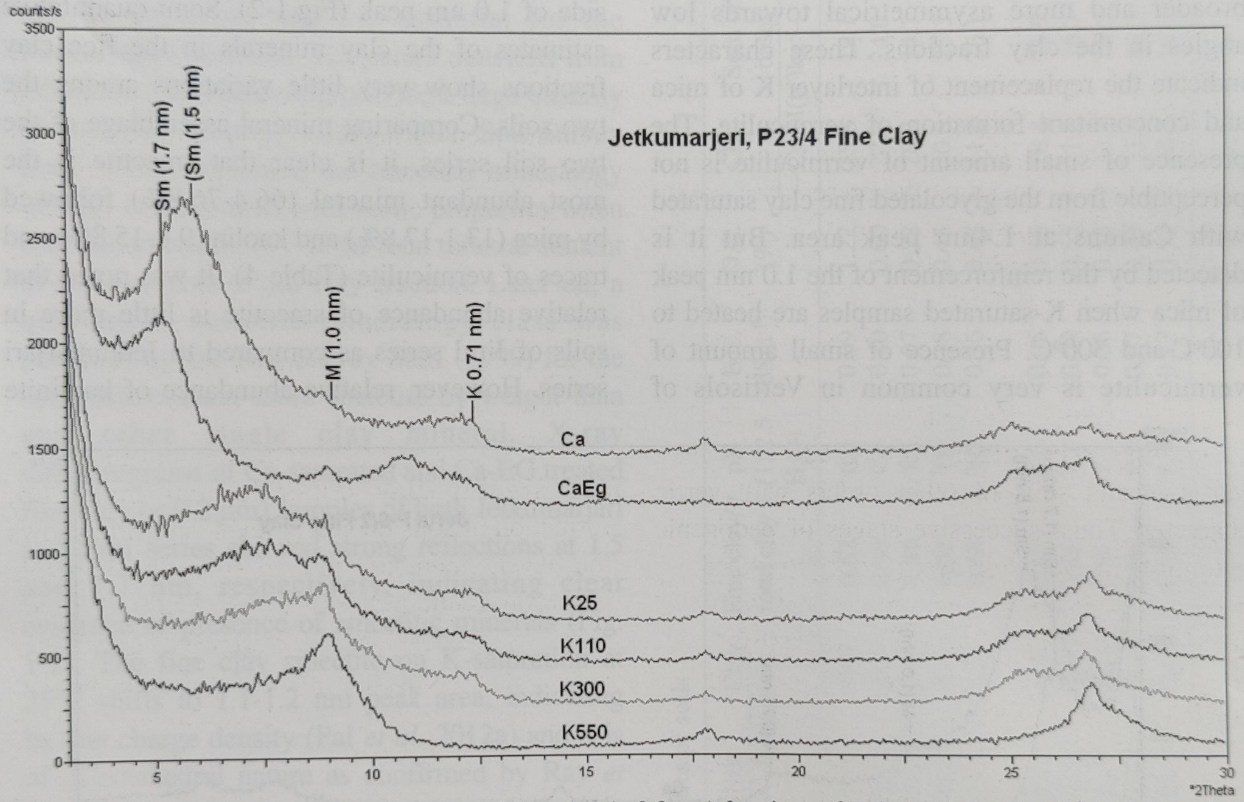


Fig. 2. Representative X-ray diffractograms of fine clay (< 0.2 μm) fractions of Jetkumarjari series (4th horizon): Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K25/110/300/550 °C = K-saturated and heated to 25, 110, 300, 550 °C; Sm = Smectite; K = Kaolinite; M-Mica.

Table 4. Semi-quantitative mineral assemblage of the soils

Soil Series	Depth (cm)	Relative %			Ratio d001/ d002	Remarks
		Smectite	Mica	Kaolinite		
Jetkumarjari	20-53	66.4	17.8	15.8	2.6	The dominant mineralogy is smectitic with mica and kaolin
	82-108	75.0	13.5	11.5	2.5	
	108-150	75.9	13.1	11.0	2.7	
Jirul	19-45	71.6	15.8	12.6	2.6	The dominant mineralogy is smectitic with mica and kaolin
	89-120	73.2	15.9	10.9	2.6	
	120-150	76.8	13.4	9.8	2.7	

et al., 1989, 2012a) and extra-peninsular regions (Ray *et al.*, 2006).

Pedogenic considerations

The pedogenic consideration of these two soils may be highlighted based on mineralogical investigations. The low charge di-octahedral smectitic parent materials derived from the weathering Rajmahal Trap basalt in the upper reaches are deposited as alluvium during the previous geological period as evidenced from the presence of weathering product of smectite as kaolin. However, weathering of smectite to kaolin did not continue for a long geological time because of the presence of small amount of kaolin (Herbillon *et al.,* 1981). Had such weathering continued for a long time the presence of kaolin would have been in dominant amount as reported by Bhattacharyya *et al.,* (1993, 1997) for soils of the humid Western Ghat areas. The similarity in mineralogy in both the soils indicates their preservation in the present dry sub-humid climate in the foot hills of Rajmahal Trap. The U.S. Soil Taxonomy recognizes 'intergrade' between Vertisols and soils of other orders with vertic character. Thus, successive stages of pedogenic evolution in Vertisols were conceptualized by Blokhuis (1982), who proposed that Vertisols would lose their vertic characters and subsequently convert to non-vertic soils under strong leaching conditions. However, soils with vertic character in the present study indicates that the soils of Jetkumarjari series are still young in age and yet to develop as Vertisols with time under the present climate (Pal *et al.,* 2012a) and this fact is reflected in their classification as *fine, smectitic, hyperthermic* family of *Vertic Endoaquepts*, On the other hand Jirul series is a matured soils and thus are classified as *fine, smectitic, hyperthermic* family of *Typic Haplusterts* owing to the occurrence of "Bss" horizon with clear evidence of slickenside formations and bearing more prominent cracking characteristics as compared to Jetkumarjari series. Jirul soils are formed in nearly level landscape of older alluvial plains, whereas, Jetkumarjari soils are formed in very gentle slope. Stability in level landforms appears to have possible effect in the development of matured Jirul soils than in Jetkumarjari in gentle slope.

Conclusions

Mineralogical studies of both the soils helped in developing a comprehensive insight of their genesis in micro-topographic variations in Rajmahal Trap. Clay minerals (hydroxy-interlayered smectite, kaolin) present in Jharkhand soils in the alluvium of Rajmahal Trap indicate their formation in humid climate of the geological past and are preserved in the present dry sub-humid climate. Mica is added from non-basaltic rocks present in the study area whereas the very small amount of vermiculite is the weathering product of biotite during the post depositional period of soil formation under the present climate.

Despite having dominant amount of smectite and similar clay mineralogical make up, formation of soils on nearly level landform shows the development of matured soils like Vertisols while on gentle slope an Inceptisols with vertic character did develop. The presence of low charge di-octahedral smectite, micas (especially biotite) and vermiculite thus may have implications in both nutrient and water management in soils of Jharkhand. For efficient agricultural land use planning in soils of this area, adequate knowledge of clay minerals may help land resource managers to take appropriate decision to maintain soil health for posterity.

References

Ball, V. 1877. Geology of The Rajmahal Hills. Memories of the GSI, 13(ii), pp 155-248.

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1993. Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and Vertisols) soils on Deccan Basalt in the Western Ghats, India. *Journal of Soil Science,* **44**:159–171.

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1997. On kaolinitic and mixed mineralogy classes of shrink-swell soils. *Australian Journal of Soil Research,* **35**:1245–1252.

Bhattacharyya, T., Ray, S.K., Pal, D.K.,and Chandran, P. 2009. Mineralogy class of calcareous zeolitised Vertisols. *Clay Research,* **28**:73–82.

Blokhuis, A.A. 1982. Morphology and genesis of Vertisols. In: Vertisols and rice soils in the tropics. Transactions 12th international congress of soil science, New Delhi, pp 23–47.

Brown, G. 1961. 'The X-ray Identification and Crystal Structure of Clay Minerals', (Mineralogical Society, London).

Chatterjee, S.C. 1946. Physiographic Evolution of Chhotanagpur, *Calcutta Geographic Review.,* Vol. VII, No.3&4.

Coulombe, C.E., Wilding, L.P.,and Dixon, J.B. 1996. Overview of Vertisols: characteristics and impacts on society. In: Sparks DL (ed) *Adv. Agron.,* **57**: 289–375.Academic Press, New York.

Hajek, B.F. 1985. Mineralogy of Aridisols and Vertisols. Proceedings 5th international soil classication. Soil Survey Administration, Khartoum, Sudan, pp 221–230.

Herbillon, A.J., Frankert, A. and Vielyoyte, L. 1981. An occurrence of interstratified kaolinite-smectite minerals in a red-black soil toposequence. *Clay Mineralogy,* **16**: 195·201.

Jackson, M. L. 1979. 'Soil Chemical Analysis - Advance Course'. (University of Wisconsin, Madison), pp 27-95.

Jackson, M.L. 1956. Soil Chemical Analysis - Advanced Course; University of Wisconsin, Madison, USA.

Mandal, P.K. 2018. Geological Study of Rajmahal Trap Area and Its Resource Base: A Regional Perspective. *IOSR Journal of Applied Geology and Geophysics (IOSR-JAGG),* **6** : 23-27.

Mermut, A.R., Padmanabham, E., Eswaran, H. and Dasog, G.S. 1996. Pedogenesis. In:Ahmad, N, Mermut, A.R. (eds).Vertisols and technologies for their management. Elsevier, Amsterdam, pp 43–61.

Murthy, R.S., Bhattacharjee, J.C., Landey, R.J. and Pofali, R.M. 1982. Distribution, characteristics and classication of Vertisols. In: Vertisols and rice soils of the tropics, Symposia paper II, 12th international congress of soil science, New Delhi. Indian Society of Soil Science, pp 3–22.

Myers, R.J.K. and Pathak, P. 2001. Indian vertisols: ICRISAT's research impact —past, present and future. In: Syers, J.K., Penning de Vries, F.T., Nyamudeza, P. (Eds.), The Sustainable Management of Vertisols. CAB International Publishing, Wallingford, pp. 203–219.

Pal, D.K., Deshpande, S.B., Venugopal, K.R., and Kalbande, A.R. 1989. Formation of di- and trioctahedral smectite as an evidence for paleoclimatic changes in southern and central Peninsular India. *Geoderma*, **45**:175–184.

Pal, D.K., Wani S.P., and Sahrawat, K.L. 2012a. Vertisols of tropical Indian environments: Pedology and Edaphology. *Geoderma,* 189–**190**: 28–49.

Pal, D.K., Bhattacharyya, T., Sinha, R., Srivastava, P., Dasgupta, A.S., Chandran, P., Ray, S.K., and Nimje, A. 2012b. Clay minerals record from late quaternary drill cores of the Ganga plains and their implications for provenance and climate change in the Himalayan Foreland. *Palaeogeography Palaeoclimatology Palaeoecology,* **356–357**: 27–37.

Pal, D.K. 2017. Cracking Clay Soils (Vertisols): Pedology, Mineralogy and Taxonomy. In: Chapter II of *A Treatise of Indian and Tropical Soils.* Springer International Publishing AG 2017. (DOI 10.1007/978-3-319-49439-5_2), pp 9-35.

Piper, C.S. 1966. Soil and Plant Analysis. Hans Publisher, Bombay, India.

Prasad, N. 1965. The Physical Landscape of Chotanagpur: A Study in Regional Physiography, Geog. Outlook, Vol. IV, Ranchi.

Prasad, N. 1971. Geomorphology in Chhotanagpur, Geography of Chhotanagpur (Bihar), Dept. of Geography, Ranchi University.

Ray Chowdhury, P.E. 1965. Bihar District Gazetteers Santahal Pargana. Secretariat Press, Patna, Bihar. P 7-9 and 36.

Roy, S.K., Bhattacharyya, T., Chandran, P., Sahoo, A.K., Sarkar, D., Durge, S.L., Raja, P., Maurya, U.K. and Pal, D.K. 2006. On the formation of cracking clay soils (Vertisols) in West Bengal. *Clay Research*, **25:** 141-152.

Smith, G.D. 1986. *The Guy Smith Interview:* Rationale for concepts in Soil Taxonomy. *SMSS* Technical Monograph No. 11, SMSS, SCS, USDA.

Soil Survey Staff. 1975. Soil taxonomy: a basic system of soil classication for making and interpreting soil surveys. Agriculture hand book no. 436, Soil Conservation Service, US Dept. of Agriculture.

Soil Survey Staff .1999. Soil taxonomy: a basic system of soil classication for making and interpreting soil surveys, USDA-SCS agricultural handbook no 436, 2nd Edn. U.S. Govt, Printing Office, Washington, DC.

Soil Survey Staff. 2014. *Keys to soil Taxonomy*, 12th Edition. NRCS, USDA, Washington DC.

Sparks, D.L. 1996. In Methods of Soil Analysis, Part-III: Chemical Methods, SSSA Book Series No. 5, Madison, Wisconsin.

Velayutham, M., Mandal, D.K., Mandal, C. and Sehgal, J.L. 1999. Agro-ecological Sub Regions of India for Planning and Development, NBSS Publ. 35, ICAR-NBSS & LUP, Nagpur, Maharashtra.

Walkley, A. and Black, I. A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method, *Soil Science*, **37** : 29-38.

Yerima, B.P.K., Calhoun, F.G., Senkayi, A.L., and Dixon, J.B. 1985. Occurrence of interstratied kaolinite - smectite in El Salvador Vertisols. *Soil Science Society of American Journal,* **49**: 462-466.

(Received June 2018; Accepted August 2018)

Clay Research, Vol. 36, No. 2, pp. 64-76 (2017)

X-ray Derived Crystallite Size of Mica Particles in Genetically Different Soil profiles of India in Relation to Potassium Release

THANGA PANDIAN AND SAMAR CHANDRA DATTA

Division of Soil Science & Agricultural Chemistry , IARI

Abstract–*Profile soil samples from an Alfisol, a Vertisol and an Entisols were collected and fractionated into coarse clay(0.2-2.0 µm) and fine clay (< 0.2 µm) fractions. X-ray diffractogram of each sample was deconvoluted and curve fitted to get full width at half maximum (FWHM) of corresponding mica peak which were transformed to crystallite size. The crystallites of micaceous minerals were found to be largest in coarse clay fractions of Entisols followed by Alfisols and Vertisols. In almost all the profiles of Alfisol, Vertisols and Entisols, the crystallite size of micaceous minerals was found to increase along the depth of the profile. Crystallite size was found to be related to release of non exchangeable K from soil by oxalic acid extraction and to that released by intensive Sudan grass cropping .*

Introduction

Crystallographically, two factors, crystallite size and lattice strain or disorder, largely determine the profile of a diffraction peak from a polycrystalline, homogeneous phase (Klug and Alexander, 1974). Peak broadening measured by the full width at half maximum intensity (FWHM) which is equivalent to integral breadth (area of the peak divided by maximum intensity) is largely contributed by (a) instrumental effects, (b) crystallite size i.e., the coherent X-ray scattering domains) and (c) lattice strain, disorder or imperfections. All these three sources of broadening are folded or convoluted together and results the observed peak width (FWHM). When broadening occurs only due to smaller crystallite size, the profile shape function follows Lorentzian (L) equation and broadening due to smaller crystallite size β_{size} obtained as :

$$\beta_{size} = B - b$$

where,

B is the observed peak width in the sample b is instrumental broadening which is taken as the observed peak width in the reference sample which should be coarse (powdered) and well crystalline. The crystallite size (Nd) is obtained from the well known Scherrer equation as follows:

$$Nd = \frac{k\lambda}{\beta\cos\theta}$$

where K is a constant (0.9), λ is the X ray wavelength (1.54184 Å for CuKα), d is the inter planar spacing for a given diffraction peak (10 Å for mica or illite) θ is the Bragg diffraction angle (in radians) and N is the effective average number of 10 Å layer in a crystallite (i.e. the coherent X-ray scattering domains).

On the other hand , when broadening occurs only due to strain in the crysrtal the profile shape function follows Gaussian equation and broadening due to strain (β_{strain}) is obtained by

$$\beta_{strain} = (B)^2 - (b)^2$$

The amount of strain in the crystallite is being calculated from bstrain using the following relationship :

$$\text{Strain} = \beta_{strain} / 57.3 \ (2 \tan \theta)$$

***Corresponding Author Email :** samar1953@yahoo.com

where,

θ = Bragg angle

However, since the effective (after eliminating instrumental broadening) total peak broadening has been the result of coherent X ray scattering by the coherent domain of crystallite, this can be used as a measure of particle crystallinity. In the present investigation, instead of using FWHM as it is , it has been converted to equivalent crystallite size by Scherrer equation and has been used as a measure of X-ray coherent domain of mica particles or crystallinity. The more the size of crystallites the more is the crystallinity.

Mica and micaceous minerals are major source of potassium in soils. Although these are rich in potassium, but it is not always true that mica with high potassium content will release potassium with high rate. Potassium release rate depends on nature of mica particles, e.g., dioctahedral or trioctahedral and its crystallinity or crystallite size.

Deconvolution of XRD peaks and the least square method of curve fitting through parameter optimization have been attempted to determine broadening caused by particle size and crystal strain in micaceous minerals of soils varying in clay mineralogy. By adopting above technique the micaceous minerals in the Ustochrept was characterised as coarser and more crystalline in nature than the vertic Ustochrept and Typic Haplustalf (Datta, 1996).

There are very little work reported on the nature of micaceous particles, such as crystallite size in genetically different Indian soils, such as black soil(Vertisol), red soil(Alfisol) and recent alluvial soil (Entisol). Hence the present investigation is aimed at studying crystallinity in terms of crystallite sizes of micaceous particles in soils at different depths of different soils and their effect on potassium release to crops or towards organic acid extractant.

Materials and Methods

Experimental soils

Profile soil samples were collected from nine different identified locations representing three major soil orders of India viz., Alfisols from Rannchi cultivated field(A1), Ranchi uncultivated field(A2), Coimbatore (A3); Vertisols from Nimone(V1), Nirmal Pimpri (V2) and Coimbatore(V3) and Entisols from Pandunagar (E1), Hisar(E2), Chhattarpur Delhi(E3). The details of the location and taxonomy of soil samples, physico-chemical properties of soil samples, various forms of soil potassium viz., water soluble K, exchangeable K, non-exchangeable K, mica K and total K, clay mineralogical compositions of the soil samples have been described in an earlier publication (Thanga Pandian and Datta 2009)

Different mechanical size fractions of soil such as sand (>20 µm), silt (2-20 µm), coarse clay (0.2-2.0 µm) and fine clay (< 0.2 µm) were separated and prepared for X-ray diffraction analysis as per the methodology proposed by Jackson (1956).

X-ray diffraction analysis

X-ray diffraction analysis of soil fractions was done following the standard methodology of Jackson (1956). For each clay sample four treatments are given, viz., a) Mg-saturated – air dried, b) K-saturated- air dried, c) Mg-saturated and glycerol solvated and d) K-saturated and heated to 550^0C for identification and semiquantification and described in Thangapandian and Datta (2009)

X-ray diffraction profile of coarse clay and fine clay were deconvoluted using APD (Philips Automated Powder Diffractometry) software which deconvolutes the X-ray profile into component peaks, their position, intensity, area and FWHM (Full width at half maximum), so that the overlapping portion of two or three peaks get resolved.

The FWHM of 10Å peak of mica were recorded for each clay sample and the average crystallite size of each sample was calculated using Scherrer equation after subtracting the instrumental broadening. For instrumental broadening determination silt size mica was scanned by X-ray and the FWHM of the 10Å peak were noted which was found to be 0.2 °2θ.

Potassium release on oxalic acid extraction

A continuous extractant flow system by adjusting the hydraulic head of delivering end was devised, where the extractant flows drop by drop due to hydraulic pressure difference. 20 grams of surface (S1) and subsurface (S2) profile samples were taken into a glass funnel fitted with Whatman No. 42 filter paper. The soil samples were extracted by continuous flow of 100 ppm oxalic acid pH adjusted to 5.0. The flow volume of oxalic acid was maintained at 35-40 ml per hour by placing a screw type stop cork at the delivering end of the rubber tube. The extract was collected in a 500 ml conical flask.

The amount of potassium released was estimated at intervals of 6, 12, 24, 48, 72, 96, 120, 144, 168, 192, 216 and 240 hours by flame photometer. The cumulative K released was plotted against time and the data points were fitted at different kinetic equations.

The cumulative K release data obtained in both oxalic acid with respect to time were fitted in the following four kinetic models,

First order : $ln\,(K0 - Kt) = a - bt$

Parabolic diffusion : $Kt/K0 = a + bt1/2$

Elovich equation : $Kt = a + b\,ln\,t$

Power function : $ln\,Kt = ln\,a + b\,ln\,t$

where,

Kt is the cumulative K released at time t,

Ko is the maximum K released,

a and b are constants,

t is the time.

The determination coefficients (r2 values) and the values of the constants a and b for the above four equations were tabulated.

Non-exchangeable K uptake by Sudan grass

The surface (S1) and sub surface (S2) soil samples of nine profiles were cropped in triplicate with potassium exhaustive cropping with Sudan grass (*Sorghum sudanensis*), as par the methodology given by Arnold and Close (1961) and Talibudeen and Dey (1968). The rationale of choosing sudan grass as test crop is attributed to its higher potassium requirement with enhanced root density and root biomass production. The seeds of sudan grass variety SSG-1006 were used in the potassium experiment.

600 grams of air dried, 2 mm sieve passed surface(S1) and subsurface(S2) soil samples were mixed with 400 g of acid washed, potassium free quartz sand (2-4 mm diameter) for potting. 3-4 sudan grass seeds were sown per hill in such a way that each pot having three hills uniformly. No external dose of potassium was applied either as basal or in irrigation water. The plants were fertilized periodically with potassium free modified Hogland solution. In order to avoid leaching of potassium, the pots were irrigated to field capacity by deionising irrigation water.

