ISSN 0255-7193

CLAY RESEARCH

Vol. 30, No. 1

June 2011

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

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Annual Institutional Subscription Rates Inclusive of Air Mail and Handdling 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

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Clay Research, Vol. 30, No. 1 pp. 1-13 (2011)

Synthesis of cyclohexanone using surfactant-immobilized manganate, chromate clay and cation exchanged clays impregnated with manganate and chromate species

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Abstract: *Oxidation of cyclohexanol to cyclohexanone has been carried out in the presence of manganate, chromate and metal cation exchanged clays, dried at 100° C. Effect of amount of modified clays and the reaction time on the yield of cyclohexanone has been investigated. The activity of the clays after regeneration has also been studied.*

Cyclohexanone is a colourless oily liquid with an acetone like smell. Cyclohexanone is also known as oxocyclohexane, pimelic ketone, ketohexamethylene, cyclo-hexylketone or ketocyclohexane. Cyclohexanone is used as an industrial solvent and as an activator in oxidation reactions. It is also used in the production of adipic acid, caprolactam and Nylon-6 (Lebedev, 1984). Cyclohexanone finds application in electronic industry. Since it reacts with various classes of compound, it is used as a starting material for synthesis of additive for electronic industry. It is also used in manufacture of pesticides, magnetic tapes, paints and cleaning agents as paint remover and painting inks (Pybus *et al.*, 1999; Verma, 2002). Many methods have been reported for synthesis of cyclohexanone from cyclohexanol. These methods involve use of corrosive chemicals like concentrated sulphuric acid. In pursuit of safer and hazard free reagents, claycatalysts have been used in the synthesis of cyclohexanone. Clay catalysts are more advantageous than the ones used in conventional methods because clay occurs abundantly in nature and it is ecofriendly. It has high surface area, high selectivity, sorptive, ion-exchange properties, low cost, reusable and simplicity in operation (Haq *et al.*, 2003; Cornelis *et al.*, 1985).

The main objective of the present work is to bring about oxidation of cyclohexanol to cyclohexanone using surfactant immobilized interlayered manganate and chromate clays and impregnated metal cation exchanged clays. Moreover, reactions will also be carried out to study the effect of variation of reaction time and amount of clay on percentage yield of cyclohexanone. Studies on the reproducibility and reusability of the clays will also be attempted in this study.

Materials and Methods

Chemicals used for the reaction

Cyclohexanol and ethyl acetate were obtained from SD Fine Chemicals. Cyclohexanol was purified by distillation before use. The solvents were dried and distilled over calcium chloride before use.

Modified clays used for the reaction

The modified clays used for oxidation of cyclohexanol are surfactant immobilized manganate, chromate clays and different metal cation exchanged bentonite clays impregnated with manganate and chromate clays.

Preparation of modified clay Preparation of surfactant immobilized manganate and chromate clays [HDTMA-Mn(VII)clay and HDTMA-Cr(VI)clay]

Surfactant immobilized manganate / chromate clay was prepared by adding hexadecyl trimethylammonium bromide to clay followed by treatment with $KMnO_4$ / $K_2Cr_2O_7$ in water.

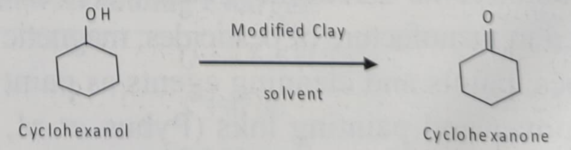
Preparation of metal cation-exchanged clays impregnated with manganate and chromate [M^{n+}-bent-Mn (VII) / Cr (VI) clays]

Metal cation-exchanged clay was prepared by adding a salt solution containing the respective cation to bentonite clay at specific pH. This was treated with $KMnO_4$ / $K_2Cr_2O_7$ in water.

Typical reaction procedure

The liquid phase oxidation reaction was carried out in a 100 ml round-bottomed flask fitted with a reflux condenser. 14mmol of cyclohexanol was taken in the flask. 15ml of ethyl acetate solvent and a known weight of modified clay samples were added to the alcohol. The reaction mixture was refluxed for 12 hrs. The flask was cooled and the clay was separated by filtration. The filtrate, was distilled under reduced pressure to get the solvent. The product left behind in the distillation flask was identified by infrared spectroscopy (Nicolet AVATAR 320 FTIR and further confirmed by gas chromatography.

Reaction: Scheme 1



Scheme 1: Schematic representation of oxidation of cyclohexanol in the presence of modified clay

Characterization

The products obtained from the reactions using manganate and chromate clays were identified by TLC using an authentic sample. This was confirmed by infrared spectroscopy (Nicolet AVATAR 320 FTIR). The products formed were further confirmed by Gas chromatography spectra.

Analysis from Infrared spectroscopy IR spectral analysis of the product from manganate clay

and the peak at 596.61cm^{-1} indicates presence of aromatic ring (Williams *et al*., The IR spectrum of the product obtained from reaction using manganate clay showed peaks at 3352.97, 2999.34, 2972.86, 1757.40, 1156.70 and 596.61 cm^{-1}. The peak at 3352.97 cm^{-1} is due to -OH group stretching, the peaks at 2999.34 and 2972.86 cm^{-1} indicate C-H stretching, the peak at 1757.40 cm^{-1} indicates presence of C=O group, the peak at 1156.70 cm^{-1} indicates C-O stretching 1991).

IR spectral analysis of the product from chromate clay

The IR spectrum of the product obtained from the reaction using chromate clay showed peaks at 3397.68, 2999.34, 2972.86, 1757.40, 1196.43 and 589.78 cm^{-1}.

The peak at 3397.68 cm^{-1} is due to -OH group stretching, the peak at 2999.34 and 2972.86 cm^{-1} indicate C-H stretching, the peak at 1757.40 cm^{-1} indicates the presence of C=O group, the peak at 1196.43 cm^{-1} indicates C-O stretching and the peak at 589.78 cm^{-1} indicates the presence aromatic ring. By comparing with the IR spectrum of authentic sample, the product obtained in the reaction was confirmed to be cyclohexanone (Figs 1.1a and 1.1b) (Williams *et al.*, 1991).

Analysis from gas chromatography Analysis of the product by gas chromatography

Fig 1.2a and 1.2b Gas chromatograms for authentic samples of cyclohexanol and cyclohexanone are presented in figures 1.2a and 1.2b respectively.

The gas chromatograms of the products obtained on oxidation of cyclohexanol using HDTMA-immobilized-interlayer-Mn (VII) clay and HDTMA-immobilized-interlayer-Cr(VI) clay respectively are shown in figures 1.2c and 1.2d respectively. By comparing the area of the peak for known amount of authentic sample and the area of the peak for the product in the GC plot, the percentage yield of the products were determined. The area of the peak for the product obtained from GC plot was 3064035.24 and the area of the peak for authentic sample was 4863548.