The root and leaf biomass were harvested at every four weeks interval and the pots were resown with Sudan grass immediately after every harvest. The soils were exhausted continuously for six months or until the plants show visual potassium deficiency symptoms combined with low biomass production. The dry matter production per pot was recorded after drying the biomass at 70 °C and the plant samples were analysed for total potassium uptake from the soil.

The non-exchangeable K released from soils were determined from the following equation :

Release of non-exchangeable K = (Total K uptake by grass + K in roots and stubbles) – (Fall in exchangeable K in soil).

Results and Discussions

Deconvoluted X-ray profiles

Fig 1, 2 and 3 show the deconvoluted X-ray profiles of fine clay fractions of Alfisol A2, Vertisol, V2 and Entisol E2, respectively. It is clear from the figures that deconvolution helped in finding exact shape of mica peak(10 Å) from the overall envelop and subsequently determining HWFM. Before deconvolution, the peak which appeared to be a single peak, resolved in more than one peaks after deconvolution which helped in proper seiquantification of component minerals

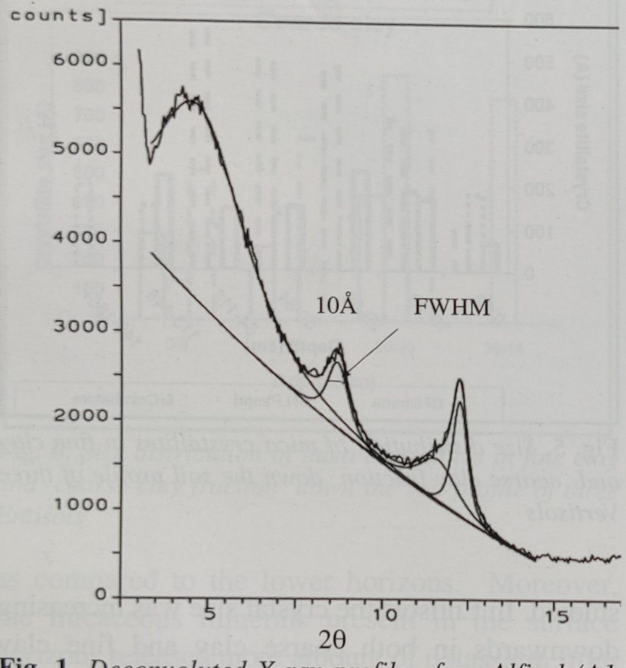


Fig. 1. *Deconvoluted X-ray profile of an Alfisol (A1, Ranchi uncultivated) fine clay from 3 to 15°2θ*

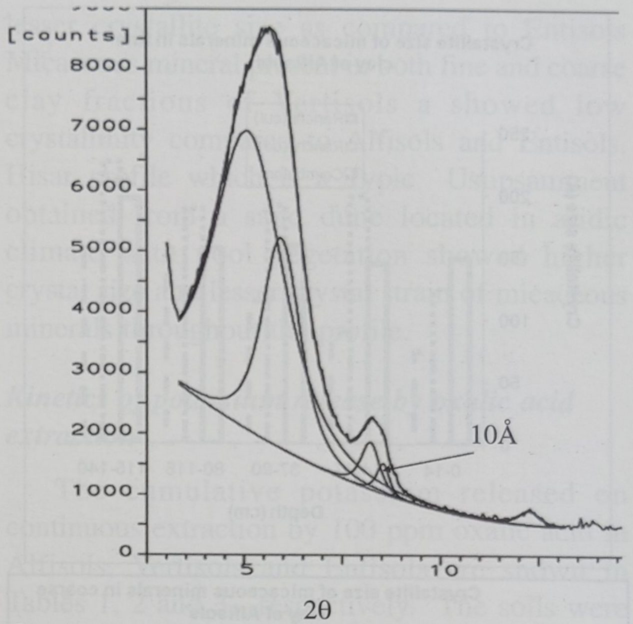


Fig. 2. *Deconvoluted X-ray profile of a Vertisol (V2, Nirmal Pimpri) fine clay from 3 to 15°2θ*

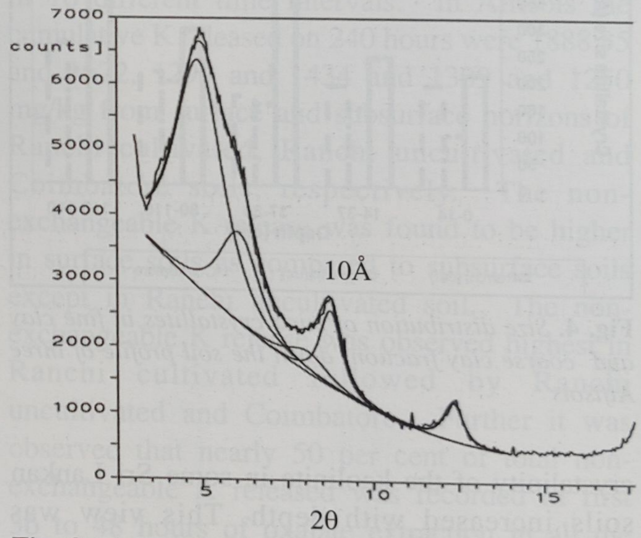


Fig. 3. *Deconvoluted X-ray profile of an Entisol (E1, Pandunagar) fine clay from 3 to 15°2θ*

Crystallite size of micaceous minerals

Crystallite size (Å) of micaceous minerals calculated from FWHM of mica peak in different clay size fractions of Alfisols, Vertisols and Entisols have been shown in Fig. 4, 5 and 6, respectively. Crystallite size of micaceous minerals in fine clay of Alfisols ranged from as small as 74 Ã in Coimbatore profile to 225 Å in lower horizon of Ranchi uncultivated profile. Similarly the crystallite size of coarse clay fractions were of 101 Å in the surface hrozion of Ranchi uncultivated to 375 Å of Ranchi cultivated profile. In general the crystallite size of the micaceous minerals increased with depth. Especially, the crystallite size of lower most horizons were higher as compared to the surface horizons. This trend was found to be common in both coarse clay and fine clay fractions. De Alwiz and Pluthv (1976) showed that the

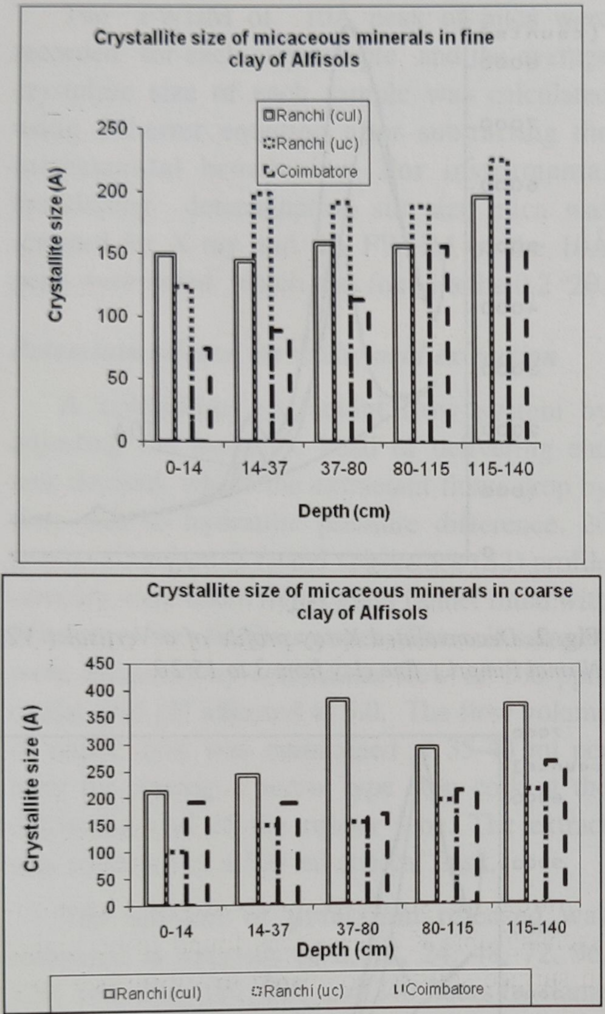


Fig. 4. *Size distribution of mica crystallites in fine clay and coarse clay fraction down the soil profile of three Alfisols*

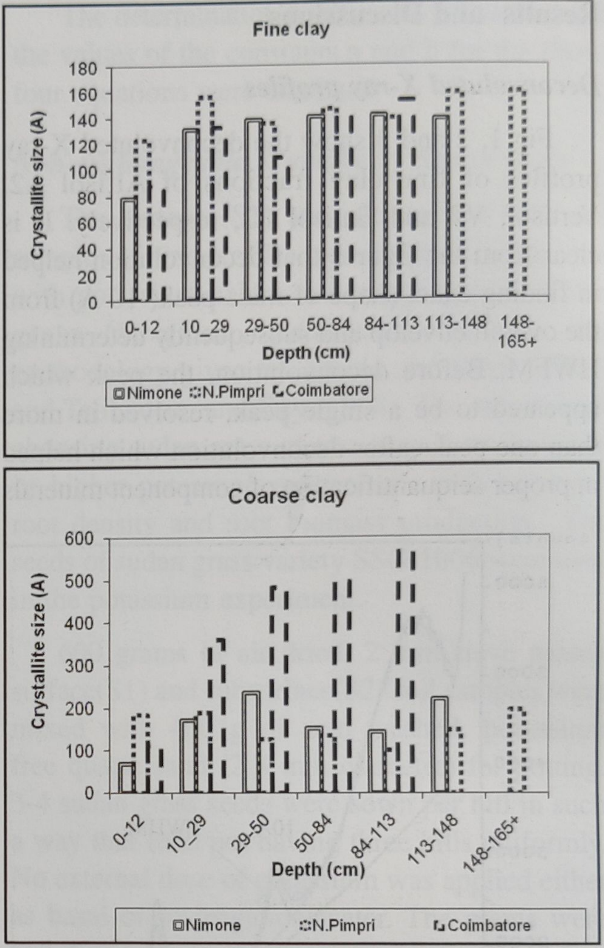


Fig. 5. *Size distribution of mica crystallites in fine clay and coarse clay fraction down the soil profile of three Vertisols*

crystalinity of the kaolinite in some Sri Lankan soils increased with depth. This view was supported by Hughes and Brown (1979) that the crystallinity index of kaolinitic minerals increasing downwards through the profile.

The crystallite size of micaceous minerals in profiles of Vertisols were comparitively smaller than the Alfisols. The size of micaceous minerals in fine clay and coarse clay fractions of Vertisols ranged from 78 to 156 Å and 69 to 564 Å respectively. Micaceous minerals present in the coarse clay fractions of Coimbatore soils showed the greatest sized crystals among the black soils studied. In Entisols the crystal size was increasing downwards in both coarse clay and fine clay fractions. The coarse clay fraction of the Chattarpur profile showed crystals with a size as big as 857 Å. The surface soils are having low crystallite size in general. The crystallite size of micaceous minerals increased with depth. Entisols contained highest amount of micaceous minerals in their profiles followed by Alfisols and Vertisols. Crystallite size of the micaceous minerals was found to depend on the stage of weathering and the rate of potassium released from the mineral edges and surfaces.

In general the impact of pedogenic factors on surface horizons of a profile is predominant

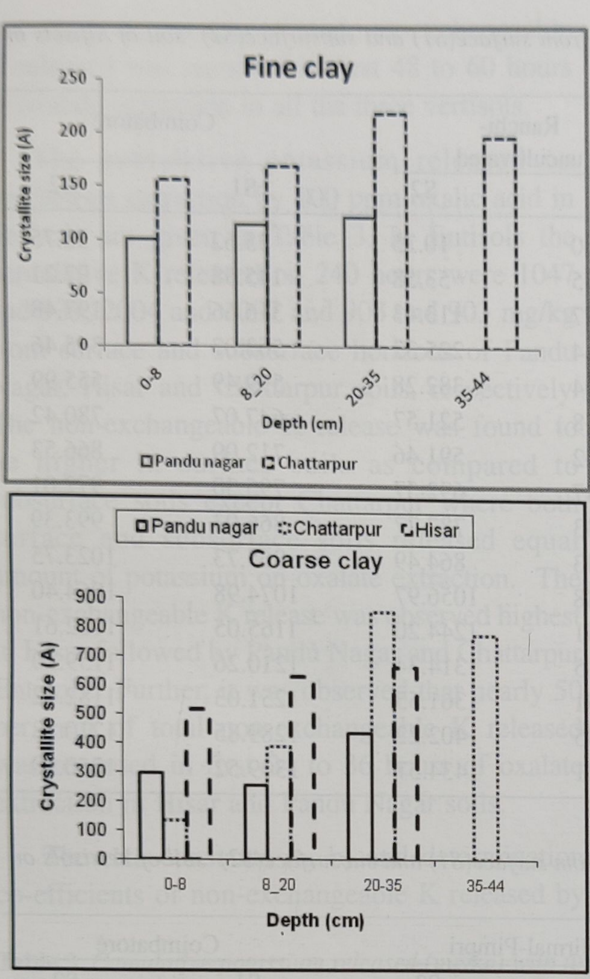


Fig. 6. *Size distribution of mica crystallites in fine clay and coarse clay fraction down the soil profile of three Entisols*

as compared to the lower horizons. Moreover, the micaceous minerals present in the surface horizons released more amount of potassium from the mineral edges and interlayers towards soil solution and plant uptake. The crystallite size of micaceous minerals in coarse clay fractions reached their maximum, in Chattarpur (857 Å) and Hisar (667 Å). The reason behind this observation is that the Chattarpur and Hisar profiles were characterised as Typic Ustorthent and Typic Ustipsamment respectively. These soils showed poor horizon development and the micaceous minerals present in the lower horizons are less afftected by forces of weathering. Conversely, the micaceous minerals present in the coarse fractions of Ranchi profiles showed lesser crystallite size as compared to Entisols Micaceous mineral present in both fine and coarse clay fractions of Vertisols a showed low crystallinity compared to Alfisols and Entisols. Hisar profile which is a Typic Ustipsamment obtained from a sand dune located in aridic climate with pool vegetation showed higher crystal size and lesser crystal strain of micaceous minerals throughout the profile.

Kinetics of potassium release by oxalic acid extraction

The cumulative potassium released on continuous extraction by 100 ppm oxalic acid in Alfisols, Vertisols and Entisols are shown in Tables 1, 2 and 3, respectively. The soils were extracted continuously by 100 ppm oxalic acid for 240 hours and the K released was observed in 16 different time intervals. In Alfisols the cumulative K released on 240 hours were 1888.35 and 1672, 1299 and 1434 and 1309 and 1250 mg/kg from surface and subsurface horizons of Ranchi cultivated, Ranchi uncultivated and Coimbatore soils, respectively. The non-exchangeable K release was found to be higher in surface soils as compared to subsurface soils except in Ranchi uncultivated soil. The non-exchangeable K release was observed highest in Ranchi cultivated followed by Ranchi uncultivated and Coimbatore. Further it was observed that nearly 50 per cent of total non-exchangeable K released was recorded in first 36 to 48 hours of oxalate extraction in all the three Alfisols.

K released on 240 hours were 1107 and 968, 723 and 1170 and 1559 and 978 mg/kg from surface and subsurface horizons of Nimone, Nirmal-Pimpri and Coimbatore soils, respectively (Table 2). The non-exchangeable K release was found to be higher in surface soils as compared to subsurface soils except in Nirmal-Pimpri soil. The non-exchangeable K release was observed highest in Coimbatore followed by Nirmal-Pimpri and Nimone vertisols. Further, it was observed

Table 1. *Cumulative potassium released (mg/kg) with time from surface(S1) and subsurface(S2) soil of Alfisols on continuous extraction by oxalic acid*

Time (t) (hrs)	Ranchi-cultivated		Ranchi-uncultivated		Coimbatore	
	S1	S2	S1	S2	S1	S2
2	22.33	34.20	25.50	10.25	35.62	32.75
6	168.05	159.00	124.25	53.58	145.58	97.21
12	432.60	354.21	281.77	113.43	316.66	197.48
24	838.34	666.83	530.64	225.32	563.07	345.46
36	950.93	877.83	745.94	382.28	599.49	555.99
48	1069.57	1006.45	881.58	521.57	647.07	780.42
60	1212.06	1053.70	917.02	591.46	712.09	866.53
72	1361.67	1116.96	958.47	692.57	795.30	972.01
84	1441.37	1241.08	1002.33	787.77	866.03	993.39
96	1534.09	1384.77	1052.43	864.49	965.73	1023.75
120	1626.34	1470.32	1151.88	1056.97	1074.98	1064.40
144	1735.01	1549.67	1164.51	1244.20	1165.05	1122.61
168	1792.82	1574.96	1222.15	1314.34	1210.26	1159.20
192	1829.54	1623.63	1244.51	1361.55	1251.03	1182.62
216	1867.99	1648.92	1276.05	1402.22	1289.85	1210.38
240	1888.35	1672.84	1299.71	1434.57	1309.52	1250.90

Table 2. *Cumulative potassium released (mg/kg) with time from surface(S1) and subsurface(S2) soil of Vertisols on continuous extraction by oxalic acid*

Time (t) (hrs)	Nimone		Nirmal-Pimpri		Coimbatore	
	S1	S2	S1	S2	S1	S2
2	28.52	15.53	6.34	16.42	43.10	27.60
6	98.99	61.25	32.82	74.09	254.34	87.06
12	231.60	217.80	78.43	192.54	571.51	173.38
24	412.33	420.49	148.93	358.38	1060.08	317.63
36	484.38	563.15	239.24	488.93	1106.09	353.17
48	566.03	632.10	341.52	661.29	1159.23	407.64
60	593.36	675.33	376.43	702.84	1189.55	486.99
72	641.79	703.00	416.67	756.43	1226.63	574.40
84	685.83	725.17	443.04	801.43	1255.66	607.80
96	746.43	766.89	469.38	865.90	1315.58	650.15
120	859.13	842.30	522.26	947.26	1391.72	741.15
144	934.35	886.05	620.90	994.41	1444.44	804.65
168	983.97	903.60	645.03	1059.21	1477.73	861.05
192	1023.60	923.85	672.81	1101.05	1503.05	894.53
216	1066.44	948.27	697.23	1138.07	1529.69	940.17
240	1107.07	968.92	723.37	1170.99	1559.95	978.39

that nearly 50 per cent of total non-exchangeable K released was recorded in first 48 to 60 hours of oxalate extraction in all the three vertisols.

The cumulative potassium released on continuous extraction by 100 ppm oxalic acid in Entisols are given in Table 3. In Entisols the cumulative K released on 240 hours were 1047 and 939, 2004 and 1097 and 903 and 903 mg/kg from surface and subsurface horizons of Pandu Nagar, Hisar and Chattarpur soils, respectively. The non-exchangeable K release was found to be higher in surface soils as compared to subsurface soils except Chattarpur where both surface and subsurface soils released equal amount of potassium on oxalate extraction. The non-exchangeable K release was observed highest in Hisar followed by Pandu Nagar and Chattarpur Entisols. Further, it was observed that nearly 50 per cent of total non-exchangeable K released was recorded in first 24 to 36 hours of oxalate extraction in Hisar and Pandu Nagar soils.

The rate constants (a, b) and determination co-efficients of non-exchangeable K released by oxalic acid extraction fitted with four types of equations are shown in Table 4. In general, the First order equation showed good agreement to oxalate extracted data compared to power function

On the basis of determination coefficients (r2) and standard error (SE) the non-exchangeable potassium release kinetics was best explained by first order equation followed by parabolic diffusion and power function. The fitted first order curves for one Entisol and one Vertsol are shown in Fig. 7 and Fig. 8, respectively.

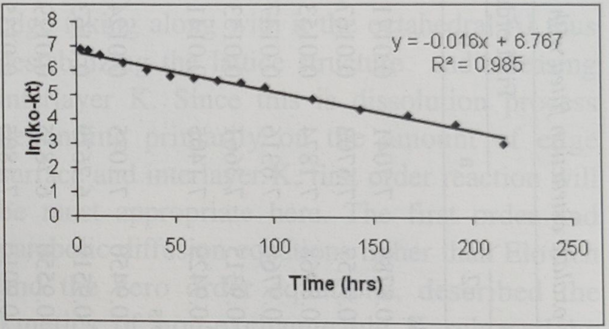


Fig. 7. *First order kinetics of K release from a Vertisol (Nimone) by continuous extraction by Oxalic acid*

Table 3. *Cumulative potassium released (mg/kg) with time from surface(S1) and subsurface(S2) soil of Entisols on continuous extraction by oxalic acid*

Time (t)	Pandu Nagar		Hisar		Chattarpur	
(hrs)	S1	S2	S1	S2	S1	S2
2	32.40	26.88	82.91	60.59	22.48	7.75
6	94.05	81.47	307.41	143.74	73.73	54.24
12	234.31	148.47	613.59	241.16	168.31	108.24
24	399.69	251.09	1125.95	356.47	349.44	190.22
36	546.67	333.65	1199.01	406.67	421.08	279.83
48	632.22	411.59	1275.2	478.18	495.02	414.51
60	712.72	479.90	1417.21	571.69	530.34	453.03
72	794.21	554.11	1514.27	680.62	571.08	493.39
84	840.91	600.03	1659.01	768.47	615.26	547.01
96	869.81	656.82	1775.91	872.13	665.66	607.24
120	913.87	728.07	1834.03	931.56	752.37	655.69
144	956.58	788.15	1875.52	970.23	801.82	718.62
168	985.35	832.56	1906.70	1006.79	825.48	799.64
192	1011.80	867.55	1937.03	1035.52	859.50	840.47
216	1035.16	908.11	1972.24	1072.08	884.72	873.23
240	1047.41	939.13	2004.24	1097.94	903.86	903.56

In Vertisols the cumulative

Table 4. *Rate constants (a, b) and determination coefficients (r2) of K release by oxalate extraction fitted with different kinetic equations*

Soil		Elovich equation			Power function			First order			Parabolic diffusion		
		a	b	r2	a	b	r2	a	b	r2	a	b	r2
						Alfisols							
Ranchi	S1	-523.48	440.05	0.9766	35.82	0.8046	0.8789	7.7041	0.0171	0.9772	0.0305	0.0711	0.9396
Cultivated	S2	-469.05	389.91	0.9706	42.07	0.7410	0.9157	7.5703	0.0167	0.9878	0.0247	0.0715	0.9421
Ranchi	S1	-332.21	300.08	0.9765	33.48	0.7413	0.8968	7.1874	0.0153	0.9824	0.0594	0.0693	0.9089
Uncultivated	S2	-621.00	343.92	0.8578	8.22	1.0054	0.9768	7.6316	0.0147	0.9407	-0.1759	0.0800	0.9849
Coimbatore	S1	-351.60	290.28	0.9515	41.55	0.6782	0.9315	7.3661	0.0153	0.9567	0.0054	0.0699	0.9753
	S2	-391.02	298.79	0.9484	28.77	0.7544	0.9429	7.1405	0.0141	0.9817	0.0012	0.0731	0.9121
						Vertisols							
Nimone	S1	-312.04	241.65	0.9482	29.85	0.7033	0.9450	7.1075	0.0124	0.9736	-0.0165	0.0692	0.9850
	S2	-182.47	136.69	0.9380	16.30	0.7070	0.9519	6.7679	0.0163	0.9857	0.0543	0.0694	0.9083
Nirmal-	S1	-275.85	169.60	0.9127	6.11	0.9388	0.9550	6.7835	0.0129	0.9682	-0.1092	0.0758	0.9859
Pimpri	S2	-375.09	271.00	0.9553	19.00	0.8193	0.9010	7.1805	0.0135	0.9777	-0.0306	0.0725	0.9671
Coimbatore	S1	-178.51	327.43	0.9690	77.35	0.6164	0.8134	7.1457	0.0148	0.9692	0.1981	0.0600	0.8194
	S2	-304.95	215.51	0.9228	24.81	7.0182	0.9715	0.0182	0.0121	0.9721	0.0547	0.0711	0.9927
						Entisols							
Pandu nagar	S1	-180.40	162.02	0.9670	32.29	0.6130	0.9545	6.9448	0.0184	0.9839	0.0407	0.0709	0.9248
Delhi	S2	-311.22	212.42	0.9225	22.19	0.7228	0.9798	7.0041	0.0128	0.9734	-0.0671	0.0730	0.9894
Hisar	S1	-356.83	441.03	0.9828	106.10	0.5945	0.8940	7.5567	0.0164	0.9913	0.1298	0.0652	0.8910
	S2	-313.73	245.66	0.9164	48.23	0.6009	0.9843	7.1573	0.0145	0.9822	-0.0207	0.0717	0.9715
Chattarpur	S1	-265.61	206.21	0.9610	22.58	0.7299	0.9416	6.9459	0.0145	0.9755	-0.0069	0.0713	0.9685
Delhi	S2	-336.59	208.44	0.9085	8.60	0.9114	0.9497	7.0128	0.0163	0.9857			

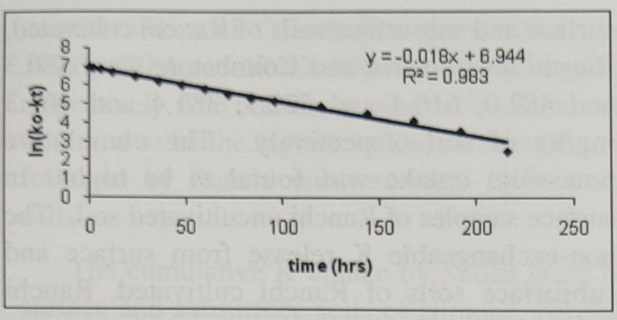


Fig. 8. *First order kinetics of K release from Entisol (Chattarpur) by continuous extraction by Oxalic acid*

The mechanism K release by oxalic acid extraction is that of a combination of proton and ligand promoted dissolution and is quite different from that of diffusive-exchange reaction in case of sodium tetraphenyl boron extraction. In case of oxalic acid extraction both proton dissocitated from oxalic acid and oxalate ions are involved in the minerals dissolution process. In proton promoted dissolution, protons migrating through edges (010 and 100 faces) attach on the apical oxygen liking tetrahedral and octahedral shhets and reduce negative layer charge which stimulate ejection of octahedral Al or Fe thus destabilizing the lattice structure and releasing interlayer K. Oxalate on the other hand being weak acid anion are adsorbed on edge surface by donating its electron to exposed octahedral Al or Fe in a ligand exchange process. In the next step the surface adsorbed oxalate separates out from the edge taking along with it the octahedral Al thus destabilizing the lattice structure and releasing interlayer K. Since this is dissolution process depending primarily on the amount of edge surface and interlayer K, first order reaction will be most appropriate here. The first order and parabolic diffusion equations rather than Elovich and the zero order equations, described the kinetics of non-exchangeable K released by boiling HNO_3, which is also a dissolution process, from a number of soils (Martin and Sparks, 1983; Elkhatib and Hern,1988).

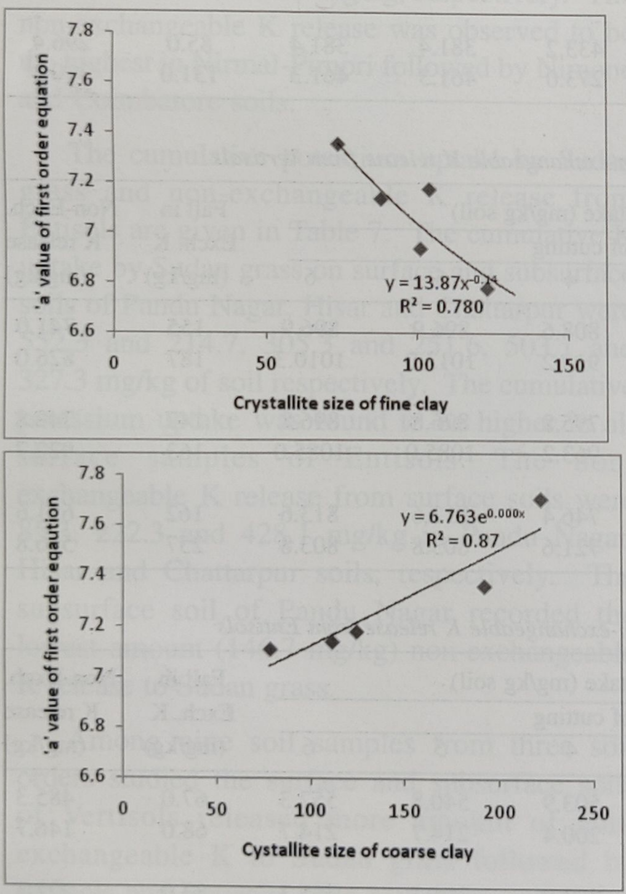


Fig. 9. *Relationship between 'a' value of first order kinetic equation of K release from oxalic acid extraction and average crystallite size of A) Fine clay, B) Coarse clay*

Relationship between crystallite size and K release by oxalic acid extraction

'a' value of the first order equation *ln* (K0 - Kt) = a – bt is related to maximum extractable K as shown below

At t=0, Kt = 0 , then a= $\ln K_0$. Thus well crystallized large mica particles having more extractable K should be positively related with 'a' value of the equations fitted to data of oxalic acid extraction. On the other hand small sized crystallite in the fine clay fraction have depleted of interlayer K should be negatively related with 'a' value of fitted equations. Fig 9 shows positive relationship of crystallite size of coarse clay fraction of all the soils and negative relationship of crystallite size of fine clay fraction of all the soils with 'a' value of the fitted first order equation.

Uptake of non-exchangeable potassium by exhaustive cropping

The cumulative potassium uptake by Sudan grass and non-exchangeable K release from Alfisols, Vertisols and Entisols are given in Tables 5, 6 and 7, respectively.

The cumulative K uptake by Sudan grass on surface and subsurface soils of Ranchi cultivated, Ranchi uncultivated and Coimbatore were 486.3 and 482.0, 610.4 and 522.3, 381.4 and 461.3 mg/kg of soil respectively. The cumulative potassium uptake was found to be higher in surface samples of Ranchi uncultivated soil. The non-exchangeable K release from surface and subsurface soils of Ranchi cultivated, Ranchi

Table 5. *Cumulative potassium uptake by Sudan grass and non-exchangeable K release from Alfisols*

Soil		Cumulative K uptake (mg/kg soil) Number of cutting 1	2	3	4	5	6	Fall in Exch. K (mg/kg)	Non-Exch. K release (mg/kg)
Ranchi uncultivated	S1	165.9	316.8	408.6	452.8	486.3	486.3	86.0	400.3
	S2	151.0	277.8	360.7	421.6	482.0	482.0	103.0	379.0
Ranchi-uncultivated	S1	247.5	387.7	515.8	568.7	610.4	610.4	140.0	470.4
	S2	186.7	321.9	421.1	490.6	522.3	522.3	132.0	390.3
Coimbatore	S1	129.1	234.9	309.3	433.2	381.4	381.4	85.0	296.4
	S2	164.6	293.6	383.3	273.0	461.3	461.3	131.0	330.3

Table 6. *Cumulative potassium uptake by Sudan grass and non-exchangeable K release from Vertisols*

Soil		Cumulative K uptake (mg/kg soil) Number of cutting 1	2	3	4	5	6	Fall in Exch. K (mg/kg)	Non-Exch. K release (mg/kg)
Nimone	S1	261.6	540.6	731.0	808.6	896.9	896.9	155	741.0
	S2	292.5	602.2	801.8	913.2	1013.0	1010.3	187	826.0
Nirmal-pimpri	S1	272.2	527.9	680.9	795.8	896.8	896.8	147	749.8
	S2	338.9	647.1	852.9	963.2	1085.0	1085.0	163	922.7
Coimbatore	S1	213.2	478.6	646.3	746.4	812.6	813.6	162	651.6
	S2	227.7	458.6	601.6	721.6	803.8	803.8	257	546.8

Table 7. *Cumulative potassium uptake by Sudan grass and non-exchangeable K release from Entisols*

Soil		Cumulative K uptake (mg/kg soil) Number of cutting 1	2	3	4	5	6	Fall in Exch. K (mg/kg)	Non-Exch. K release (mg/kg)
Pandu nagar	S1	147.5	304.0	424.9	503.9	540.8	552.3	67.0	485.3
Delhi	S2	92.3	156.1	180.9	200.4	214.7	214.7	68.0	146.7
Hisar	S1	101.5	176.7	241.6	273.0	305.3	305.3	83.0	222.3
	S2	76.5	130.0	190.7	230.3	251.6	251.6	81.0	170.6
Chattarpur	S1	175.0	298.4	366.3	449.5	503.1	503.1	75.0	428.1
Delhi	S2	118.8	213.8	265.1	302.7	327.3	327.3	133.0	198.3

uncultivated and Coimbatore were 400.3 and 379.0, 470.4 and 390.3, 296.4 and 330.3 mg/kg, respectively. The non-exchangeable K release was observed to be the highest in Ranchi uncultivated followed by Ranchi cultivated and Coimbatore soils.

The cumulative K uptake by Sudan grass on surface and subsurface soils of Nimone, Nirmal-Pimpri and Coimbatore were 896.9 and 1010.3, 896.8 and 1085.0, 813.8 and 803.8 mg/kg of soil, respectively. The cumulative potassium uptake was found to be higher in subsurface samples except Coimbatore Vertisol. The non-exchangeable K release from surface and subsurface soils of Nimone, Nirmal-Pimpri and Coimbatore were 741.0 and 826.0, 749.8 and 922.7, 651.6 and 546.8 mg/kg, respectively. The non-exchangeable K release was observed to be the highest in Nirmal-Pimpri followed by Nimone and Coimbatore soils.

The cumulative potassium uptake by Sudan grass and non-exchangeable K release from Entisols are given in Table 7. The cumulative K uptake by Sudan grass on surface and subsurface soils of Pandu Nagar, Hisar and Chattarpur were 552.3 and 214.7, 305.3 and 251.6, 503.1 and 327.3 mg/kg of soil respectively. The cumulative potassium uptake was found to be higher in all surface samples of Entisols. The non-exchangeable K release from surface soils were 85.3, 222.3 and 428.1 mg/kg in Pandu Nagar, Hisar and Chattarpur soils, respectively. The subsurface soil of Pandu Nagar recorded the lowest amount (146.7 mg/kg) non-exchangeable K release to Sudan grass.

Among nine soil samples from three soil orders studied the surface and subsurface soils of Vertisols released more amount of non-exchangeable K to Sudan grass followed by Alfisols and Entisols. The higher release of non exchangeable K from Vertisols was attributed to its smaller crystallite size and pool crystallinity of K-bearing minerals. The subsurface soils of Entisols supplied remarkably low amount of potassium to Sudan grass as compared to subsurface soils of Alfisols and Vertisols.

Sudan grass cropping and crystallite size of coarse clay and total clay of different soils

Fig 10 shows inverse relationship of K release from Sudan grass cropping with crystallite size of coarse clay and total clay. This is quite expected because in stressed condition plants release organic acid in the rhizosphere which initiates release of non exchangeable K by ligand promoted dissolution mechanism which is centered on edge surface. So more the edge surface more will be the K release. Thus smaller crystallites having more specific surface area, rather more edge surface will cause more K release

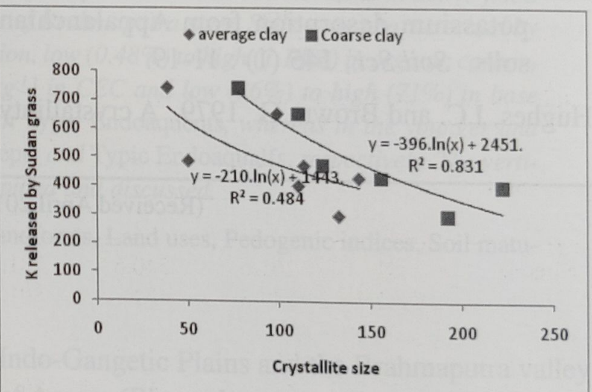


Fig. 10. *Relationship between release of non-exchangeable K during*

Conclusion

The crystallites of micaceous minerals were found to be largest in coarse clay fractions of Entisols followed by Alfisols and Vertisols. In almost all the profiles of Alfisol, Vertisols and Entisols, the crystallite size of micaceous minerals was found to increase along the depth of the profile. Release of non exchangeable K to crops seems to be largely controlled by finer crystallites of mica.

References

Arnold, P.W. and Close, B.M. 1961. Release of non-exchangeable potassium from some British soils cropped in the glasshouse. *J. Agric. Sci.,* **57** : 295-304.

Datta, S.C. 1996. Characterization of micaceous minerals in soils for strain and size of crystallites through deconvolution and curve fitting of XRD profile. *Clay Research,* **15** (1) : 20-27.

De Alwis, K.A. and Pluth, D.J. 1976. The red latosols of Sri Lanka : I. Macromorphological, physical and chemical properties, genesis and classification. II. Mineralogy and weathering. *Soil Sci. Soc. Am. J.,* **40** : 912-928.

Elkhatib, E.A. and Hern, J.L. 1988. Kinetics of potassium desorption from Appalanchian soils. *Soil Sci.,* **145** (1) : 11-19.

Hughes, J.C. and Brown, G. 1979. A crystallinty index for soil kaolins and its relation to parent rock, climate and maturity. *J. Soil Sci.,* **30** : 557-563

Klug, H.P. and Alexander, L.E. 1974. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials.* A Wiley – Interscience Publication. John Wiley & Sons. New York. p 618.

Martin, H.W. and Sapiks, D.L. 1983. Kinetics of non-exchangeable potassium release from two coastal plain soils. *Soil Sci. Soc. Am. J.,* **47** : 883-887.

Talibudeen, O. and Dey, S.K. 1968. Potassium reserves in British soils. I. The Rothamsted classical experiments. *J. Agric. Sci. Camb.,* **71** : 95-104.

Thanga Pandian and Datta 2009. Potassium Release Behavior of Soil Clays in Relation to Trioctahedral Components of Mica *Clay Research.* **28** (1&2) : 53-71.

(Received April 2018; Accepted July 2018)

Clay Research, Vol. 36, No. 2, pp. 77-89 (2017)

Pedogenesis of Some Hydromorphic Soils of Upper Brahmaputra Valley Region, Assam, India

SILADITYA BANDYOPADHYAY*, P. RAY[1], S. RAMACHANDRAN[1], R.K. JENA[1], S.K. SINGH[2] AND S.K. RAY[1]

National Bureau of Soil Survey and Land Use Planning (ICAR), R.C., Kolkata- 700091, India
[1]National Bureau of Soil Survey and Land Use Planning (ICAR), R.C., Jorhat – 785004, India
[2]National Bureau of Soil Survey and Land Use Planning (ICAR), Nagpur – 440033, India

Abstract–*Hydromorphic soils and their properties are key to address various issues of the waterlogged regions related to its productivity and conservation. The present investigation is aimed to investigate the pedogenesis of some hydromorphic soils of the Upper Brahmaputra valley region of Assam. Six pedons from North West Jorhat Development block were selected and examined for the purpose. Detail morphological, physical and chemical characteristics of the hydromorphic soils under different landforms and land uses were done through land resource inventorization (at 1:10000 scale) using and fine resolution satellite image. The study showed change in soil characteristics with micro-topographic variation. Wide variability in particle size is attributed to frequent occurrence of lithologically discontinued soil horizons in active flood plains due to fluvial processes and changes in the course of Brahmaputra river. Soils were characterized by strongly acidic (pH 4.74) to neutral (pH 6.7) in soil reaction, low (0.48%) to high (1.14%) in organic carbon, low [3.13 cmol (p^+) kg^{-1}] to medium [11.90 cmol (p^+) kg^{-1}] in CEC and low (26%) to high (71%) in base saturation status. Active flood plains were endowed with* Typic Endoaquents, *whereas in the younger and older flood plains, soils formed were* Fluventic Endoaquepts *and* Typic Endoaqualfs, *respectively. The vertical distribution of different pedogenic indices were computed and discussed.*

Key words: Brahmaputra valley, Hydromorphic soils, Landforms, Land uses, Pedogenic indices, Soil maturity, etc.

The genesis of hydromorphic soils have been studied world-wide (Bouma, 1983; Bouma *et al.*, 1988; 1990). These soils varied in wide spectrum of orders from Entisols to Histosols. They have been locally classified under peat, muck and bog soils with occurrence of characteristics *Sapric* materials (Soil Survey Staff, 2003). In India, such hydromorphic soils are mainly distributed along the coasts, river deltas, river islands and their tributaries (Soil Resource Mapping, 1994). Some are also confined to anthropogenic water bodies. The Indian hydromorphic soils are mostly confined to Entisols and Inceptisols orders with aquic moisture regime (*aquepts*) (Bhattacharyya *et al.*, 2004; 2013a) and mostly spread over the Indo-Gangetic Plains and the Brahmaputra valley of Assam (Bhattacharyya *et al.*, 1997). However, soils belonging to other orders also exist in a scattered form (Ray *et al.*, 1997; Bhattacharyya *et al.*, 2004). These soils have endo-saturated sub-surface horizons with dark gray to light gray coloured matrix (2.5 Y to 10 YR hue, chroma of 2 or less). The lower sub-surface horizons are often gleyed with formation of reduction mottles and depletions of iron and manganese. The gleyed sub-surfaces horizons are often stratified with alternate sand and silt deposits due to fluvial cycles. The hydromorphic soils of Brahmaputra valley region are confined to marshy lands and younger, older and active flood plains (Vadivelu

---

***Corresponding Author Email:** siladitya_555@yahoo.co.in

et al., 2003; Bhaskar *et al.*, 2007; 2010) and are mainly classified to *Typic Endoaquepts* and *Fluvaquentic Endoaquepts* sub group. However, these informations are limited to small scale dataset (Sen *et al.*, 1999) and lack detailed information on their genesis. These soils are formed as a result of continuous cycles of saturation (dominantly Endosaturation). But the knowledge about the factors responsible for their formation and pedogenesis requires investigation of pedogenic indices. It is noteworthy that among the pedogenic indices, obtained from ratios, *viz.*, exchange ratio (ER) (Pratt and Alvahydo, 1966), fine sand/ total sand (FS/ TS) and very fine sand/ total sand (VFS/ TS) (Schaetzl and Thompson, 2015) are the direct indicators influencing pedogenesis, whereas, the indices obtained from the ratios like sand/ silt, silt/ clay (Schaetzl and Thomson, 2015), index of weathering (IW) (Martini, 1970) and CEC/clay (Smith, 1986) influence inversely the pedogenesis in soils. An attempt has been made here to understand the variability of these direct and inversely related pedogenic indices on soil formation of the hydromorphic soils. Therefore, the present study has been undertaken to understand the characteristics of saturated soils with the objectives (i) to characterize and classify some hydromorphic soils of upper Brahmaputra valley region of Assam and (ii) to study their pedogenesis by pedogenic indexing.