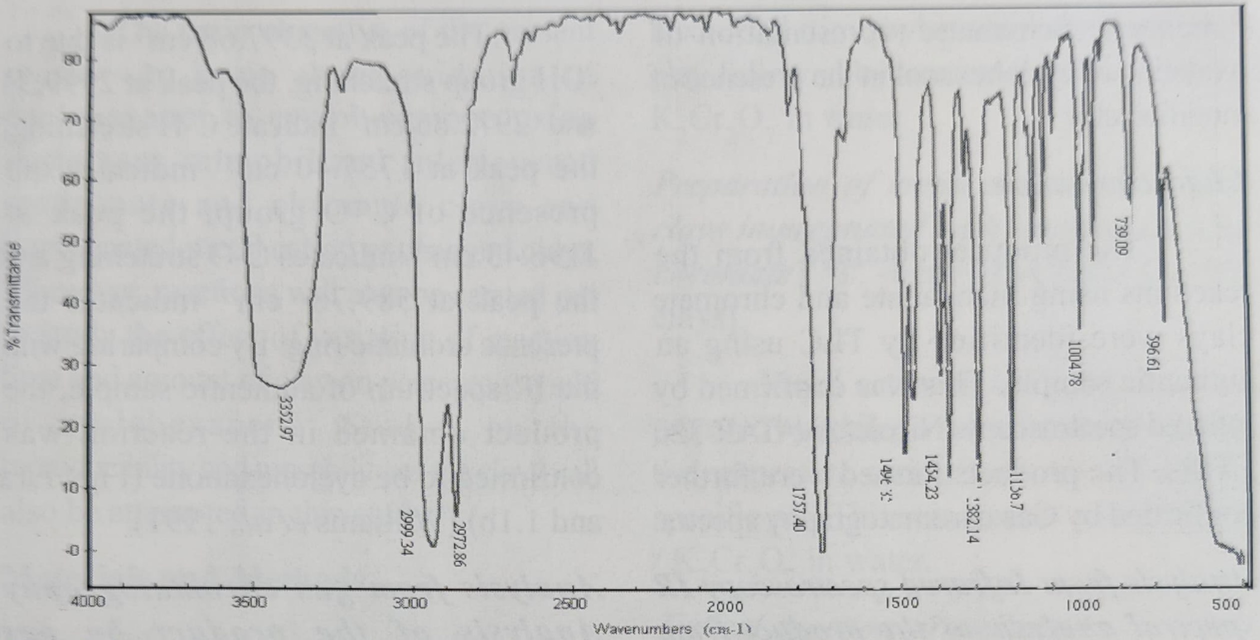


Fig. 1.1a. *IR spectra of reaction mixture cyclohexanol and cyclohexanone from manganate clay.*