Materials and Methods

Study Area

The study was concentrated in North West Jorhat Development Block of Jorhat District, Assam in between the geographic extent from 26°35'N to 26°55'N Latitudes and 93°55'E to 94°15'E Longitudes and covering an area of about 30,700 ha (Fig. 1). The general topography varied from almost flat to very gently sloping (slope varied from 0-1% to 1-3%). The climate is humid sub tropical with mean annual rainfall of 2262 mm (ACP, 2015). The mean annual soil temperature is 24.5°C, mean summer soil temperature is 26.3°C and mean winter soil temperature is 19.1°C. The soil temperature regime is *Hyperthermic* and soil moisture regime is *Aquic* (Soil Survey Staff, 2003). The agro-ecological sub region is 15.4 (Upper Brahmaputra Valley Zone, hot, moist per-humid climate with length of growing period of more than 300 days) (Velayutham *et al.,* 1999). The study area is under rain-fed paddy (*kharif*) as the major crop along with sporadically grown mustard / vegetables (*rabi*). Irrigation is mainly open sourced (*viz.*, open well, scattered water bodies, drainage streams and rivulets of Brahmaputra) (Statistical Handbook, 2015). The study area is characterized by three broad landform units viz., (i) very gently sloping active flood plains (AFP) (1-3% slope), (ii) nearly level younger flood plains (YFP) (0-1% slope) and (iii) very gently sloping older flood plains (OFP) (1-3% slope). Each of older and younger flood plains comprise two types of land use systems viz., paddy (*Kharif*)-fallow (*Rabi*) and currently fallow marshy lands, while, active flood plains consist of two land uses namely, mustard/ vegetables (*Rabi*)-fallow (*Kharif*) and currently fallow marshy lands. Six hydromorphic pedons were identified from each of the landform and land use units for examination of their morphological, physical and chemical characteristics (Fig. 2).

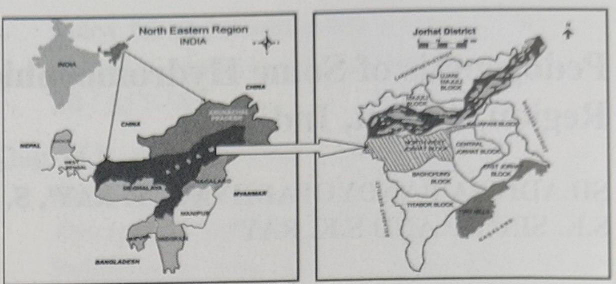


Fig. 1. *Location map of the study area*

Methodology of soil survey

A detailed soil survey on 1:10,000 scale was undertaken in the study area using Survey of India

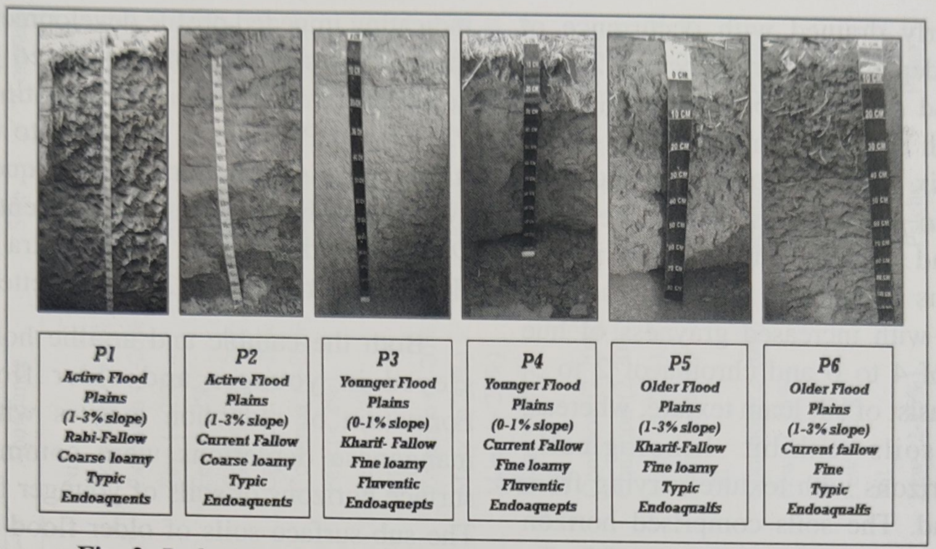


Fig. 2. *Pedons in different landforms and land use systems of the study area*

(SoI) topographical sheets (83 F/13, 14, J/1, 2), IRS (LISS-IV) multispectral data and Cartosat-1 data as base maps (Srivastava and Saxena, 2004, Nagaraju *et al.,* 2014). The landforms corresponding to the hydromorphic soils were identified on the base map by ground truth verification. The morphological characteristics of soils were studied by soil profile examination at specific sites where hydromorphic soils existed (Buol *et al.,* 1997; Soil Survey Staff, 2003) taking special care to note the soil hydromorphological indicators. Laboratory analysis of soil physical and chemical parameters were done which included mechanical analysis by International Pipette method (Jackson, 1973), pH (1: 2.5 H_2O) (Piper, 1966), soil organic carbon (SOC) by wet digestion method (Walkley and Black, 1934), cation exchange capacity (CEC) and exchangeable bases by neutral 1 *N* ammonium acetate solution (Sparks, 1996; Page *et al.,* 1982) and exchangeable aluminium was done by 1 *N* KCl (van Reeuwijk, 1993). Base saturation was calculated by both sum of cations as well as by sum of cations method (Soil Survey Staff, 1998). ECEC by sum of extractable bases plus exchangeable aluminium, pH dependent CEC by CEC of sum of cations subtracted from ECEC) (Pratt and Alvahydo, 1966) and base saturation by sum of bases divided by CEC and multiplied by 100. Soils were classified after interpretation of morphological, and laboratory analytical data using Soil Survey Staff (2003, 2014).

Pedogenic index

The ‘pedogenic index’, originally used to quantitatively express the changes which occurred in soils during their development, has been applied essentially in study of pedogenesis (Arnaud, 1988). In the present study, pedogenic indices have been calculated to throw some light on the genesis of soils of the study area. This was obtained by computing various indices from some soil properties, *viz.,* particle size ratios including sand/silt, silt/clay, fine sand/total sand (FS/ TS), very fine sand/total sand (VFS/ TS) (Schaetzl and Thompson, 2015), CEC/Clay, ECEC (sum of cations plus exchangeable aluminium), exchange ratio (ER) (pH dependent CEC/ ECEC) (Pratt and Alvahydo, 1966) and weathering index (CEC/ square of clay and multiplied by 100) (IW) (Martini, 1970).

Results and Discussions

Morphological characteristics of soils

Soils occurring on active flood plains were very deep, poorly drained with occurrence of redoximorphic depletions started below 20 cm from surface and continued beneath it. Gleying started at a depth below 20 cm in P1 and 40 cm in P2. The matrix colour in surface ranged from yellowish grey to grayish yellow with hue of 10 YR, value 5 and chroma 2 to 3. Soils in sub surface horizons comprised different sets of colour matrices with increased grayness of hue (2.5 Y), value of 4 to 6 and chroma of 2 to 3. Surface soils consist of silt loam texture, whereas, sub surface soils exhibit lithologically discontinued horizons with texture varying from silt loam to sand. The soils comprised horizon sequence of Ap-2ACg-3Cg in P1 and P2. On younger flood plains, the soils were very deep and imperfectly drained with occurrence of strong and brownish redoximorphic mottling started at a depth of 18 cm in P3 and 23 cm in P4. The soils comprised yellowish brown to dark gray colour with hue of 10 YR in surface and 10 YR to 2.5 Y in sub surface, value of 4 to 5 and chroma of 1 to 3. The surface soils have silt loam texture, whereas, sub surface soils varied from sandy loam to silty clay loam texture. The horizon sequence of P1 was Ap-Bwg-2Bwg and P2 was Ap-Bwg, signifying the occurrence of deep gleyed cambic horizons below surface. Sudden increase in clay content below 90 cm in P3 indicated profile discontinuity. Soils on older flood plains were very deep and very poorly drained with occurrence of redox depletions below 25 cm. The colour of the matrix ranged in hue of 2.5 Y to 5Y with value of 4 to 7 and chroma of 1, exhibiting dark gray coloured soil matrix. Occurrence of stress features and faint and patchy cutans in the forms of iron (Ferrans) and manganese concentrations (Mangans). In sub surface layers gleyed cambic (Bwg) followed by gleyed argillic (Btg) horizons were formed indicates gradual clay illuviation processes. The horizon sequences were Ap-Bwg-Btg-2Cg ad Ap--Btg for P5 and P6, respectively (Table 1). It is noteworthy that lithological discontinuity has been seen in P5 below 100 cm from the surface, indicating impeded profile development, whereas, the horizon sequence of P6 showed gradual soil development. Lithological discontinuity of P1, P2, P3 and P5 may be attributed to the juvenile stages of soils formation due to frequent flooding cycles and their genesis from recent origin *i.e.*, *Quaternary* deposits of Brahmaputra alluvium of Holocene period (GSI, 2009; Gazetteers, 1979).

Both the cambic and argillic horizons were gleyed in younger and older flood plains. Formation of reduction mottles with iron and manganese depletions were common in sub-surface horizons of soils of younger flood plains. The sub-surface soils of older flood plains were characterized by formations of stress features followed by ferrans and mangans indicating that the process of agrillization preceeded much earlier than the process of gleyization (Bhaskar *et al.,* 2007; Vadivelu *et al.,* 2003). On the other hand, soils of active flood plains showed negligible horizon development because of the frequent fluvial influence of Brahmaputra river as evidenced by lithologic discontinuity (LD). Micro-depressions in the southern bank of the river may be attributed to faster gleyization process in active flood plains, which probably retarded the pedogenic processes. LD in these soils is one of the major factors influencing pedogenesis, particularly in soils of active and younger flood plains, where LD was found to decline from active flood plains to older flood plains. Thus LD can be attributed as an indicator of soil formation in the Brahmaputra valley; more frequent is the presence of LD, younger is the soil.

Physical and chemical characteristics of soils

The sand, silt and clay content of soils ranged from 1.0 to 90.8%, 5.2 to 74.3% and 3.8 to 52.4%, respectively. Such wide range of variability in particle size clearly depicts textural versatility of soils and lithological discontinuity due to frequent fluvial activities of the mighty river Brahmaputra. Older flood plains have

Table 1. Morphological characteristics of soils of the study area

Landforms	Pedons	Depth (cm)	Horizon	Matrix colour	Texture	Diagnostic features of sub-surface (mottles/ cutans/ stress features/ depletions)			
						Kind/ type	Abundance	Size	Contrast
Active flood plains (1-3% slope)	P1	0-20	Ap	10 YR 5/2 (M)	Silt loam	Nil	Nil	Nil	Nil
		20-40	2Acg1	2.5 Y 5/2 (M)	Silt loam	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		40-75	2Acg2	2.5 Y 4/2 (M)	Loamy sand	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		75-105	3Cg1	2.5 Y 4/2 (M)	Loamy sand	Fe-Mn depletion	Few (< 2%)	Medium	Faint
		105-130	3Cg2	2.5 Y 6/2 (M)	Loamy sand	Fe-Mn depletion	Few (< 2%)	Medium	Faint
Active flood plains (1-3% slope)	P2	0-20	Ap	10 YR 5/3 (M)	Silt loam	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		20-40	2Acg1	10 YR 5/2 (M)	Silt loam	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		40-60	2Acg2	2.5Y 5/3 (M)	Sandy loam	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		60-75	3Cg1	2.5Y 6/2 (M)	Loamy sand	Fe-Mn depletion	Few (< 2%)	Medium	Faint
		75-125	3Cg2	2.5 Y 6/2 (M)	Sand	Fe-Mn depletion	Few (< 2%)	Medium	Faint
Younger flood plains (0-1% slope)	P3	0-18	Ap	10YR 5/3 (M)	Silt loam	Not observable	Nil	Nil	Nil
		18-40	Bwg1	10YR 5/3 (M)	Sandy loam	Redox mottles	Common (2-20%)	Medium	Distinct
		40-70	Bwg2	10YR 5/2 (M)	Silt loam	Redox mottles	Many (> 20%)	Medium	Prominent
		70-90	Bwg3	10YR 5/2 (M)	Silt loam	Redox mottles	Many (> 20%)	Medium	Prominent
		90-136	2Bwg1	2.5Y 4/1 (M)	Silty clay loam	Redox mottles	Many (> 20%)	Coarse	Prominent
Younger flood plains (0-1% slope)	P4	0-23	Ap	10YR5/3 (M)	Silt loam	Not observable	Nil	Nil	Nil
		23-46	Bwg1	10YR5/3 (M)	Silt loam	Redox mottles	Common (2-20%)	Medium	Distinct
		46-90	Bwg2	10YR5/3 (M)	Silt loam	Redox mottles	Common (2-20%)	Medium	Distinct
		90-121	Bw3	10YR5/2 (M)	Sandy loam	Redox mottles	Many (> 20%)	Medium	Prominent
		121-153	Bwg4	10YR5/2 (M)	Sandy loam	Redox mottles	Many (> 20%)	Medium	Prominent
Older flood plains (1-3% slope)	P5	0-25	Ap	2.5Y 4/1 (M)	Loam	Not observable	Nil	Nil	Nil
		25-48	Bwg1	2.5Y 5/1 (M)	Silty clay loam	Fe-Mn depletion	Common (2-20%)	Medium	Distinct
		48-70	2Btg1	2.5 Y6/1 (M)	Silty clay loam	Ferrans/ Mangans	Few (2-25%)	Patchy	Faint
		70-100	Btg2	2.5 Y6/1 (M)	Silty clay loam	Ferrans/ Mangans	Few (2-25%)	Patchy	Faint
		100-115	2Cg1	2.5Y 7/1 (M)	Loamy sand	Fe-Mn depletion	Few (< 2%)	Medium	Faint
Older flood plains (1-3% slope)	P6	0-25	Ap	5Y 5/1 (M)	Silty clay loam	Not observable	Nil	Nil	Nil
		25-55	Btg1	5Y 5/1 (M)	Silty clay	Stress features	Few (2-25%)	Patchy	Faint
		55-85	Btg2	5 Y6/1 (M)	Silty clay	Ferrans/ Mangans	Few (2-25%)	Patchy	Faint
		85-120	Btg3	5 Y6/1 (M)	Silty clay	Ferrans/ Mangans	Few (2-25%)	Patchy	Faint

generally more clay content in sub surface (28.1-52.4%) compared to that younger (10.0-38.2%) and active flood plains (3.8-20.1%). Lithological discontinuity has been found more prominent in sub-surfaces of soils on active flood plains with high sand contents (75.6-90.8%) compared to that in other landforms. Thus, it is noteworthy to say that varying particle size fractions are good enough to explain the micro-topographic variability of the study area (Birkland, 1984; Gerrard, 1992). The soils were slightly acidic to neutral in reaction (pH 6.3-6.7) on active flood plains, strongly to moderately acidic (pH 5.3-6.1) on younger flood plains and very strongly to moderately acidic (pH 4.7-6.1) on older flood plains. Strong to moderate soil acidity in older and younger flood plains may be attributed to little influence of exchangeable aluminium {0.11-0.59 cmol (p^+) kg^{-1}. Higher side of pH in soils of active flood plains may be attributed to presence of considerable amount of bases in coarser particle size (sand and silt) fraction of soils. The soils comprise low (0.48%) to medium organic carbon (0.64%) on active flood plains, medium (0.62%) to high (0.79%) on younger flood plains and high (0.89-1.14%)-on older flood plains. The gradual increase in organic carbon from P1 to P6 indicates that the older is the landform the more is the soil aggregation. Frequent fluvial activities and flooding hazards by Brahmaputra appears to hinder organic matter accumulation and thereby restrict the process of humification in surface soils of active flood plains. CEC of soils varied from 3.13 cmol (p^+) kg^{-1} on active flood plains to 10.56 cmol (p^+) kg^{-1} on older flood plains (Table 3). CEC of sum of cations ranged from 4.35 cmol (p^+) kg^{-1} in active flood plains to 10.73 cmol (p^+) kg^{-1} in older flood plains. CEC of sum of cations was more than CEC by ammonium acetate method is most of the horizons of all the pedons (P1 to P6), attributing to the little influence of exchangeable aluminium in soils, even at higher pH. Lower CEC in soils on active flood plains and its subsequent increase in soils of younger and older flood plains may again attribute to the subsequent increase in clay content of soils. The soils comprised medium to high base saturation in active flood plains (42-71%), high base saturation on younger flood plains (51-71%) and low to medium base saturation in older flood plains (26-44%). The base saturation percentage had a general declining trend from active flood plains to older flood plains. Relatively low base saturation status in soils older flood plains may be attributed to low CEC content, which reflects the presence of considerable amount of low activity clays in these soils (Bhattacharyya *et al.*, 2010; 2013b). On the contrary, younger and active flood plains comprise soils with relatively higher base saturation status due to presence of considerable amount of extractable bases, especially calcium and magnesium (Bhaskar *et al.*, 2007).

Among the physical and chemical characteristics of the soils, silt, clay, CEC and base saturation were the major influencing factors for the formation of hydromorphic soils. High CEC and base saturation of soils in younger flood plains may be attributed to higher silt and clay content, resulting in impeded sub-surface drainage condition in all the soils (Table 2). The soils of older flood plains have high clay and low sand and silt fractions with low CEC/ clay ratio compared to that in other two landforms (Table 2). This may justify the presence of considerable amount of low activity clays in these soils with presence of kaolin group of minerals being interstratified with HIV (Bhattacharyya *et al.*, 2010; 2013b). This favours the assumption that these soils were formed much earlier (during *Pleistocene* period or more older) the soils of younger and active flood plains. The hydromorphic characters of these soils might have built-up recently *i.e.*, during the late *Holocene* period (GSI, 2009; Gazetteers, 1979) due to shifting of courses of Brahmaputra more and more towards southern direction.

Table 3. *Physical and chemical characteristics of soils of the study area*

Pedons	Depth (cm)	Sand	Silt	Clay	pH (1: 2.5 H_2O)	O.C. (%)	CEC			Sum of bases	Exch. Aluminium	ECEC	BS (%)
							1*N* NH_4Oac	Sum of cations	pH dependent				
		%					cmol (p^+) kg^{-1}						
P1	0-20	35.2	52.5	12.3	6.6	0.64	7.04	7.14	3.12	3.80	0.22	4.02	54
	20-40	16.7	65.4	17.9	6.4	0.49	7.34	7.99	3.12	4.55	0.32	4.87	62
	40-75	75.6	18.0	6.4	6.4	0.13	4.41	5.46	2.71	2.53	0.22	2.75	57
	75-105	80.7	14.2	5.1	6.6	0.05	4.45	5.53	2.49	2.88	0.16	3.04	65
	105-130	87.7	6.9	5.4	6.7	0.13	4.59	4.35	1.69	2.55	0.11	2.66	56
P2	0-20	15.2	71.3	13.5	6.5	0.48	6.77	7.45	3.72	3.42	0.31	3.73	51
	20-40	15.2	64.7	20.1	6.4	0.43	7.47	6.57	3.19	3.16	0.22	3.38	42
	40-60	58.3	32.5	9.2	6.3	0.16	4.95	6.4	3.19	3.10	0.11	3.21	63
	60-75	87.7	6.1	6.2	6.5	0.14	3.13	5.14	2.80	2.23	0.11	2.34	71
	75-125	90.8	5.4	3.8	6.5	0.11	3.23	4.52	2.66	1.75	0.11	1.86	54
P3	0-18	28.3	52.4	19.4	6.1	0.79	5.83	7.82	3.89	3.68	0.25	3.93	63
	18-40	63.1	26.9	10.0	5.9	0.11	5.23	7.12	3.79	3.02	0.31	3.33	58
	40-70	3.0	74.3	22.8	6.0	0.32	5.77	7.84	4.27	3.26	0.31	3.57	56
	70-90	41.9	47.9	10.2	5.6	0.17	4.97	7.16	4.01	2.84	0.31	3.15	57
	90-136	6.8	55.0	38.2	6.0	0.72	9.29	12.41	6.49	5.41	0.51	5.92	58
P4	0-23	15.1	58.4	26.5	5.4	0.62	6.98	9.24	3.69	4.96	0.59	5.55	71
	23-46	21.5	57.6	20.9	5.4	0.18	4.67	7.47	4.40	2.76	0.31	3.07	59
	46-90	16.2	59.6	24.2	5.3	0.25	4.72	7.25	4.11	2.83	0.31	3.14	60
	90-121	83.5	5.2	11.3	5.5	0.04	3.36	6.28	4.25	1.78	0.25	2.03	53
	121-153	72.3	10.2	17.5	5.4	0.22	3.90	6.31	4.01	1.99	0.31	2.3	51
P5	0-25	56.7	27.2	16.1	4.7	0.89	5.05	6.14	3.93	1.86	0.35	2.21	37
	25-48	15.8	55.4	28.8	5.1	0.23	5.45	5.43	3.69	1.44	0.30	1.74	26
	48-70	17.2	51.5	31.3	5.4	0.14	5.96	6.23	4.27	1.66	0.30	1.96	28
	70-100	14.1	55.3	30.6	5.2	0.09	6.67	7.47	4.36	2.65	0.46	3.11	40
	100-115	80.7	14.2	5.1	5.3	0.04	4.76	4.63	1.36	2.11	0.16	2.27	44
P6	0-25	1.0	74.0	25.0	5.3	1.14	10.56	10.73	5.82	4.64	0.27	4.91	44
	25-55	4.3	46.2	49.6	6.1	0.42	9.79	9.33	5.45	3.72	0.16	3.88	38
	55-85	6.4	41.2	52.4	6.0	0.29	7.87	9.78	6.45	3.22	0.11	3.33	41
	85-120	4.0	53.9	42.1	6.1	0.18	5.47	8.23	5.82	2.25	0.16	2.41	41

Pedogenic index

The vertical distribution of some soil properties in each pedon as well as across the landforms was the basis for development of pedogenic indices (Table 3, Fig 3) and are described below:.

Particle size ratio

The average sand/silt ratio followed the sequence of P2 (6.69) > P4 (4.81) > P1 (4.70) > P5 (1.73) > P3 (0.78) > P6 (0.08). The lower the sand/silt ratio, the higher is the maturity of soils indicating relatively higher profile development as is evidenced in soils of older flood plains under current fallow land use (P6). Whereas, soils of active flood plains under current fallow land use have least developed horizons. The sand/ silt ratio had a gradual increasing trend with depth in soils of active flood plains (P1 and P2) (Sidhu *et al.,* 1976; Ray *et al.,* 1997). Vertical distribution of sand/ silt ratio in soils of younger flood plains had an irregularly increasing trend with depth of soils, indicating little influence of pedogenic processes in the formation of soils of active flood plains. In soils of older flood plains, lithological discontinuity has only been seen in P5 at a depth below 100 cm, which was absent in P6. As a result, a gradual increasing trend of sand/ silt ratio with depth of soil has been observed in both P5 and P6 in soil control section, showing relatively higher degree of maturity as compared to soils of the other two landforms. Silt/ clay ratio had a sequence of P1 (2.96) = P3 (2.96) > P1 (2.89) > P5 (1.97) > P4 (1.69) > P6 (1.49). Though, soils on older flood plains had lower silt/ clay ratio as compared to that in younger and active flood plains, an irregularity in their vertical distribution was observed in all the profiles. Secondly, the dominance of silt fraction over the clay in most of the sub-surface horizons of younger and older flood plains resulted in irregularity in silt/clay ratios with increasing depth. VFS/ TS (0.44-2.98) and FS/ TS (0.24-1.12) showed an increasing trend from active flood plains to older flood plains. Average value of FS/ TS followed the sequence of P6 (0.70) > P5 (0.69) > P4 (0.58) > P2 (0.54 > P3 (0.51) > P1 (0.31), whereas, VFS/ TS follows the order of P6 (2.11) > P3 (2.05) > P5 (1.83) > P4 (1.21) > P2 (1.08) > P1 (0.58). Least values of VFS/ TS and FS/ TS in active flood plains were indicative of least profile development and hence least maturity of soils. Presence of finer sand fraction in soils of older flood plains is once again, indicative of their more relative maturity of soils as compared to other landforms.

The interpretation of particle size ratio showed that there was a relative increase in coarse fractions (sand and silt) soils in active flood plains and finer fractions (clay, fine and very fine sands) in younger and older flood plains. The

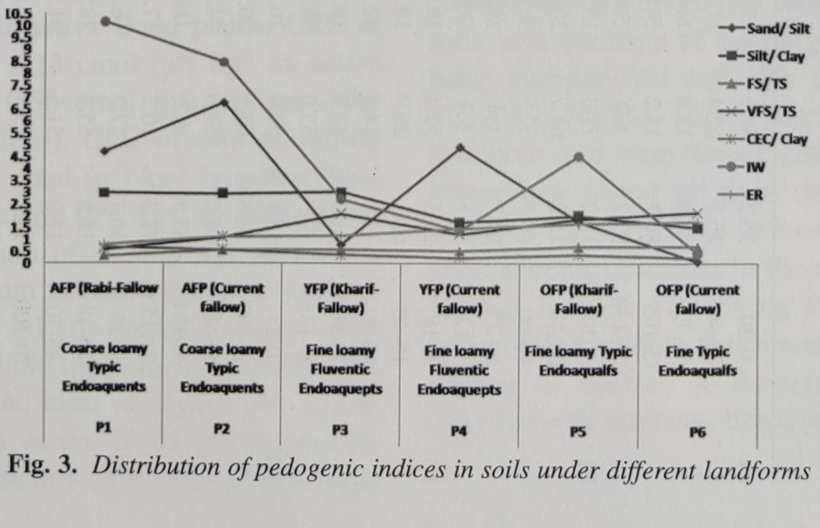


Fig. 3. *Distribution of pedogenic indices in soils under different landforms*

hydromorphic behaviour was persistent even under the predominance of coarse fractions of soils due to prolonged inundation of soils under active flood plains. On the other hand, translocation of finer fractions in soils of younger and older flood plains facilitates developing impeded drainage situations.

Chemical and exchange ratio

The weighted average of CEC/ clay ratio in control section (0-100 cm) all soils were more than 0.20, indicating mixed mineralogy of soils in P1 to P6 (Smith, 1986). The higher values of average CEC/ clay ratio (0.55-0.68) in soils of active flood plains may be attributed to the presence of hydroxy-interlayered vermiculite (HIV) (Bhattacharyya *et al.,* 1997), whereas, in younger and older flood plains, the average values of the same were lower (0.23-0.37), indicating the presence of low activity clays in terms of kaolinite interstratified mixed minerals (Bhattacharyya *et al.,* 2010; 2013b). The CEC/ clay ratio followed the sequence of P1 (0.68) > P2 (0.68) > P5 (0.37) > P3 (0.36) > P4 (0.24) > P6 (0.23). Occurrence of low activity clays in soils of older flood plains (P6) indicates that the soils of this landform are relatively mature compared to the other landforms. It is interesting to note that weathering index followed similar trend that of the CEC/ clay ratio in the sequence, P1 (10.11) > P2 (8.38) > P5 (4.46) > P3 (2.66) > P4 (1.35) > P6 (0.40). It is noteworthy that P5 had an intermediate position, which may be attributed to the occurrence of lithological discontinuity below 100 cm depth. Exchange ratio followed the sequence, P6 (1.74) > P5 (1.64) > P4 (1.45) > P3 (1.14) > P2 (1.11) > P1 (0.77) indicating that soils of active flood plains showed least profile development, whereas soils of older flood plains exhibited higher degree of profile development. The weathering index (IW) values followed the trend, P1 > P2 > P5 > P3 > P4 > P6 (Martini, 1970) indicating that the soils of the older alluvium in general, show higher maturity in profile development compared to the active alluvial plain. There is an exception in the IW value for profile P5 which is higher compared to P3 and P4 which may be attributed to the presence of higher clay per cent.

Classification of hydromorphic soils

Soils on active flood plains (P1 and P2) belonged to coarse loamy textural family owing to having weighted average of clay in the soil control section (0-100 cm) of less than 18%, whereas as, soils on younger flood plains were characterized by fine loamy textural class with weighted average clay content between 18 to 35%. On older flood plains, both fine loamy and fine textural classes (> 35% of weighted average of clay in soil control section) were found. Higher clay content on older flood plains and their increasing trend with depth of soils clearly indicated that clay illuviation is one of the major soil forming processes and the clay increase and its distribution suffices to classify these soils as Alfisols. On the other hand, lithological discontinuity in active flood plains appears to have restricted clay illuviation processes resulting in the formation of Entisols. Soils of younger flood plains showed the presence of cambic B horizon and thus these soils were classified to Inceptisols. Whereas the soils of P1 and P2 (Ap-2ACg-3Cg type of horizon) with hue of 2.5 Y and chroma of 2 or less in sub-surface horizon, having an aquic moisture regime, enabled to classify these soils to Entisols and can be generalized as *Coarse loamy, mixed, hyperthermic* family of *Typic Endoaquents*. Soils of younger flood plains were Inceptisols having cambic and gleyed (Bwg) sub surface horizons with horizon type of Ap-Bwg with aquic moisture regime and presence of endo-saturation were classified as *Fine loamy, mixed, hyperthermic* family of *Typic Endoaquepts,* showing their more relative maturity over the soils on active flood plains. Soils on older flood plains were more matured than younger flood plains as they have both gleyed cambic (Bwg) as well as gleyed argillic (Btg) horizons with dark gray hue (2.5-5Y) and chroma of 1. Formation of stress features in sub surface horizons with occurrence of faint and patchy ferrans and mangans indicate that these soils are Alfisols and can be classified as *Fine loamy, mixed, hyperthermic* family of *Typic Endoaqualfs* (P5) and *Fine, mixed, hyperthermic* family of *Typic Endoaqualfs* (Vadivelu *et al.*, 2003; 2004). The fact that these soils could also be Alfisols has been a revelation in this study (Bandyopadhyay *et al.*, 2014; 2018).

Discussions

It is noteworthy that all these soils comprised endo-saturation with hue 5Y to10 YR and

Table 4. *Pedogenic considerations of soils of the study area*

Pedons	Depth (cm)	Sand/ Silt	Silt/ Clay	FS/ TS	VFS/ TS	CEC/ Clay	ER	IW
P1	0-20	0.67	4.27	0.24	0.44	0.57	0.78	4.65
	20-40	0.26	3.65	0.36	0.67	0.41	0.64	2.29
	40-75	4.20	2.81	0.38	0.70	0.69	0.99	10.77
	75-105	5.68	2.78	0.26	0.48	0.87	0.82	17.11
	105-130	12.71	1.28	0.32	0.59	0.85	0.64	15.74
	Average	**4.70**	**2.96**	**0.31**	**0.58**	**0.68**	**0.77**	**10.11**
P2	0-20	0.21	5.28	0.24	0.47	0.50	1.00	3.71
	20-40	0.23	3.22	0.52	1.03	0.37	0.94	1.85
	40-60	1.79	3.53	0.71	1.41	0.54	0.99	5.85
	60-75	14.38	0.98	0.82	1.63	0.50	1.20	8.14
	75-125	16.82	1.42	0.43	0.86	0.85	1.43	22.37
	Average	**6.69**	**2.89**	**0.54**	**1.08**	**0.55**	**1.11**	**8.38**
P3	0-18	0.54	2.70	0.45	1.58	0.30	0.99	1.55
	18-40	2.35	2.69	0.45	1.58	0.52	1.14	5.23
	40-70	0.04	3.26	0.78	2.76	0.25	1.20	1.11
	70-90	0.87	4.70	0.67	2.37	0.49	1.27	4.78
	90-136	0.12	1.44	0.56	1.97	0.24	1.10	0.64
	Average	**0.78**	**2.96**	**0.58**	**2.05**	**0.36**	**1.14**	**2.66**
P4	0-23	0.26	2.20	0.40	0.95	0.26	0.66	0.99
	23-46	0.37	2.76	0.48	1.13	0.22	1.43	1.07
	46-90	0.27	2.46	0.48	1.13	0.20	1.31	0.81
	90-121	16.06	0.46	0.56	1.32	0.30	2.09	2.63
	121-153	7.09	0.58	0.64	1.51	0.22	1.74	1.27
	Average	**4.81**	**1.69**	**0.51**	**1.21**	**0.24**	**1.45**	**1.35**
P5	0-25	2.08	1.69	0.46	1.22	0.31	1.78	1.95
	25-48	0.29	1.92	0.49	1.29	0.19	2.12	0.66
	48-70	0.33	1.65	0.74	1.97	0.19	2.18	0.61
	70-100	0.25	1.81	0.64	1.69	0.22	1.40	0.71
	100-115	5.68	2.78	1.12	2.98	0.93	0.72	18.30
	Average	**1.73**	**1.97**	**0.69**	**1.83**	**0.37**	**1.64**	**4.46**
P6	0-25	0.01	2.96	0.70	2.11	0.42	1.19	0.40
	25-55	0.09	0.93	0.64	1.94	0.20	1.41	0.29
	55-85	0.16	0.79	0.61	1.86	0.15	1.94	0.31
	85-120	0.07	1.28	0.83	2.53	0.13	2.41	0.59
	Average	**0.08**	**1.49**	**0.70**	**2.11**	**0.23**	**1.74**	**0.40**

Abbreviations: FS/TS-Fine sand/ total sand; VFS/ TS-very fine sand/ total sand; ER-Exchange ratio; IW-Weathering index

Chroma of 2 or less in at least two or more subsurface horizons. Formation of gleyed cambic and argillic horizons were common in these soils. The hydromorphic behaviour is indicated from gleyed sub-surface horizons in all the pedons with occurrence of reduction mottles, iron and manganese depletions in P1, P2, P3 and P4, as well as stress features, ferrans and mangans in P5 and P6. They have been classified under Entisols, Inceptisols and Alfisols orders in successive stages of pedogenesis from active flood plains, younger flood plains to older flood plains. Worldwide, hydromorphic soils are known in varying orders with the commonest one as Histosols (Bouma *et al.,* 1990). Though, in Brahmaputra valley region of Assam, the hydromorphic soils were confined only to three soil orders. The humid sub-tropical climate of the study area may not be conducive for the formation of Histosols, since the soils experiences rapid pedogenic events. Thus, it is apparent that there is a steady pedogenic change in these hydromorphic soils from *Endoaquents* to *Endoaqualfs* with micro-topographic variability of the landscapes. The relatively higher elevation and being at a distance proximity from the fluvial agents, facilitated clay illuviation compared to that for the younger and active flood plains which are in close proximity to the agents of fluvial action.

The hydromorphic behaviours in soils under three different landforms are very complex in nature. The endo-saturation in older flood plains occurred much earlier than it happened in younger and active flood plains. In active flood plains, micro-climatic depressions may be responsible for hydromorphic behaviour of soils. Soils of younger flood plains show an intermediate stage of endo-saturation between that of active and older flood plains. Hence, this study shows that local topographic and micro-climatic variability in the region can greatly influence the hydromorphic behaviour of soils *vis-a-vis* their pedogenesis.

Conclusions

The presence investigation stresses that micro-topographic variations, changes in textural and exchange properties and lithological discontinuity have been identified as the recognizable factors to describe the pedogenesis of hydromorphic soils. The relative elderliness of soils depended upon the pedogenic indices across the landforms and land uses of the study area. The vertical distribution of these indices showed lithological discontinuity in the younger and soils of the active plains was detrimental for the higher pedogenic development in such soils. This type of study can unveil the crucial information needed for proper management and restoration of these soils for their optimal use.

Acknowledgement

The authors gratefully acknowledge the institutional support from the Director, ICAR-NBSS&LUP to conduct the present research work under the project on "Land resource inventory of North West Jorhat development block of Jorhat district, Assam (on 1: 10, 000 scale) using geo-spatial technique".

References

Agricultural Contingency Plan (ACP) - Jorhat District (Assam). 2012. *http://www.crida.in/cp-2012/index.html.* ICAR-CRIDA, Hyderabad, Telengana.

Arnaud, R.J. St. 1988. Application of the 'Pedogenic Index' to soil fertility studies, Saskatchewan. *Geoderma,* **43 (1)**: 21-32.

Assam District Gazetteers. 1979. Gazetteers of India, Assam State. Govt. of Assam, Guwahati, Assam, India.

Bandyopadhyay, S., Dutta, D., Chattopadhyay, T., Reza, S.K., Dutta, D.P., Baruah, U., Sarkar, D. and Singh, S.K. 2014. Characterization and classification of some tea-growing soils of Jorhat district, Assam. *Agropedology,* **24 (2):** 138-145.

Bandyopadhyay, S., Ghosh, B.N., Ray, P, Ramachandran, S., Jena, R.K., Deb Roy, P., Singh, S.K., Mukhopadhyay, S., Nayak, D.C. and Ray, S.K. 2018. Impact assessment of land resource inventory towards optimizing land use plan in Brahmaputra valley ecosystem, Assam, India. *Indian Journal of Soil Conservation,* **46 (1):** 11-24.

Bhaskar, B.P., Baruah, U., Vadivelu, S., Raja, P. and Sarkar, D. 2007. Characterization of depositional soils in dynamic fluvial landforms of Majuli island for land use-related issues. *Agropedology,* **17 (2):** 33-43.

Bhaskar, B.P., Baruah, U., Vadivelu, S., Raja, P. and Sarkar, D. 2010. Remote sensing and GIS in the management of wetland resources of Majuli Island, Assam, India. *Tropical Ecology,* **51 (1):** 31-40.

Bhattacharyya, T., Sarkar, D., Dubey, P.N., Ray, S.K., Gangopadhyay, S.K., Baruah, U. and Sehgal, J. 2004. Soil Series of Tripura. NBSS Publ. No. 111 NBSS&LUP, Nagpur, pp. 115.

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1997. On kaolinitic and mixed mineralogy classes of shrink–swell soils. *Australian Journal of Soil Research,* **35:** 1245–1252.

Bhattacharyya, T, Sarkar, D., Pal, D.K., Mandal, C., Baruah, U., Telpandey, B. and Vaidya, P. H. 2010. Soil information system for resource management – Tripura as a case study. *Current Science,* **99(9):** 1208-1216.

Bhattacharyya, T., Pal, D. K., Mandal, C., Chandran, P., Ray, S.K., Sarkar, Dipak, Velmourougane, K., Srivastava, A., Sidhu, G. S., Singh, R. S., Sahoo, A.K., Dutta, D., Nair, K.M., Srivastava, R., Tiwary, P., Nagar, A.P. and Nimkhedkar, S.S. 2013a. Soils of India: historical perspective, classification and recent advances. *Current Science,* **104** (10): 1308-1323.

Bhattacharyya, T., Pal, D.K., Chandran, P, Ray, S.K., Sarkar, D., Mandal, C. and Telpande, B. 2013b. The Clay Mineral Maps of Tripura and their Application in Land Use Planning. *Clay Research,* **32 (2):** 147-158.

Birkland, P.W. 1984. Topography-soil relationship in Soils and Geomorphology. Oxford University Press, pp. 234-259.

Bouma, J, Fox, C.A. and Miedema, R. 1990. Micromorphology of Hydromorphic Soils: Applications for Soil Genesis and Land Evaluation. *Developments in Soil Science* **19**: 257-278.

Bouma, J. 1983. Hydrology and soil genesis of soils with aquic moisture regimes. L.P. Wilding, N.E. Smeck, G.F. Hall (Eds.), *Pedogenesis and Soil Taxonomy. **I** Concepts and Interactions,* Elsevier, Amsterdam (1983), pp. 253-281

Bouma, J. 1988. Using soil survey data for quantitative land evaluation. In: Advances in Soil Science. B.A. Stewart (Ed.), **Vol. 9:** 177-215.

Gerrard J. 1992. *Soil Geomorphology. An integration of pedology and geomorphology.* Chapman and Hill, p. 269.

Jackson, M.L. 1973. Soil Chemical Analysis. Prentice Hall of India Pvt. Ltd., New Delhi, 498.

Martini, J. A. 1970. Allocation of cation exchange capacity to soil fractions in seven surface soils from panama and the application of a cation exchange factor as a weathering index. *Soil Science,* **109** (5): **324-331.**

Nagaraju, M. S. S., Nirmal Kumar, R. Srivastava and Das, S.N. 2014. Cadastral-level soil mapping in basaltic terrain using Cartosat-1-derived products. *International Journal of Remote Sensing*, **35**, 3764-3781.

Page, A. L., Miller, R.H. and Keeney, D.R. 1982. Methods of Soil Analysis. Part-II. Chemical and Microbiological Properties. *American Society of Agronomy*, Madison, Wisconsin, USA.

Pratt, P.F. and Alvahydo, R. 1966. *Cation exchange characteristics of soils of Saopaulo, Brazil.* IRI Research Institute, Inc., Bull. **31,** New York, p. 31.

Piper, C.S. 1966. Soil and Plant Analysis. Hans Publisher, Bombay, India.

Ray, S.K., Reddy, R.S. and Budihal, S.L. 1997. Vertisols and associated soils development and lithological discontinuity in Coastal Godavari delta region. *Journal of the Indian Society of Coastal Agricultural Res*earch XV(1): 1-14.

Schaetzl, R.J. and Thompson, M.L. 2015. *Soils - Genesis and Geomorphology*. 2nd Edition. Cambridge University Press, New York.

Sen, T.K., Chamuah, G.S., Sehgal, J. and Velayutham, M. 1999. Soils of Assam for Optimizing Land Use. NBSS Publ.66b (Soils of India Series), National Bureau of Soil Survey and Land Use Planning, Nagpur, India, - 51p.

Sidhu, P.S., Hall, G.E. and Sehgal, J.L. 1976. Studies on some soils at varying stages of Pedogenic Development in the Central Punjab. *Journal of Reseach (P.A.U)* **13** (1) : 23-33.

Singh, S.K., Chaterjee, S., Chattaraj, S. and Butte, P.S. 2016. Land Resource Inventory on 1:10000 scale, Why and How? *NBSS Publ.* **172,** *ICAR-NBSS&LUP, Nagpur, India*, 94 p.

Smith, G.D. 1986. *The Guy Smith Interview:* Rationale for concepts in Soil Taxonomy. *SMSS Technical Monograph No.* **11**, SMSS, SCS, USDA.

Soil Survey Staff. 2003. *Soil Taxonomy*. Agricultural Handbook, **436**, 3rd Edition, USDA, Washington, DC.

Soil Survey Staff.1998. Soil taxonomy: a basic system of soil classication for making and interpreting soil surveys, USDA-SCS Agricultural Handbook No. **436,** 2nd edn. U.S. Govt, Printing Ofce, Washington, DC.

Soil Survey Staff. 2014. *Keys to soil Taxonomy*, 12th Edition. NRCS, USDA, Washington DC.

Sparks, D.L. 1996. *Methods of Soil Analysis.* Part 3: *Chemical Methods.* Soil Science Society of America Inc., American Society of Agronomy Inc., Madison, Wisconsin, USA.

Srivastava, R. and Saxena, R.K. 2004. Techniques of large scale soil mapping in basaltic terrain using satellite remote sensing data. *International Journal of Remote Sensing*, **25 (4):** 679-688.

Statistical Handbook, Assam. 2015. Directorate of Economics and Statistics, Planning & Development Department, Guwahati, Assam.

Vadivelu, S., Baruah, U., Bhaskar, B.P., Thampi, J., Walia, C.S., Sarkar, D. and Nayak, D.C. 2003. A land use plan for Jorhat district of Assam. *Agropedology* **13,** 1-10.

Vadivelu, S., Baruah, U., Bhaskar, B.P., Mandal, C., Sarkar, D., Walia, C.S. and Gajbhiye, K.S. 2004. *Soil Resource Atlas, Jorhat District (Assam),* NBSS Publ. **107**, ICAR-NBSS & LUP, Nagpur, India.