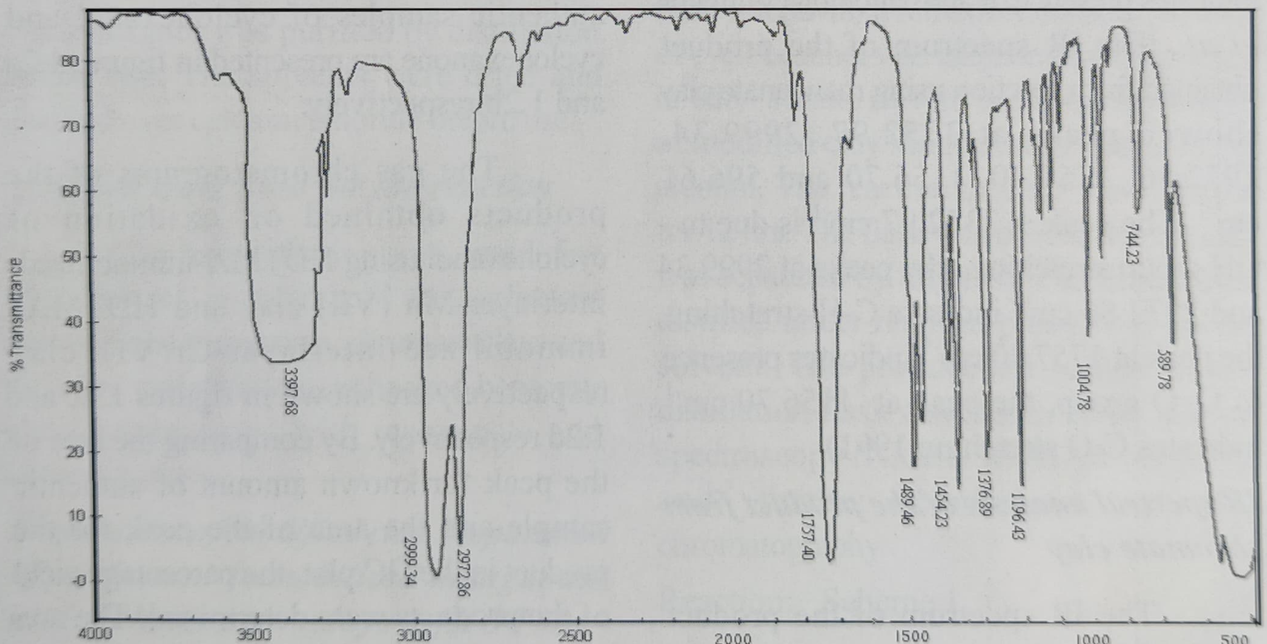


Fig. 1.1b. *IR spectra of reaction mixture cyclohexanol and cyclohexanone from chromate clay.*