Van Reeuwijk, L.P. 1993. *Procedures for Soil Analysis*. ISRIC. Wageningen, the Netherlands.

Velayutham, M., Mandal, D.K., Mandal, C. and Sehgal, J.L. 1999. *Agro-ecological Sub Regions of India for Planning and Development. NBSS Publ.* **35**, NBSS & LUP (ICAR), Nagpur, India.

Walkley, A. and Black, I. A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science,* **37**, 29-38.

(Received June 2018; Accepted August 2018)

Clay Research, Vol. 36, No. 2, pp. 90-105 (2017)

Ca-zeolites as Transitory Eco-System Engineers: Hydro-Pedological Evidence in Cracking Clay Soils (Vertisols) of Semi-Arid Marathwada Region, Maharashtra

SWATI P. ZADE*[1], P. CHANDRAN [2]AND D. K. PAL[3]

[1]Assistant Professor, College of Agriculture, Vasantrao Naik Marathwada Krishi Vidyapeeth, Parbhani
[2]Present and [3]Former Principal Scientist, Indian Council of Agricultural Research-National Bureau of Soil Survey and Land Use Planning, Nagpur

Abstract– *Out of the area under cracking clay soils (Vertisols) in Peninsular India, nearly 5.6 % is occupied by Vertisols in the state of Maharashtra. Research endeavors on the genesis and management of Vertisols of semi-arid tropical (SAT) climate was accomplished during the last few decades for major regions of Maharashtra except Marathwada. But such effort needs to be extended to this region as precise information on the physical and chemical characteristics associated with the hydro-pedology of Vertisols developed in the alluvium of the Deccan trap basalt of the Marathwada region is not adequate enough to suggest appropriate management protocols to enhance their productivity. Majority of the Marathwada region support rain-fed agriculture with low productivity. Therefore, systematic studies on the SAT Vertisols of Marathwada region are warranted to know the extent of regressive pedogenetic processes that are operative in SAT Vertisols of this region and also to develop cause-effect relationship of natural soil degradation (if any) in presence of soil modifiers or ecosystem engineers like Ca-zeolites. Ten SAT Vertisols were selected in the districts of Buldhana, Parbhani, Osmanabad, Beed, Jalna and Aurangabad of Maharashtra state. These Vertisols contain Ca-zeolites in their basaltic parent materials. Ca- zeolites are considered as prolonged ecosystem engineers in supporting the successful enterprise for forestry, horticultural and cereal crops, and spices in non-calcareous and acidic Vertisols, Alfisols and Mollisols developed on the Deccan basalt or in its alluvium under the humid tropical climate of the Western Ghats and Satpura Regions for the several millions of years. In contrast, SAT Vertisols of Marathwada showed contrasting physical and chemical characteristics so much that their US Soil Taxonomic classes are Typic Haplusterts and Sodic Haplusterts. Due to the dominant pedogenetic processes like the formation of pedogenic $CaCO_3$ (PC) and illuviation of Na-saturated fine clays, some Typic Haplusterts showed more exchangeable Mg percentage (EMP) than exchangeable Ca percentage (ECP) in their Bss horizons, which caused lowering of saturated hydraulic conductivity (sHC) at a value little over 10 mm hr^{-1}, preventing strong swelling of plasmic fabric and rise of pH near to 8.2 and above. Zeolites could not prevent the lowering of exchangeable Ca/Mg ratio < 1.5 almost throughout depth, rise in pH, exchangeable Na percentage (ESP) and EMP, weak swelling of plasmic fabric and reducing the sHC $<< 10$ mm hr^{-1} in Sodic Haplusterts. This anomalous chemical environment in SAT Vertisols appears to be related to zeolite reserve and the rate of Ca ions release from zeolites amidst the formation of PC as the major pedogenetic process. Selective analytical method to quantify the amount of soil Ca-zeolites is still not available and in its absence the anomalous situation will continue to baffle the researchers. The rate of formation of PC must have been much higher than the rate of release of Ca ions from zeolites in SAT environments as evidenced from the impaired soils' hydraulic properties. This kind of hydro-pedological process would not support the irrigationpractice to raise agricultural crops including sugarcane in the Marathwada region of Maharashtra. Ca-zeolites have proved their worthiness as prolonged ecosystem engineers while supporting successful enterprise for various land uses in the Deccan basalt derived non-calcareous and acidic soils of the humid tropical (HT) climate. Since Ca-zeolites losetheir significance in the*

Corresponding Author Email : spzade@yahoo.co.in

contemporary dominant hydro-pedological processes (regressive pedogenesis) theywould remain as transitory ecosystemengineers in SAT Vertisols of the Peninsular India in general and Marathwada region in particular.

Key words: SAT Vertisols, Marathwada, Maharashtra, Zeolites as eco-system engineers, Hydro-pedological evidence, Regressive pedogenesis, Natural soil degradation

Cracking clay soils (Vertisols) occupy 26.62% of the total geographical area of Peninsular India, andMaharashtra has a share of 5.6% of this area (Pal *et al*., 2012a). Extensive research on the genesis and management of Vertisols of SAT climate has been made during the last two and a half decades (Pal, 2017) for major regions of Maharashtra except in the Marathwada region. Precise information on the physical and chemical characteristics associated with pedogenetic processes of Vertisols developed in the alluvium of the Deccan trap basalt of the Marathwada region is scanty. Adequate knowledge in this regard forms the basic necessity forplanning better use and management of SAT soils because in the present SAT climate, Ca^{2+} ions are removed from exchangeable complex and get precipitated as pedogenic carbonates (PC) due to reduced pCO_2 in the soil system (Pal *et al*., 2000, Pal *et al*., 2001, Srivastava *et al*., 2002). This has resulted in the increase in ESP and EMP with depth, which cause dispersion of fine clay smectites, and thus pose problem of blocking macro- and micro pores and poor drainage. Such unfavorable physical and chemical environments make SAT Vertisols less productive for agricultural crops. However, due to the improvement in hydraulic properties caused by the occasional presence of natural modifiers like Ca-zeolites (as constituents of the basaltic parent material), many agricultural crops often grow well in these soils under both rain-fed and irrigation conditions. Ca-zeolites provide enough of Ca^{2+} ions in soil solution and improve the hydraulic properties of the soils even in high ESP (>5) and also in preventing the enhancement of pH and ESP or EMP (Pal *et al*., 2003a).

Majority of the SAT Vertisols of Marathwada region support rain-fed agriculture with low productivity and there are several challenges in improvingthe livelihoods of the rural poor. Therefore, systematic studies on the SAT Vertisols of Marathwada region are warranted to develop cause-effect relationship of natural soil degradation (if any) in probable presence of Ca-zeolites. It is also not known yet how long Ca-zeolites can act as ecosystem engineers in improving hydraulic properties that can help in better movement of rain water in the soil profile, and storing in the subsoils and releasing the stored soil water for crops between the rains. Obviously, this knowledge base is likely to help in making proper management interventions to improve their soil properties conducive for better agricultural land uses.

Materials and Methods

Ten SAT Vertisols were selected in the districts of Buldhana, Parbhani, Osmanabad, Beed, Jalna and Aurangabad, representing the major districts of Marathwada region (Table 1) that are developed in the alluvium of the Deccan basalt. The characteristics of each pedon and its individual horizons were described following the standard procedure (Soil Survey Division Staff, 1993). Particle size distribution was determined by the international pipette method after the removal of organic matter, $CaCO_3$ and free Fe oxides. Sand (2000-50 µm), silt (50-2 ìm) and clay fractions (<2 µm and <0.2 ìm)were separated using the size segregation procedure of Jackson (1979). Soil saturated soil paste was made and the saturation extracts were prepared as per procedure outlined by Richards (1954). The EC of the saturation extract were (ECe) determined by using conductivity bridge. Saturation extract were analyzed for their ionic composition as described by Richards (1954).

The $CaCO_3$, pH, cation exchange capacity (CEC), exchangeable Na and K were determined on total fine earth (<2mm) by standard methods (Richards, 1954). Carbonate clay (Shields and Meyer, 1964) was determined by gravimetric loss of carbon dioxide using Collin's calcimeter. Exchangeable calcium and magnesium were determined from <2 mm sieved samples by leaching with 1N NaCl solution (Piper, 1950) and titrating the leachate against saturated EDTA solution as per the method of Richards (1954).The saturated hydraulic conductivity (sHC) was determined by constant head method as describedby Richards (1954). For identification of clay minerals, the silt and clay fractions were subjected to X-ray examinations of the parallel oriented samples saturated with Ca and K, using a Philips diffractometer with Ni filtered CuKα radiation at a scanning speed of 2 degree 2ε/ min. Glycolation and different thermal pretreatments as required were given to distinguish and confirm the type of minerals present (Jackson, 1979). Undisturbed soil blocks (8cm long, 6cm wide and 5cm thick) were collected from soil horizons, and thin sections were prepared by the methods of Jongerius and Heintzberger (1975). They were described according to the nomenclature of Bullock *et al.* (1985).

Results

Morphological Properties

Vertisols under study are deep to very deep (100 to more than 150 cm), very darkgray to dark yellowish brown (10YR 3/1.5 to 10YR 4/ 4), moderately to highly calcareous throughout the depth and have peds that broke into small sub angular blocky to angular blocky peds.Both sphenoids and slickensides observed in the field confirm the presence of slickensided B horizons (Bss) (Soil Survey Staff, 1999), which also occur beyond 100cm (Table 1). Typical cracks of Vertisols were 2 to 5 cm wide at the surface and extended upto a depth to 60 cm and beyond.Such deep cracklings are generally seen when subsoils are alkaline and have impaired drainage (Pal, 2017). Detailed morphological descriptions are available elsewhere (Zade, 2007; Zade *et al.*, 2017).

Physical Properties

These soils contain very small amount of sand (<5%) but are highly clayey containing < 40 % to as high as 75% < 2µm clay fractions. The fine clay fractions (< 0. 2µm) constitute from 30% to 76 % of the < 2µm clay (Table 2). The total clay content shows more than 8% clay in the Bss horizons than in the Ap horizons. The ratio of fine clay to total clay (FC/TC) in the Bss horizons is greater than 1.2 times than the ratio in the Ap horizon. Depth distribution of total and fine clays suggests the clay illuviation process which enriched the Bss horizons (Soil Survey Staff, 2003).The fine clays are low charge di-octahedral smectites and nearer to montmorillonite in the montmorillonite-nontronite series (Zade *et al.*, 2017).This suggests that any management protocol to enhance the hydrological properties of these SAT soils requires due attention to the presence of this type of smectite with very high co-efficient oflinear expansion (COLE) (0.2-0.3, Zade, 2007), especially when soils may have unfavorable cations like Mg and Na on their exchange complex (Pal, 2017).

The saturated hydraulic conductivity (sHC) of soils varies enormously within and among the ten Vertisols(Table 2). It decreases gradually with depthin soils at Chandaj of Parbhani district (Pedon 1), Satgaon of Buldhana district (Pedon 2), Adgaon of Jalna district (Pedon 4), Patrud of Beed district (Pedon 12), Raurgaon of Beed district (Pedon 13) and its weighted mean (WM) value within first 1m soil depth ranges from 17

Table 1: *General properties of the Vertisols selected from different districts and their mean annual rainfall (MAR)*

Pedon No.	Soil Series (Soil Taxonomy) (District)	Parent Material	Latitude	Longitude	*MAR (mm)
1	Chandaj (Typic Haplusterts) (Parbhani)	Basaltic alluvium with zeolites	19°32'42" N	76°42'20" E	957
2	Satgaon (Typic Haplusterts) (Buldhana)	Basaltic alluvium with zeolites	20°23'53" N	76°13'45" E	899
3	Kalegaon (Sodic Haplusterts) (Jalna)	Basaltic alluvium with zeolites	19°49'15" N	75°59'57" E	840
4	Adgaon (Typic Haplusterts) (Jalna)	Basaltic alluvium with zeolites	20°27'32" N	75°49'20" E	840
5	Khasgaon (Sodic Haplusterts) (Osmanabad)	Basaltic alluvium	18°14'59" N	75°29'31" E	809
6	Nali Wadgaon (Sodic Haplusterts) (Osmanabad)	Basaltic alluvium with zeolites	18°35'58" N	75°30'29" E	809
10	Bhalgaon (Sodic Haplusterts) (Aurangabad)	Basaltic alluvium with zeolites	19°49'38" N	75°28'42" E	792
11	Babhulgaon (Sodic Haplusterts) (Aurangabad)	Basaltic alluvium with zeolites	20°02'40" N	74°58'03" E	792
12	Patrud (Typic Haplusterts) (Beed)	Basaltic alluvium with zeolites	19°04'15" N	76°12'10" E	685
13	Raurgaon (Typic Haplusterts) (Beed)	Basaltic alluvium with zeolites	18°45'43" N	75°42'20" E	685

*MAR – Mean Annual Rainfall

to 44mm hr^{-1} (Table 2). On the contrary, the decrease of sHC is very sharp in soils at Kalegaon of Jalna district (Pedon 3), Khasgaon of Osmanabad district (Pedon 5), at Nali Wadgaon of Osmanabad district (Pedon 6), at Bhalgaon of Aurangabad district (Pedon 10) and Babhulgaon of Aurangabad district (Pedon 11). Its WM value ranges from< 1 to 9 mm hr^{-1}. Pal *et al.* (2006) brought out a fact that an optimum yield of cotton in Vertisols of SAT part of Central India can be obtained when the soils are non-sodic (ESP<5) and have sHC ≥ 20 mm h^{-1}. These authors also reported 50% reduction in yield in the sodic (ESP>5) soils and with sHC<10mm $h^{"1}$,and this study also permitted to advocate a value of sHC<10mm h^{-1} in distilled water(weighted mean in 0–1m depth of soil) to define a sodic soil. The differential hydraulic properties of Vertisols under study clearly indicate that both physical and chemical environments are not similar even though these Vertisols are developed in SAT environment. It is expected that the possible presence of Ca-zeolites might have modified soil properties (Pal *et al.*, 2006).

Chemical Properties

Vertisols under study contain around 1% organic carbon (OC) in their surface horizons (Zade, 2007) and are mildly to strongly alkaline in reaction.Soils those are strongly alkaline in nature (pH > 8.5), show very low sHC (< 10 mm hr^{-1}), and their exchangeable sodium percentage (ESP) ranges from > 5 to > 15. And soils those are moderately alkaline (pH ≤ 8.5), have sHC >> 10 and their ESP values are < 5. Soils are not saline as their ECe values are much less than 4 dS m^{-1} (Tables 2 and 3). Although all soils are calcareous, soils with pH > 8.5, contain more $CaCO_3$ (< mm) than soils those have pH < 8.5, and their clays (< 2μm) also contain $CaCO_3$ (Table 3). The CO_3 clay constitutes as high as 31% of the total soil $CaCO_3$ content, suggesting that the calcification is the major pedogenetic process. It is interesting to note that although

Table 2: *Some physical and sodicity related chemical properties of soils*

Depth (cm)	Exch. Ca/Mg	ECP	EMP	ESP	sHC mm hr^{-1}	< 2µm clay fraction %	< 0.2µm clay fraction %	< 0,2µm clay /< 2µm clay %
Pedon 1 : Chandaj (Parbhani) –Typic Haplusterts								
Ap(0-13)	4.8	80	17	0.8	30	64	19	30
Bw1(13-28)	5.8	83	14	0.5	49	69	25	36
Bw2(28-45)	5.2(4.6)*	82	16	0.5	56(44)**	70	42	60
Bss1(45-75)	4.5	80	18	0.4	42	70	45	64
Bss2(75-108)	3.7	77	21	0.6	42	70	47	67
Pedon 2 : Satgaon (Buldhana) - Typic Haplusterts								
Ap(0-6)	3.1	73	23	1.3	15	65	31	48
Bw1(6-19)	2.9	73	25	1.2	84	64	33	51
Bw2(19-35)	2.9(2.1)*	73	25	1.6	40(43)**	66	34	51
BC(35-51)	2.2	67	31	1.7	50	66	37	56
Bss(51-118)	1.5	58	39	1.6	34	74	46	62
Crk(118-130+)	1.3	53	42	3.7	9	60	22	37
Pedon 3 : Kalegaon (Jalna) – Sodic Haplusterts								
Ap(0-14)	2.0	65	32	1.4	10	42	13	31
Bw1(14-36)	1.6	57	36	4.8	12	46	15	33
Bw2(36-57)	1.3(1.2)*	51	39	7.9	4(5)**	47	16	34
Bss1(57-87)	0.8	37	48	12.5	.0..3	49	20	41
Bss2(87-114)	0.7	34	47	17.9	0.3	44	16	36
C(114-130+)	0.8	38	44	17.7	1	13	9	69
Pedon 4 : Adgaon (Jalna) Typic Haplusterts								
Ap(0-12)	2.9	71	24	1.0	17	49	13	26
Bw1(12-33)	1.9	63	33	1.1	32	53	24	45
Bw2(33-49)	1.4(1.5)*	56	40	1.6	33(32)**	67	34	51
Bss1(49-82)	0.9	46	51	1.9	41	77	31	40
Bss2(82-105)	1.1	50	46	2.5	24	78	32	41
C(105-129+)	1.1	51	45	2.4	25	45	13	29
Pedon 5 : Khasgaon (Osmanabad)- Sodic Haplusterts								
Ap (0-14)	2.0	64	32	3.2	08	59	38	64
Bw1(14-30)	1.8	61	33	4.5	10	58	39	67
Bw2(30-53)	2.6(2.4)*	68	26	6.1	12(9)**	62	44	71
Bss1 (53-77)	2.9	68	27	7.2	10	63	48	76
Bss2(77-102)	2.3	64	28	7.6	9	60	44	73
Bw1 (102-150)	1.5	56	36	5.9	9	56	33	59
Pedon 6 : Nali Wadgaon (Osmanabad) – Sodic Haplusterts								
Ap (0-13)	1.4	56	40	3.0	12	50	35	70
Bw1 (13-33)	1.0	48	46	4.1	11	52	15	29
Bw2 (33-53)	0.8(0.76)*	41	53	5.7	9(9)**	57	43	75
Bss1 (53-82)	0.5	31	63	4.6	8	62	47	76
Bss2(82-99)	0.5	33	61	5.2	5	61	46	75
Bss3 (99-150)	0.6	34	60	4.7	4	67	48	72
Pedon 10 : Bhalgaon (Aurangabad)- Sodic Haplusterts								
Ap (0-12)	1.4	48	35	12.9	2	30	8	27
Bw1 (12-33)	0.9	38	43	14.8	0.1	37	12	32
Bw2 (33-62)	0.8(0.83)*	33	41	22.6	0.8(<1)**	39	14	36
Bss1 (62-88)	0.8	31	39	25.4	0.8.	42	16	38

Table 2. *Continued*

Depth (cm)	Exch. Ca/Mg	ECP	EMP	ESP	sHC mm hr^{-1}	< 2µm clay fraction %	< 0.2µm clay fraction %	< 0,2µm clay /< 2µm clay %
Bss2(88-123)	0.5	24	44	29.1	0.1	51	18	35
Bss3 (123-150)	0.5	20	40	37.3	0.1	46	17	37
Pedon 11 : Babhulgaon (Aurangabad) - Sodic Haplusterts								
Ap (0-15)	1.1	48	45	2.4	5	33	11	33
Bw1 (15-34)	0.8	41	49	4.0	.5	32	13	40
Bw2 (34-72)	0.5(0.62)*	27	58	11.1	1(2)**	38	16	42
Bss1(72-97)	0.4	21	60	15.8	1	39	18	46
Bw3 (97-130)	0.3	22	65	9.7	1	29	13	49
Bw4 (130-160)	0.4	22	63	12.5	1	26	13	50
Pedon 12 : Patrud (Beed)- Typic Haplusterts								
Ap (0-13)	4.6	79	17	1.1	7	43	14	32
Bw1 (13-36)	3.2	75	23	0.7	14	49	17	35
Bw2(36-61)	2.8(2.8)*	72	25	0.3	14(26)**	48	16	33
Bss1 (61-104)	2.1	65	31	0.9	27	49	16	33
Bss2 (104-140)	1.5	60	39	0.2	42	51	16	31
Bss3 (140-160)	1.7	61	35	0.9	34	59	24	41
Pedon 13 : Raurgaon (Beed) - Typic Haplusterts								
Ap (0-14)	3.1	73	24	0.5	31	69	24	35
Bw1 (14-28)	2.1	66	32	0.9	29	71	30	42
Bw2 (28-43)	1.7(1.5)*	62	35	1.5	19(17)**	72	35	49
Bss1 (43-85)	1.1	50	46	1.8	10	72	35	49
Bss2 (85-130)	0.6	38	59	1.4	8	75	38	51
Bss3 (130-150)	0.5	33	63	2.8	6	58	21	36

*Weighted mean value of exchangeable Ca/Mg in the 0-1m depth of soil

**Weighted mean value of sHC in the 0-1m depth of soil

sodification of SAT Vertisols under study is observed but it is restricted in soils of Jalna (Pedon 3), Osmanabad (Pedon 5 and Pedon 6) and Aurangabad (Pedons 10 and 11) districts, and the soils of Parbhani (Pedon1), Buldhana (Pedon2), Jalna (Pedon 4) and Beed (Pedon 12 and Pedon 13) are free from sodicity. Judging by their pH, ECe and sHC, soils of pedons 3, 5, 6, 10 and 11 qualify as Sodic Haplusterts, and the soils of pedons 1, 2, 4, 12 and 13 as Typic Haplusterts on the basis of observations made by Pal *et al*. (2006) who advocated a value of sHC<10mm h^{-1} (as weighted mean in the first 1m of soil) instead of ESP or sodium adsorption ratio (SAR) to define a sodic soil. Their study reaffirms a fact that the decisive feature of soil classification must be evidently the crop performance because it indicates the nature of soil much more explicitly than any other arbitrary definition and nomenclature possibly can claim to do.

Zeolites and their Implication in sHC

Several reviews have been published about the occurrence and properties of zeolites in soils (Pal *et al.*, 2013a; Bhattacharyya *et al.*, 2015). Among the commonly occurring species of zeolites, Si-poor Ca -rich heulandite is widely distributedin cracking clay soils developed in the alluvium of the weathering Deccan basalts (Bhattacharyya *et al.*, 2015). Zeolites have the ability to hydrate and dehydrate reversibly and to exchange some of their constituent cations and thus, can influence the pedo-chemical and hydro-pedological environments during the formation of soils.

It is a fact that there is no selective method to quantify the heulandite in soils which have other clay minerals. But the qualitative presence of heulandite in soils developed in Deccan basalt alluvium could be made by a simple method (Bhattacharyya *et al.*, 1999). These researchers determined the CEC and extractable bases that provide indications for the possible presence of zeolites in soils. They determined the CEC of acidic and zeolitic soils using 1 N NaOAc (pH 7) for saturating the soils, and 1 N NH_4OAc (pH 7) for exchanging the Na^+ ions; and the CEC was determined by estimating the adsorbed Na^+ ions (Richards 1954). But for the calcareous, and slight to moderately alkaline Vertisols, determination of extractable Ca and Mg is done following 1 N NaCl solution extraction method (Piper 1966) and for Na and K, 1 N NH_4OAc (pH 7) (Pal *et al.*, 2006) is used. The base saturation (BS) calculated using CEC and extractable bases exceeds ≥ 100 either throughout the pedon depth or in the sub-soils. Vertisols under study have BS ≥ 100 (Table 3), confirming the presence of zeolites in general and heulandite in particular. Presence of zeolites in the silt and coarse clay fractions along with other clay and primary minerals, was further confirmed by the XRD technique (Figs. 1 and 2)as demonstrated by Bhattacharyya *et al.*(1993,1999). Micro morphological soil thin sections studies also indicated the presence of zeolites (Fig. 3).

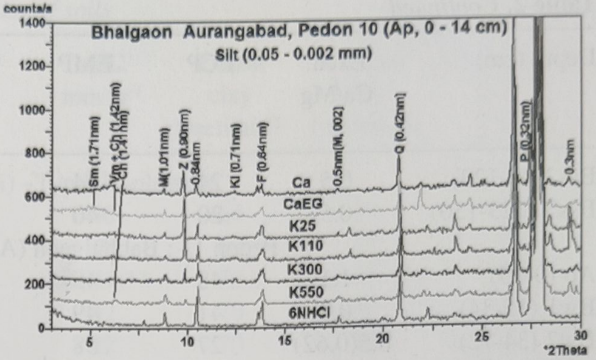


Fig. 1. *XRD patterns of the silt fraction as representative of Typic and Sodic Haplusterts. Ca=Ca saturated, CaEG=Ca saturated plus glycol vapour, 25/110/300/550°C=K saturated and heated to 25°C, 110°C, 300°C and 550°C, 6NHCl= HCl treated silt, Sm=Smectite, Vm=Vermiculite, Ch=Chlorite, M=Mica, Kl=Kaolin, F=Feldspar, Q=Quartz, Z=Zeolite, P=Plagioclase*

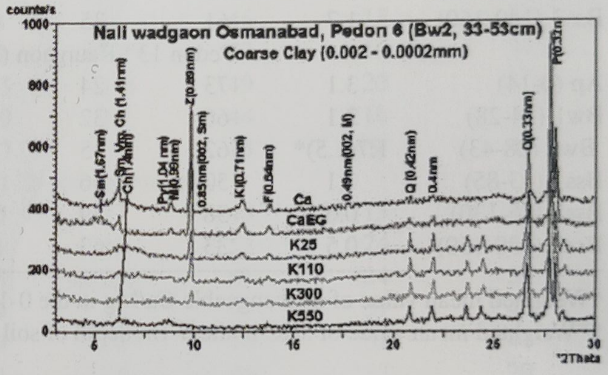


Fig. 2. *XRD patterns of the coarse clay fractions as representative of Typic and Sodic Haplusterts. Ca = Ca-saturated, CaEG = Ca-saturated plus glycol vapour, K25/110/300/550°C = K-saturated and heated to 25°C, 110°C, 300°C and 550°C, K300EG= K-saturated plus ethylene glycol vapour and heated at 300°C, Sm= smectite, Vm=vermiculite, Ch=chlorite, Py=palygorskite, M=mica, Z=zeolite, Kl=kaolin, Q = quartz, F=feldspars, P=plagioclase.*

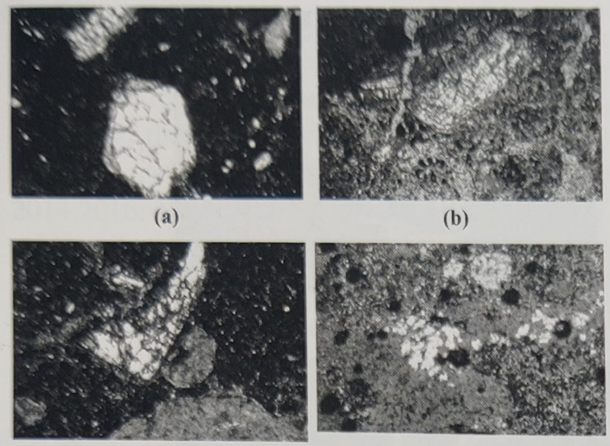
It is well known that many productive Vertisols under rainfed conditions have been rendered unproductive for agriculture when they are irrigated in thelonger-term. However, some zeolitic SAT Vertisols at Pahur and Loni of Yavatmal district, and at Vasmat of Hingoli district (Pal *et al.*, 2003a) have been irrigated through canals for the last twenty years toproduce sugarcane. These soils lack salt-efflorescence on the surface unlike the sodic soils of the NW parts of the Indo-Gangetic Alluvial Plains, and are not waterlogged at present. This may apparently suggest that these soils are notdegraded due to their better drainage even these soils are nowSodic Haplusterts in view of their pH, ECe and ESP values. Interestingly, theyhave sHC>10 mm hr^{-1}. A constant supply of Ca^{2+} ions from

Table 3. *Chemical properties of soils*

Hori-zon	Depth (cm)	pH (1:2) H_2O	ECe dS m^{-1}	O. C. %	Calcium carbonate equivalent as $CaCO_3$ <2 mm (%)	Carbonate clay % on fine earth basis	Extractable bases				Sum of cations	CEC cmol(p+) kg^{-1}	Base saturation %
							Ca	Mg	Na	K			
							←		cmol(p+)kg^{-1}		→		
Pedon 1 : Chandaj (Parbhani)-Typic Haplusterts													
Ap	0-13	8.2	1.2	0.9	6.7	2.5	52.3	10.9	0.5	1.9	65.6	61.8	106.1
Bw1	13-28	8.3	0.3	0.8	6.3	2.7	55.9	9.7	0.3	1.3	67.3	59.1	113.9
Bw2	28-45	8.3	0.4	0.8	6.5	2.7	54.9	10.6	0.3	1.1	67.0	57.5	116.6
Bss1	45-75	8.2	0.3	0.8	6.8	2.8	54.2	12.1	0.3	1.0	67.7	50.6	133.7
Bss2	75-108	8.3	0.3	0.7	6.7	2.9	51.9	14.1	0.4	1.2	67.6	56.8	119.1
Pedon 2 : Satgaon (Buldhana)-Typic Haplusterts													
Ap	0-6	8.5	0.4	1.1	6.0	2.4	47.11	15.0	0.9	1.3	64.3	68.6	93.7
Bw1	6-19	8.5	0.5	1.2	7.8	2.6	46.6	16.0	0.8	0.8	64.2	72.3	88.7
Bw2	19-35	8.5	0.5	0.9	9.5	2.9	39.8	13.7	0.8	0.3	54.5	60.4	90.3
BC	35-51	8.5	0.6	0.7	14.8	3.4	32.9	15.0	0.8	0.2	48.9	51.7	94.7
Bss	51-118	8.5	0.5	0.8	16.7	3.8	36.5	24.8	1.0	0.9	63.3	66.6	95.1
Crk	118-130+	8.6	0.7	0.2	24.9	3.2	20.6	16.3	1.4	0.5	38.8	38.4	100.9
Pedon 3 : Kalegaon (Jalna)- Sodic Haplusterts													
Ap	0-14	8.8	0.5	0.7	15.0	2.0	36.7	18.1	0.8	1.2	56.9	51.7	109.9
Bw1	14-36	8.9	0.15	0.6	14.2	2.3	32.9	21.1	2.8	0.9	57.7	54.3	106.2
Bw2	36-57	9.3	0.4	0.6	14.4	2.4	29.5	22.4	4.5	0.8	57.2	53.3	107.2
Bss1	57-87	9.3	0.7	0.6	15.5	2.6	21.1	27.3	7.2	1.4	56.9	54.4	104.7
Bss2	87-114	9.2	1.1	0.5	17.0	2.3	18.5	25.9	9.9	0.8	55.1	50.9	108.2
C	114-130+	9.6	0.30	0.1	24.4	0.7	12.6	14.7	5.6	0.08	33.3	21.8	152.7
Pedon 4 : Adgaon (Jalna) - Typic Haplusterts													
Ap	0-12	8.3	0.6	1.1	13.2	2.1	33.7	11.6	0.5	1.8	47.7	48.6	98.1
Bw1	12-33	8.7	0.4	1.0	11.7	2.1	30.8	16.2	0.5	1.0	48.6	47.4	102.4
Bw2	33-49	8.6	0.5	0.8	14.6	3.4	31.2	22.3	0.9	0.8	55.1	51.2	107.7
Bss	49-82	8.7	0.6	0.7	20.5	3.9	25.8	28.5	1.1	0.5	55.9	49.9	111.9
Bss2	82-105	8.7	0.6	0.7	21.0	4.1	29.9	27.2	1.5	0.7	59.3	54.2	109.3
C	105-129+	8.6	0.5	0.3	24.5	1.8	20.1	17.7	0.9	0.5	39.2	33.9	115.7
Pedon 5 : Khasgaon (Osmanabad) — Sodic Haplusterts													
Ap	0-14	8.4	0.5	1.0	8.6	1.9	37.8	18.9	1.9	0.6	59.2	65.4	90.6
Bw1	14-30	8.4	0.5	0.9	9.8	2.4	37.7	20.8	2.8	0.7	62.1	70.8	87.7
Bw2	30-53	8.3	0.9	0.8	10.1	2.5	42.0	15.9	3.6	0.4	62.0	64.7	95.9
Bss1	53-77	8.2	1.3	0.8	9.9	2.6	40.8	13.9	4.3	0.6	59.6	64.7	92.3
Bss2	77-102	8.6	1.6	0.7	11.4	2.5	37.8	16.4	4.5	0.5	59.2	59.3	99.8
Bw1	102-150	8.9	1.8	0.7	15.5	2.2	31.1	20.3	3.3	0.9	55.6	56.7	98.0

Table 3. *Contined ...*

Hori-zon	Depth (cm)	pH (1:2) H_2O	ECe dS m^{-1}	O. C. %	Calcium carbonate equivalent as $CaCO_3$ <2 mm (%)	Carbonate clay % on fine earth basis	Extractable bases				Sum of cations	CEC cmol(p+) kg^{-1}	Base saturation %
							Ca	Mg	Na	K			
							← cmol(p+)kg^{-1} →						
Pedon 6 : Nali Wadgaon (Osmanabad) - Sodic Haplusterts													
Ap	0-13	8.5	0.6	0.8	12.7	1.7	25.2	18.1	1.4	0.7	45.3	45.4	99.8
Bw1	13-33	8.6	0.5	0.6	13.5	1.7	23.1	22.1	1.9	0.4	47.6	47.1	100.9
Bw2	33-53	8.9	0.9	0.6	13.6	2.4	21.0	27.3	2.9	0.4	51.7	51.7	99.9
Bss1	53-82	9.1	0.5	0.6	13.8	2.7	17.0	34.1	2.5	0.6	54.2	56.5	96.0
Bss2	82-99	9.2	0.6	0.6	13.5	2.8	19.4	35.6	3.1	0.4	58.5	58.4	100.1
Bss3	99-150	8.9	0.4	0.6	18.9	3.0	20.3	35.8	2.8	0.7	59.6	55.8	106.9
Pedon 10 : Bhalgaon (Aurangabad) - Sodic Haplusterts													
Ap	0-12	8.8	1.0	0.5	12.3	1.4	20.1	14.6	5.4	1.9	42.0	34.0	123.6
Bw1	12-33	9.1	1.2	0.3	13.5	2.0	15.3	17.0	5.9	1.5	39.7	37.1	107.0
Bw2	33-62	9.1	1.3	0.3	14.2	2.1	13.4	16.6	9.2	1.5	40.6	41.6	97.5
Bss1	62-88	9.0	1.3	0.3	14.7	2.3	14.2	17.8	11.5	1.8	45.5	40.8	111.5
Bss2	88-123	8.8	1.4	0.2	11.7	2.9	12.3	22.0	14.7	1.4	50.4	44.4	113.5
Bss3	12-150	8.9	2.4	0.2	12.8	2.7	11.2	23.0	21.3	1.5	57.0	40.9	139.1
Pedon 11 : Babhulgaon (Aurangabad) - Sodic Haplusterts													
Ap	0-15	8.5	1.0	0.8	17.3	1.5	17.9	16.7	0.9	1.9	37.5	33.4	112.1
Bw1	15-34	8.5	0.7	0.8	18.5	1.6	15.2	18.3	1.5	2.2	37.2	31.5	117.8
Bw2	34-72	8.8	0.8	0.6	17.0	1.9	11.4	24.0	4.6	1.4	41.6	35.2	117.9
Bss1	72-97	9.1	0.9	0.4	17.2	2.0	8.8	24.5	6.5	1.0	40.8	35.0	116.3
Bw3	97-130	9.3	1.1	0.2	20.1	1.5	7.3	21.4	3.2	0.8	32.7	25.9	126.5
Bw4	130-160	9.3	1.0	0.2	20.2	1.2	7.3	20.7	4.1	0.8	32.9	30.5	107.6
Pedon 12 : Patrud (Beed)- Typic Haplusterts													
Ap	0-13	8.7	0.2	0.8	12.7	1.9	47.8	10.4	0.7	1.7	60.7	55.1	110.2
Bw1	13-36	8.8	0.3	0.7	13.9	2.1	44.1	13.7	0.4	0.9	59.1	54.5	108.5
Bw2	36-61	8.7	0.2	0.6	13.3	2.2	45.4	15.9	0.2	1.3	62.8	62.7	100.0
Bss1	61-104	8.5	0.4	0.5	12.6	2.4	39.1	18.7	0.5	1.6	59.9	56.6	105.9
Bss2	104-140	8.9	0.3	0.3	13.9	2.2	36.2	23.5	0.1	0.8	60.6	52.6	115.2
Bss3	140-160	8.5	0.4	0.3	11.8	2.4	37.8	21.6	0.6	1.9	61.9	60.4	102.5
Pedon 13 : Raurgaon (Beed) - Typic Haplusterts													
Ap	0-14	8.5	0.4	0.9	11.8	2.3	46.4	15.1	0.3	1.6	63.3	64.6	98.0
Bw1	14-28	8.5	0.3	0.8	12.2	2.8	43.0	20.8	0.6	1.0	65.4	65.4	100.1
Bw2	28-43	8.5	0.3	0.7	10.2	2.9	42.4	24.0	1.0	1.0	68.4	68.3	100.2
Bss1	43-85	8.6	0.4	0.7	9.9	3.1	34.5	31.6	1.2	1.0	68.3	68.5	99.6
Bss2	85-130	8.5	0.4	0.4	11.8	3.2	26.1	40.7	1.0	1.1	68.9	69.0	99.8
Bss3	130-150	8.5	0.6	0.4	1.02	2.3	22.9	44.3	2.0	1.1	70.3	67.1	104.7



(a) (b) (c) (d)

Fig. 3. *Representative photograph of zeolite minerals in cross polarized light : (a) Typic Haplusterts (Pedon 1, 88-93cm), (b) Sodic Haplusterts (Pedon 3, 110-118), (c) Sodic Haplusterts (Pedon 10, 48-56 cm), (d) Typic Haplusterts (Pedon 12, 34-66cm).*

Ca-zeolites in these soils most likely helps maintain a better drainage system. However it is be noted that the five zeolitic Vertisols (Sodic Haplusterts) under study (Pedons 3, 5, 6, 10 and 11) have sHC $\leq$ 10 mmhr^{-1} (Table 2) whereas the rest of the zeolitic Vertisols (Pedons 1, 2, 4, 12 and 13) which are Typic Haplusterts and have sHC >> 10 (Table 2). Sodic Haplusterts under study obviously are no more vibrant substrate for good agricultural land use plans because of poor hydraulic properties unlike similar soils of Yavatmal and Hingoli district.It is to be noted here that Vertisols developed in SAT climate in the zeolitic basalt alluvial material belong to two kinds of subgroups; one is Typic Haplusterts and the other is Sodic Haplusterts. In addition, Sodic Haplusterts under study though zeolitic are,however, notcomparable in terms of their hydraulic properties to those of Yavatmal and Hingoli district. This is a paradoxical situation and needs to be explained.

Plasmic fabric, sHC and Shrink-Swell phenomena

Shrinking and swelling result in a very dense groundmass exhibiting porostriated, parallel-striated, reticulate striated, granostriated,stipple-speckled, mosaic speckled and crystallitic plasmic fabric, which are observed in Vertisols of HT and SAT climatic conditions (Pal *et al.*, 2006, 2009). Vertisols of semi-arid moist (SAM) and dry(SAD) climate under study (Pedons 1, 2, 12 and 13 - Typic Haplusterts) show moderately strong plasma separation with reticulateand granostriated plasmic fabrics (Fig. 4a,b) whereas soils of semi-arid dry (SAD) climate (Pedons 3, 5, 6,10- Sodic Haplusterts) showed moderateto weakplasma separation with mosaic-speckled, stipple-speckled and crystallitic plasmic fabric (Fig.4c,d,e). Despite a high degree of clay activity, and shrink–swell process (as evidenced in high COLE values 0.2 – 0.3, Zade, 2007), the plasmic fabric is not uniform among the Vertisols of SAM and SAD bio-climates because of the difference in hydraulic properties in Typic and Sodic Haplusterts. Zeolites in Sodic Haplusterts under study could not help in improving the sHC like those of Yavatmal and Hingoli districts (Pal *et al.*, 2003a). This suggests that the release of Ca^{+2} ions from Ca-zeolite was not enough in improving the sHC, and preventing the rise in pH and ESP and EMP in the subsoils of Sodic Haplusterts under study. Because of poor sHC, free entry of rain water was prevented in to the Vertisols when they are sodic, and this situation does not provide adequate soil water in the subsoils for greater shrink-swell process to create strong plasma separation while Typic Haplusterts with a relatively better sHC could remainwith enoughsoil water to cause greater shrink-swell activity to causemoderately strong plasma separation.

Discussions

The results of the present study indicates that the SAT Vertisols of Marathwada region of Maharashtra state are calcareous and the soils with mean annual rainfall (MAR) < 1000 mm are mild to strongly alkaline and are of both

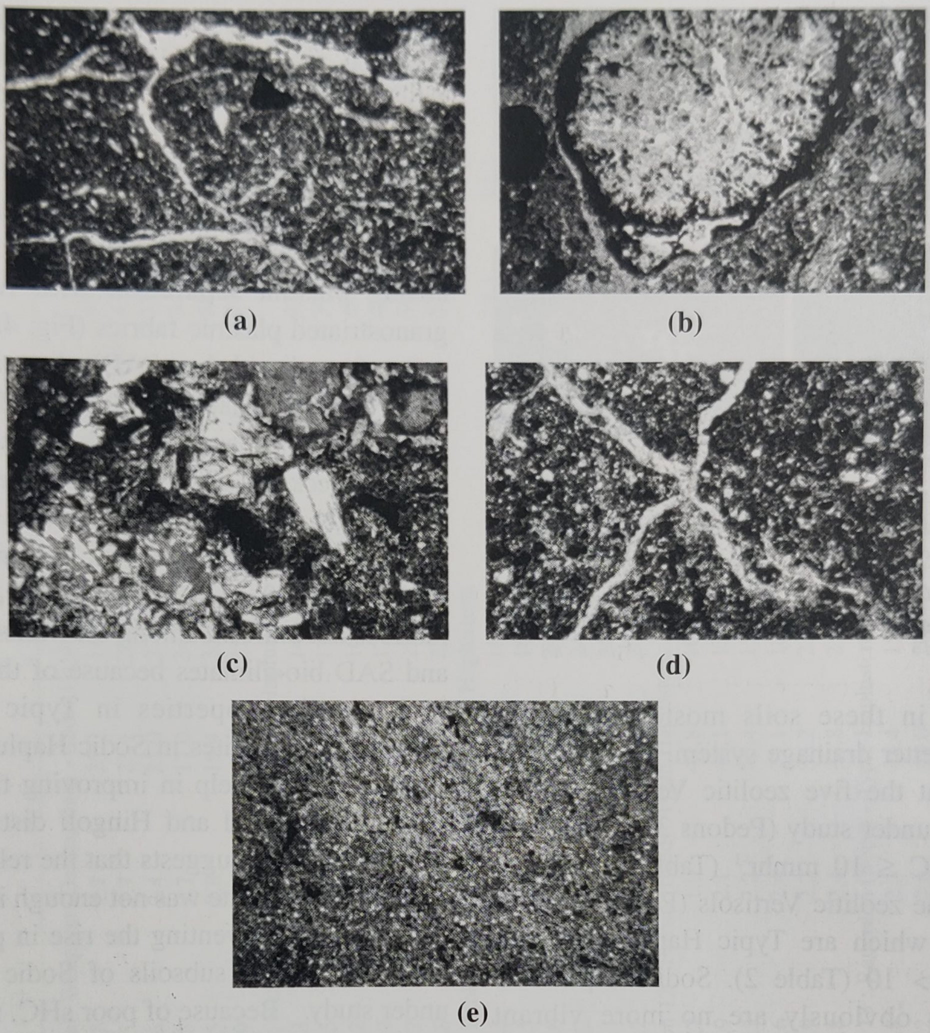


Fig. 4. *Representative photograph of plasmic fabric in cross polarized light. (a) Reticulate b-fabric of Typic Haplusterts (Pedon2, 83-91cm), (b) Granostriated b-fabric of Typic Haplusterts (Pedon 12, 97-105 cm), (c) Stipple-speckled b-fabric of Sodic Haplusterts (Pedon 3, 110-118cm), (d) Crystallitic b-fabric of Sodic Haplusterts (Pedon, 5, 66-74 cm), (e) Mosaic-speckled b-fabric of Sodic Haplusterts (Pedon 10, 91-99 cm).*

sodic and non-sodic in nature, and thus they are classed as Typic Haplusterts and Sodic Haplusterts. Calcareousness of soils is due to the presence of both pedogenic and non-pedogenic $CaCO_3$, but the pedogenic formation of $CaCO_3$ (PC) is not a favourable chemical reaction for soil health because this impairs sHC, causes high pH with concomitant enrichment of both Na and Mg ions on the soil exchange complex (Pal *et al.*, 2000; Balpande *et al.*, 1996; Bhattacharyya *et al.*, 2004). The presence of pedogenic PC that is distinguished from the pedorelict $CaCO_3$ (NPC) by the soil thin section studies (Pal *et al.*, 2000), is very common in SAT Vertisols.