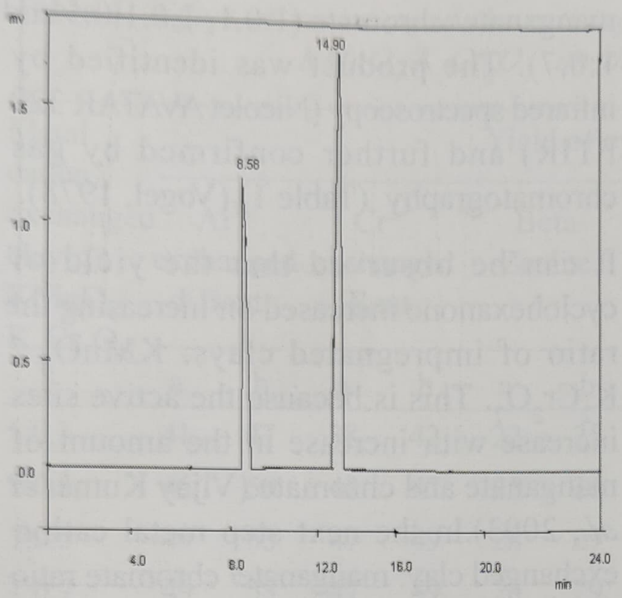


Fig. 1.2a. *GC plot for authentic sample of cyclohexanone.*

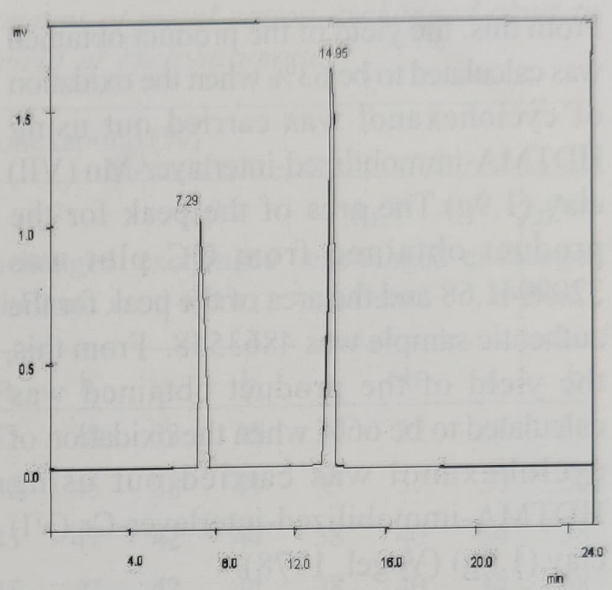


Fig. 1.2b. *GC plot for authentic sample of cyclohexanone.*

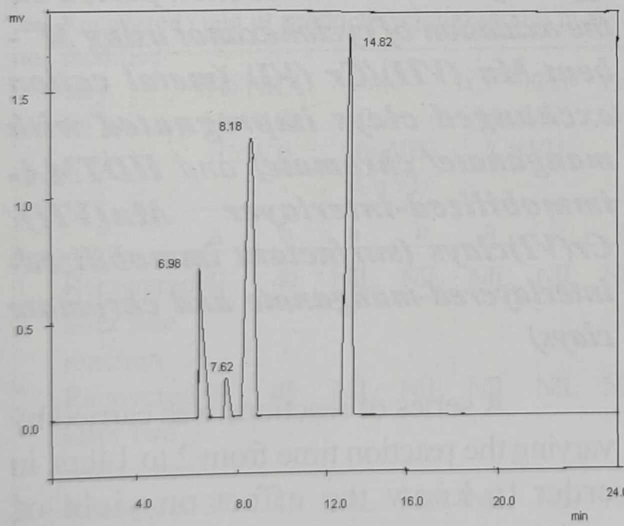


Fig. 1.2c. *GC plot obtained by oxidation of cyclohexanol using HDTMA-immobilized- interlayer-Mn(VII) clay*

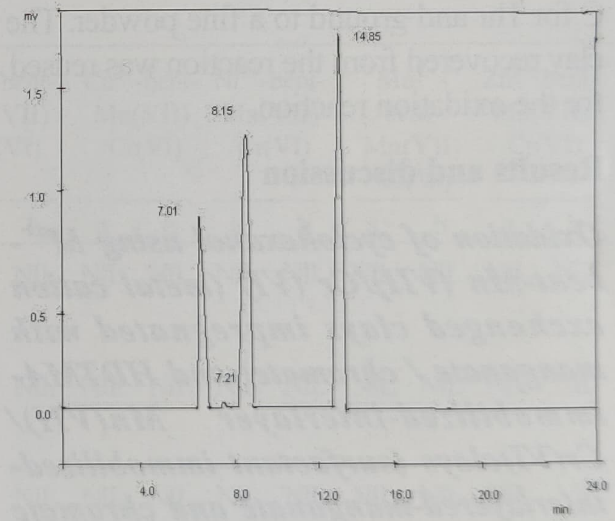


Fig. 1.2d. *GC plot obtained by oxidation of cyclohexanol using HDTMA-immobilized- interlayer-Cr(VI) clay*

From this, the yield of the product obtained was calculated to be 63% when the oxidation of cyclohexanol was carried out using HDTMA-immobilized-interlayer-Mn (VII) clay (1.9g).The area of the peak for the product obtained from GC plot was 3209941.68 and the area of the peak for the authentic sample was 4863548. From this, the yield of the product obtained was calculated to be 66% when the oxidation of cyclohexanol was carried out using HDTMA-immobilized-interlayer-Cr (VI) clay (1.9g) (Vogel, 1978).

Regeneration of clays

The clay separated from the reaction mixture was washed with solvent and several times with distilled water. It was dried at 100^0 C for 1hr and ground to a fine powder. The clay recovered from the reaction was reused for the oxidation reaction.

Results and discussion

Oxidation of cyclohexanol using M^{n+}-bent-Mn (VII)/Cr (VI) (metal cation exchanged clays impregnated with manganate / chromate) and HDTMA-immobilized-interlayer Mn(VII)/ Cr(VI)clays (surfactant immobilized-interlayered-manganate and chromate clays)

A series of reactions was carried out by varying the ratio of amount of metal cation exchanged clay samples to the amount of manganate/ chromate (1:0.1, 1:0.1:0.5 and 1:0.7). The product was identified by infrared spectroscopy (Nicolet AVATAR 320 FTIR) and further confirmed by gas chromatography (Table 1) (Vogel, 1978).

It can be observed that the yield of cyclohexanone increased on increasing the ratio of impregnated clays: $KMnO_4$ / $K_2Cr_2O_7$. This is because the active sites increase with increase in the amount of manganate and chromate (Vijay Kumar *et al.*, 2003).In the next step metal cation exchanged clay: manganate/ chromate ratio 1:0.5 was used.