The enrichment of Na ions on soil exchange complex in turn cause dispersion of the fine clay particles. The dispersed fine clays translocate as the formation of PC creates a Na^+- enriched chemical environment conducive for the deflocculation of clay particles and their subsequent movement downward. The formation of PC and the clay illuviation are thustwo concurrent and contemporary pedogenetic events, which result in an increase in relative proportion of sodium and magnesium, causing increased

ESP, EMP, pH values and a decrease in sHC and exchangeable Ca/Mg ratio with depth (Table 2). These pedogenetic processes represent a pedogenic threshold during the dry climates of the Holocene (Pal *et al.*, 2003b, 2012a, 2014,2016; Srivastava *et al.*, 2015), and clearly suggest that the formation of PC is a basic natural chemical degradation process (Pal *et al.*, 2000, 2016), which exhibits the regressive pedogenesis (Pal *et al.*, 2013b, 2016); and it also immobilizes soil carbon in unavailable form.

Vertisols under study contain Ca-zeolites in their silt and clay fractions; however their contents are not as high as are observed from their XRD intensity of the Western Ghats Vertisols of HT climate (Bhattacharyya *et al.*, 1993, 1999). Zeolites are known as effective soil modifiers as they improve sHC (Pal *et al.*, 2003a, 2006). It is however paradoxical that even in presence of Ca-zeolites, SAT Vertisols under study is not Typic Haplusterts. Even zeolites could not prevent the formation of ill drained Sodic Haplusterts with sHC << 10mmhr^{-1}. This queer scenario needs however an explanation.

It is observed that although the soils belong to Typic Haplusterts, their pH values are often close to or little over 8.5 (Table 3), indicating that the formation of PC has been an active pedogenetic process. Active calcification as PC caused greater exchangeable Mg in the Bss horizons of some Typic Haplusterts (Pedons 4, 12 and 13) and the exchangeable Mg was very close or greater than exchangeable Ca when exchangeable Ca/Mg ratio reaches a value around 1.5 or less (Table 2). In the sub soils, especially in the Bss horizons of the Sodic Haplusterts, exchangeable Ca /Mg ratio often reaches a ratio much less than 1.5 when exchangeable Mg was greater than exchangeable Ca (Table 2). It is now understood that the endowment of soil modifier like Ca-zeolites did help maintain sHC >> 10 mmhr^{-1} and moderately strong plasma separation butfailed to maintain the pH below 8.5. However, Ca-zeolites could succeed maintain in general,the exchangeable Ca/Mg ratio at 1.5 and above in Typic Haplusterts. In Sodic Haplusterts, Ca-zeolites could not improve the sHC beyond 10 mmhr^{-1}, resulting in poorplasma separation. This is however in contrast to the scenario in Hingolidistricts of Marathwada region where zeolitic Typic Haplusterts with sHC >> 10 mm hr^{-1} became Sodic Haplusterts under decade long irrigated agriculture but their hydraulic property was not impaired as it still maintains at sHC > 10 mm hr^{-1}. However, a contrasting result was observed in Yavatmal district where better drained Typic Haplusterts after irrigation turned out to be Sodic Haplusterts, which showed sHC << 10 mm hr^{-1} (Pal *et al.*, 2003a). This anomalous scenario indicates the necessity to gain knowledge on the reserve of Ca-zeolites in soil system in different bio-climates where Vertisols occur in Peninsular India (Bhattacharyya *et al.*, 2015). However, fresh research initiative is warranted to follow the dynamics on the rate of Ca ion release from zeolites in diverse soil types. At this moment it appears that Ca-zeolites actonly as transitory ecosystem engineers in making SAT Vertisols sustainable for long term productive agriculture under irrigation.

At presentit isdifficult to detect and identify small quantities of zeolite minerals in soils by the XRD method (Pal *et al.*, 2013a). The CEC procedure described by Ming and Dixon (1987) was developed to only quantify zeolite like clinoptilolite. But the authors felt that the procedure needs further modification to quantify zeolites other than clinoptilolite. Therefore, as of now, there is no selective method to quantify the heulandite (Ca-rich zeolite) content in soils which carry other clay minerals (Pal *et al.*, 2013a). Bhattacharyya *et al.* (1999) advocated specific chemical protocol to determine the CEC and extractable bases that provide indications for the possible presence of zeolites in soils. Authors demonstrated when the base saturation in excess of 50 for acidic soils and 100 for calcareous and slight to moderate alkaline Vertisols provides an evidence of the presence of zeolite. According to this criterion, Vertisols under study have BS ≥ 100.

Bhattacharyya *et al.* (1993, 1999, and 2006) highlighted the unique role of Ca-rich zeolites as ecosystem engineers in the formation and persistence of non-calcareous and acidic Vertisols, Alfisols and Mollisols in the Deccan basalt area under HT Western Ghats (WG) and Satpura Regions (SR). Natural endowment of Ca-zeolites in these soils helped in the enrichment of organic carbon(OC), adequate moisture, high base saturation(BS) and more exchangeable Ca than Mg on soil exchange complex, and moderately smectite rich clays and also a better soil drainage since the several millions years. In reality, these soils support the successful enterprise forforestry, horticultural and cereal crops, and spices. Now the question arises how long zeolites would help sustain such varied land uses? One can, however, envisage that such necessity would arise when the stocks of zeolites is depleted completely under continuing HT climate, acidic Vertisols, Alfisols and Mollisols would phase towards the base poor and OC rich Ultisols (Pal *et al.,* 2012a, 2014; Pal, 2017). In view of their weathering since the several millions years, the stock of Ca-zeolites is still not exhausted in HT soils of the WG and SR, suggesting a constant supply of Ca ions in soils. The BS >50% in general of the soils suggest that WG and SR areat present non-calcareous and acid soils,and far away from phasing towards Ultisols, which justifies the existence of Ca-zeolites in these soils as prolonged ecosystem engineers.

The present rate of formation of PC in SAT Vertisols is estimated to be around 37.5 kg ha^{-1} yr^{-1} (Pal *et al.*, 2000). Thus, it can be safely presumed that the rate of formation of PC is much faster than the rate release of Ca ions from zeolites as evident in the enrichment of exchangeable Mg more than the exchangeable Ca on the soil exchange complex in the Bss horizons of some of Typic Haplusterts, and in Sodic Haplusterts exchangeable Mg is more than exchangeable Ca in the Bw to the Bss horizons (Table 3). It is envisaged that with time and under the SAT climatic environments, the present day Typic Haplusterts would phase towards ill drained and agriculturally unproductive Sodic Haplusterts. Such phasing would be facilitated if such soils are irrigated for raising crops especially the sugarcane. Therefore, Ca-zeolites qualify to be transitory ecosystem engineers in managing and sustaining the productivity of SAT Vertisols of Marathwada region of Maharashtra. Suitable management protocols to enhance the productivity of such SAT Vertisols in rain-fed conditions needs to be followed to make them a sustaining productive system (Pal *et al.*, 2012b; Pal 2017)

Conclusions

The results of the present study indicate some interesting information on the impairment of hydraulic properties of SAT Vertisols of Marathwada region of Maharashtra even though they are endowed with Ca-zeolites. Among the major pedogenetic processes typical in SAT soils, the formation of PC mainlycaused the impairment of sHC even in the Bss horizon of the Typic Haplusterts by enriching with exchangeable Mg, and throughout depth of Sodic Haplusterts by enriching both exchangeable Mg and Na. Ca-zeolites could not prevent the rise of pH and exchangeable Mg in Typic Haplusterts and very poor sHC in Sodic Haplusterts. The rate of formation of PC must have been much higher than the rate of release of Ca ions from zeolites in SAT environments, which is not likely to support the practice of irrigation in raising agricultural crops especially the sugarcane in the Marathwada region of Maharashtra. While the Ca-zeolites can act as prolonged ecosystem engineers in supporting successful enterprise for various land uses in non-calcareous and acidic soils of the HT climate, they however will remain as transitory ecosystem engineers in SAT Vertisols of the Peninsular India in general and Marathwada region in particular.

Acknowledgements

We thank Director, ICAR-NBSS and LUP, Nagpur, India for providing facilities for this work. Help received from other colleagues in the Division of Soil Resource Studies are also thankfully acknowledged.

References

Balpande, S.S., Deshpande, S.B. and D.K. Pal. 1996. Factors and processes of soil degradation in Vertisols of the Purna valley, Maharashtra, India. *Land Degrad & Dev.,*7: 313-324.

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1993. Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and Vertisols) soils on Deccan Basalt in the Western Ghats, India.*J. Soil Sci.,* **44** : 159-171.

Bhattacharyya, T., Pal, D.K. and Srivastava, P. 1999. Role of zeolites in persistence of high altitude ferruginous Alfisols of the humid tropical Western Ghats, India. *Geoderma* **90:** 263-276.

Bhattacharyya, T., Pal, D.K., Chandran, P., Mandal, C., Ray, S.K., Gupta, R.K. andGajbhiye, K.S. 2004. Managing soil carbon stocks in the Indo-Gangetic Plains, India, Rice-Wheat Consortium for the Indo-Gangetic Plains, New Delhi, p.44.

Bhattacharyya, T., Pal, D.K., Lal, S., Chandran, P. and Ray, S.K. 2006. Formation and persistence of Mollisols on zeolitic Deccan basalt of humid tropical India. *Geoderma.* **146** : 609-620.

Bhattacharyya, T., Chandran, P., Pal, D.K., Mandal, C. and Mandal, D.K. 2015. Distribution of zeolitic soils in India. *Curr Sci.,* **109**: 1305-1313.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G. and Tursina, T. 1985. *Handbook for Soil Thin section Description.* Waine Research Walverhampton, 150.

Jackson, M.L. 1979. *Soil Chemical Analysis – Advanced Course,* 2nd. edn. Published byAuthor, University of Wisconsin MD.WI.

Jongerius, A. and Heintzberger, G. 1975. Methods in Soil Micromorphology, A Technique forthe Preparation of Large Thin Sections *Soil Survey Paper* No. 10, Netherlands Soil Survey Institute, Wageningen

Ming, D.W. and Dixon, J. B. 1987. Quantitative determination of cli-noptilolite in soils by a cation-exchange capacity method. *Clays Clay Miner.* **35** : 463–468.

Pal, D.K., Dasog, G.S., Vadivelu, S., Ahuja, R.L. and Bhattacharyya, T. 2000. Secondary calciumcarbonate in soils of arid andsemi-arid regions of India. In: Lal, R., Kimble, J.M., Eswaran,H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates.* Lewis Publishers, Boca Raton, FL,pp. 149– 185

Pal, D.K., Balpande, S.S. and Srivastava, P. 2001. Polygenetic Vertisols of the Purna Valley ofcentral India. *Catena* **43** : 231–249.

Pal, D.K., Bhattacharyya, T., Ray, S.K. and Bhuse, S.R. 2003a. Developing a model on the formation and resilience of naturally degraded black soils of the Peninsular India as a decision support system for better land use planning. *NRDMS, DST Project Report,* NBSSLUP (ICAR), Nagpur, 144p.

Pal, D.K., Srivastava, P. and Bhattacharyya, T. 2003b. Clay illuviation in calcareous soils of the semi-arid part of the Indo-Gangetic plains, India. *Geoderma,* **115:** 177-192.

Pal, D.K., Bhattacharyya, T., Ray, S.K., Chandran, P., Srivastava, P., Durge, S.L. and Bhuse, S.R. 2006. Significance of soil modifiers (Ca-zeolites and gypsum) in naturally degraded Vertisols of the peninsular India in redefining the sodic soils. *Geoderma* **136** : 210– 228.

Pal, D.K., Bhattacharyya, T., Chandran, P., Ray, S.K., Satyavathi, P.L.A., Durge, S.L., Raja, P. and Maurya, U.K. 2009. Vertisols (cracking clay soils) in a climosequence of Peninsular India: Evidence for Holocene climate changes. *Quat. Inter.,* **209** : 6–21.

Pal, D. K., Wani, S. P. and Sahrawat, K.L. 2012a. Vertisols of tropical Indian environments: Pedology and edaphology. *Geoderma.* **189-190** : 28-49.

Pal, D. K., Bhattacharyya, T. and Wani, S.P. 2012b. Formation and management of cracking clay soils (Vertisols) to enhance crop productivity: Indian Experience. In: Lal, R., B.A. Stewart, B.A. (Eds.), *World Soil Resources,* Francis and Taylor, pp. 317-343.

Pal, D.K., Wani, S.P. and Sahrawat, K.L. 2013a. Zeolitic soils of the Deccan basalt areas in India: their pedology and edaphology. *Current Sci*, **105** : 309-318.

Pal, D. K., Sarkar, D., Bhattacharyya, T., Datta, S.C., Chandran, P. and Ray, S.K. 2013b. Impact of climate change in soils of semi-arid tropics (SAT). In: Bhattacharyya, T., Pal, D.K., Wani, S.P. (Eds.), *Climate Change and Agriculture*. Studium Press, New Delhi, pp.113-121.

Pal, D.K., Wani, S. P., Sahrawat, K. L. and Srivastava, P. 2014. Red ferruginous soils of tropical Indian environments: A review of the pedogenic processes and its implications for edaphology. *Catena* **121** : 260-278. DOI:10.1016 /j. catena 2014.05.023.

Pal, D. K., Bhattacharyya, T., Sahrawat, K. L. and Wani, S. P. 2016. Natural chemical degradation of soils in the Indian semi-arid tropics and remedial measures. *Curr Sci,* **110:**1675-1682.

Pal, D. K. 2017. *A Treatise of Indian and Tropical Soils*. Springer International Publishing AG, Switzerland

Piper, C.S. 1950. *Soil and Plant Analysis*.The University of Adelaide, Adelaide, 368p.

Piper, C. S. 1966. *Soil and Plant Analysis*, Hans Publishers, Bombay.

Richards, E.A. 1954. *Diagnosis and Improvement of Saline and Alkali soils.* Agriculture Hand Book No. 60, United States Salinity Laboratory, United States Dept. of Agriculture.

Shields, L. G. and Meyer, M.W. 1964. Carbonate clay: measurement andrelationship to clay distribution and cation exchange capacity. *Soil Sci. Soc. Amer. Proc*., **28**: 416±419.

Soil Survey Division Staff. 1993. *Soil Survey Manual.* USDA Agriculture, Handbook No.18, (Department of Agriculture: Washington, DC).

Soil Survey Staff, 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys.* Agri. Handbook, USDA, 436, p. 869.

Soil Survey Staff, 2003. *Keys to Soil Taxonomy*, ninth ed. United States Department of Agriculture, Natural Resources Conservation Service, Washington, DC.

Srivastava, P., Bhattacharyya T. and Pal, D.K. 2002. Significance of the formation of calcium carbonates minerals in the pedogenesis and management of cracking clay soils (Vertisols) of India. *Clays Clay Miner.* **50**: 111-126.

Srivastava, P., Pal, D. K., Aruche, K.M., Wani, S.P. and Sahrawat, K.L. 2015. Soils of the Indo-Gangetic Plains: A pedogenic response to landscape stability, climatic variability and anthropogenic activity during the Holocene. *Earth-Science Reviews* **140** : 54-71. doi:

10.1016/j.earscirev.2014.10.010

Zade, S.P. 2007. *Pedogenetic Studies of Some Deep Shrink-Swell Soils of Marathwada Region of Maharashtra to Develop a Viable Land Use Plan*. Ph.D. Thesis. Dr. P.D.K.V. Akola, Maharashtra, India.

Zade, S.P., Chandran, P. and Pal, D.K. 2017. Role of calcium carbonate and palygorskite in enhancing exchangeable magnesium to impair drainage of Vertisols of semi-arid western India.*Clay Res.* **36** : 33-45.

(Received January 2018; Accepted March 2018)

ACKNOWLEDGEMENT

I grate fully acknowledge the help received from the followings scientists /Professors who reviewed the manuscripts for 2017 issue.

1. Dr Padikkal Chandran
2. Dr Sanjay Ray
3. Dr Goutam Goswami
4. Dr Siddhartha Mukhopadhyay
5. Dr K.M Manjaiah

INSTRUCTIONS FOR CONTRIBUTORS

CLAY RESEARCH is the official publication ofTHE CLAY MINERALS SOCIETY OF INDIA and is published twice a year, in June and December. The Journal undertakes to publish articles of interest to the international community of clay scientists, and will cover the subject areas of mineralogy, geology and geochemistry, crystallography, physical and colloid chemistry, physics, ceramics, civil and petroleum engineering and soil science.

The Journal is reviewed in *Chemical Abstracts, MineralogicalAbstracts, and Soils and Fertilizers.*

Paper (in English) should be submitted to the Editor, Clay Research **"The Clay Minerals Society of India"** Division of Soil Science and Agricultural Chemistry, I.A.R.I., New Delhi-I to 012. samar1953@yahoo.com. At least one of the authors should be member of THE CLAY MINERALS SOCIETY OF INDIA. Submission is an undertaking that the manuscript has not been published or submitted for publication elsewhere.

Manuscripts should not exceed sixteen typed (double spaced) pages including tables and illustrations. **The original and two copies of text and illustrations should be submitted.**

Form Manusciprts should be typewritten, double spaced on white paper, with wide margins. Intending contributors should consult a recent issue of CLAY RESEARCH for the standard format and style. The manuscript should have the sections ABSTRACT, introductory portion (untitled), MATERIALS AND METHODS, RESULTS and DISCUSSION and REFERENCES.

Title page should contain manuscript title, full name(s) of author(s), address (es) of the institution(s) of the author(s), a short running title not exceeding 60 characters including spaces, footnotes if any to the title, and complete mailing address of the person to whom communications should be sent.

Abstract should be a condensation of the ideas and results of the paper. It should not exceed 25'0 words. Do not make reference to the literature in the abstract.

Tables should have the simplest possible column headings. Type each table on a separate page; indicate location in the text by marking in the margin of text page.

Figures should be self-illustrative, drawn with black India ink on tracing paper or white Board. The lattering should be large enough to permit size reduction to one Journal page column width (about 7.0 cm) without sacrificing legibility. **The original tracing should be submitted**. The size of the drawing should not exceed 24 × 17 cm. Give the numbered legend on a separate sheet, not on the figure itself. Data available in the tables should not be duplicated in the form of illustrations. Indicate the location of the figure in the text by marking in the margin of the page.

Photographs should be in the form of glossy prints with strong contrast. In photomicrographs, the scale in micron or other suitable unit should be drawn on the print. Give the numbered legend on a separate sheet. Indicate the location of the photograph in the text by making in the margin of the text page.

References should be cited in the text by the name(s) of author(s) if two or less, and year of publication. If there are more than two authors, give the name ofthe first author followed by *'et al'* and year. Full references giving author(s) and initial(s), year, title of paper, (journal, volume, number if paged separately), first and last pages should be listed alphabetically at the end of the paper. Journal title should be abbreviated in accordance with the World List of Scientific Periodicals and its sequences. Examples are

Grim, R.E., Bray, R.H. and Bradley, W.R. 1937. The mica in argillaceous sediments. *Am. Miner.* **22**:813-829.

Brindley, G.W. 1961. Chlorite minerals. In *(G. Brown,* Ed.) *The X-ray Identification and Crystal Structures of Clay Minerals,* Mineralogical Society, London, pp.242-296.

Theng, B.K.G. 1974. *The Chemistry of Clay Organic Reactions,* Adam. Hilger, London, 343 pp.

Review Every manuscript submitted to CLAY RESEARCH is independently reviewed by one or more referees. Acceptance or rejection of a manuscript is the responsibility of the Editor.

Reprints No free reprints are supplied to authors. Order for priced reprints should be sent when required by the Editor.

Clay Research

Vol. 36 **December 2017** **No. 2**

CONTENTS

Printed at : Cambridge Printing Works, New Delhi-1100028. (Mobile : 9811860113)