Effect of variation in reaction period on oxidation of cyclohexanol

Effect of variation in reaction period on the oxidation of cyclohexanol using M^{+}-bent-Mn (VII)/Cr (VI) (metal cation exchanged clays impregnated with manganate/ chromate) and HDTMA-immobilized-interlayer Mn(VII)/ Cr(VI)clays (surfactant immobilized-interlayered-manganate and chromate clays)

A series of reactions was carried by varying the reaction time from 2 to 14hrs, in order to know the effect on yield of cyclohexanone. The reactions were carried out by refluxing 14mmol of cyclohexanol, 0.5g of M^{n+}-bent-Mn(VII)/Cr(VI) (impregnated different metal cation exchanged bentonite clays, where M^{n+}=Al^{3+},

Table 1. *Effect of variation in the ratio of amount of metal cation exchanged clays to $KMnO_4/K_2Cr_2O_7$ on the yield of cyclohexanone*

Metal cation exchanged clay(g): $KMnO_4$/ $K_2Cr_2O_7$	Yield of cyclohexanone (%)													
	Al^{3+} exchanged d-Bent :		Cr^{3+} exchanged -Bent :		Beta Zeolite		Cu^{2+} exchanged d-Bent :		Ni^{2+} exchanged d-Bent :		Mn^{2+} exchanged d-Bent :		Zn^{2+} exchanged d-Bent :	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b
1:0.1	41	47	38	42	22	25	35	38	33	35	30	32	27	30
1:0.3	45	50	42	47	25	26	40	45	38	41	35	37	30	36
1:0.5	49	53	47	49	28	29	45	47	42	44	38	40	34	38
1:0.7	49	53	47	49	28	29	45	47	42	44	38	40	34	38

a= MnO_4^-; b= $Cr_2O_7^{2-}$

Table 2. *Study of recovered [M^{n+}-bent-Mn(VII)/Cr(VI)] and HDTMA-Immobilized-interlayer Mn(VII)/Cr(VI)clays, modified clays on the yield of cyclohexanone*

Sl. no.	Recovered modified clay (in g)	Yield of product(cyclohexanone) in %															
		HDTMA Mn(VII) /Cr(VI)		Al^{3+} Bent-Mn(VII) /Cr(VI)		Cr^{3+}-bent-Mn(VII) /Cr(VI)		Fe^{3+}-bent-Mn(VII) /Cr(VI)		Cu^{2+}-bent-Mn(VII) /Cr(VI)		Ni^{2+}-bent-Mn(VII) /Cr(VI)		Mn^{2+}-bent-Mn(VII) /Cr(VI)		Zn^{2+}-bent-Mn(VII) /Cr(VI)	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
1	Recovered after one reaction	41	49	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
2	Recovered after two reactions	39	45	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
3	Recovered after three reactions	35	41	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
4	Recovered after four reactions	31	36	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL

a=MnO_4^--clay; b= $Cr_2O_7^{2-}$ clay

Reaction conditions used:

- Reactant: cyclohexanol(14mmol)
- clay used: M^{n+}-bent-Mn(VII)/Cr(VI)] and HDTMA-immobilized interlayer-Mn(VII)/Cr(VI)clays recovered after 158 the reaction (0.5g)
- solvent (Ethyl acetate=15ml)
- Reaction time (12hrs)

Cr^{3+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} and HDTMA immobilized-interlayer Mn(VII)/ Cr(VI) clays (surfactant immobilized-interlayered-manganate and chromate clays) using solvent (Ethyl acetate=15 ml).

In the reactions carried out with impregnated manganate and chromate clays as well as in the oxidation reactions carried out with surfactant immobilized-interlayered-manganate and chromate clays, the yield of cyclohexanone increased with increase in reaction time from 2 to 12 hrs. But, in both the cases there was a slight decrease in yield of cyclohexanone when the reaction time was 14hrs indicating that the optimum condition for oxidation of cyclohexanol is 12 hrs. When the results were compared, it was observed that the yield of cyclohexanone obtained using HDTMA-Mn(VII)/Cr(VI)-bent was more than 20% higher than the yield obtained using impregnated clays (Mahadevaiah *et al.*, 2007). This may be due to the fact that oxidant species using surfactant exhibits higher activity possibly due to the nano dispersion of the active species in the interlamellar region. The interlayer thus provides a nanoregion for the reactant the molecules to come together and interact with the active species. The active species are possibly oxides of Mn (IV) and Cr (III) (Mahadevaiah *et al.*, 2007).

Whereas in the case of impregnated clays, the manganate and chromate are present on the surface of the clay. The active species available for oxidation is less Among the, impregnated metal cation clays, it is observed that Al^{3+} and Cr^{3+} ions showed a higher yield than divalent ions. This is attributed to the small charge to radius ratio of the di-positive ions compared to that of the tri-positive ions. The low activity of Fe^{3+}-bent, although it is a tri-positive ion and having a high charge to radius ratio, may be due to the leaching of interlayer Fe^{3+}-ions possibly through Fe^{3+}-cyclohexanol complex formation (Breen, 1987).

In order to establish that manganate and chromate should either be impregnated on the surface or be immobilized in the interlayer of clay for oxidation to take place, a set of blank reactions were carried out as shown below. The reactions were conducted using reactant amount (14mmol of cyclohexanol), reaction time (12 hrs) and solvent (ethyl acetate, 15ml) (Nagendrappa, 2002).

In blank I raw clay (1.0g) was used, in blank II HDTMA-raw clay (1.0g) was used and in blank III raw clay (1.0g) and adding $KMnO_4$ /$K_2Cr_2O_7$crystals (0.03g) (amount equivalent to the amount of $KMnO_4$/$K_2Cr_2O_7$ present in modified clay) was used. But in all the three no product was obtained and cyclohexanol was regained back. This indicates that acid sites on raw clay alone are not effective in the absence of oxidizing agents. However, in blank IV where raw clay (1.0g) higher amount of $KMnO_4$/$K_2Cr_2O_7$ crystals (0.3g) (10 times of that of blank III) was taken, the yield of the product was cyclohexanone whose amount was very low (about 17%).The results indicate that, if the oxidizing agents ($KMnO_4$ and $K_2Cr_2O_7$ crystals) are added separately with raw clay, oxidation of cyclohexanol does not take place. Thus, impregnation or immobilization with manganate or chromate species is effective in bringing about the oxidation (Figs. 2.1 a and b) (Nagendrappa, 2002).

Effect of variation in the amount of modified clays on the yield of cyclohexanone

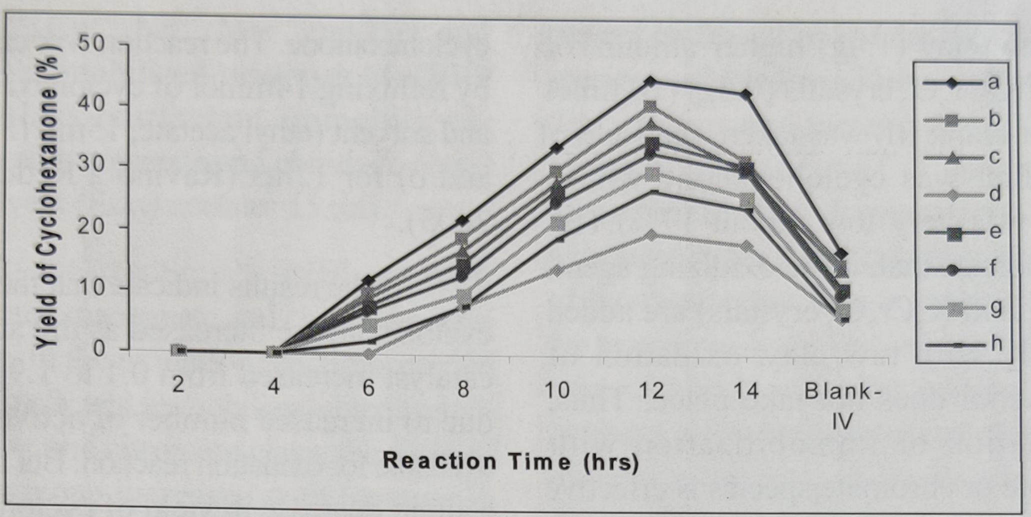
Effect of variation in the amount of M^{n+}-bent-Mn (VII)/Cr(VI) (metal cation exchanged clays impregnated with manganate/ chromate) and HDTMA-Immobilized interlayer Mn(VII)/ Cr(VI)clays (surfactant immobilized-interlayered-manganate and chromate clays on the yield of cyclohexanone

A series of reactions was carried by varying the M^{n+}-bent-Mn(VII)/Cr(VI) (impregnated with different metal cation exchanged bentonite clays *and* HDTMA-Immobilized interlayer Mn(VII)/Cr(VI) clays (surfactant immobilized-interlayered-manganate and chromate clays on the yield of cyclohexanone amount from 0.1 to 2.1g, in order know the effect on yield of cyclohexanone. The reaction was carried out by refluxing 14mmol of cyclohexanol, clay and solvent (ethyl acetate, 15ml) (Figs 2.2 a and b) for 12hrs (Ravindra Reddy *et al.*, 2005).

The results indicate that the yield of cyclohexanone increased as the amount of catalyst increased from 0.1 to 1.9g. This is due to increased number of active species available for oxidation reaction. But there was a slight decrease in yield of cyclohexanone when the amount of surfactant immobilized clays is 2.1g. This shows that optimum amount of clay for oxidation of cyclohexanol is 1.9g (Ravindra Reddy *et al.*, 2005).

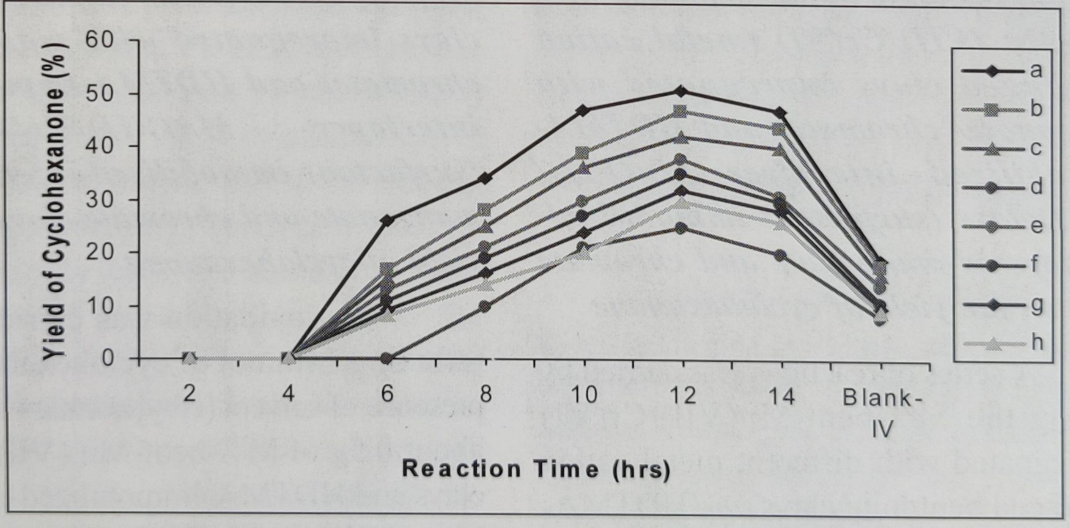
Study of use of recovered M^{n+}-bent-Mn(VII)/Cr(VI) (metal cation exchanged clays impregnated with manganate/ chromate) and HDTMA-Immobilized-interlayer Mn(VII)/Cr(VI)clays (surfactant immobilized-interlayered-manganate and chromate clays) on the yield of cyclohexanone

The oxidation was carried out by refluxing 14mmol of cyclohexanol, in the presence of solvent (ethyl acetate=15ml) and about 0.5g of M^{n+}-bent-Mn (VII)/Cr (VI) clays and HDTMA-Immobilized-interlayer Mn (VII)/Cr (VI) clays (surfactant immobilized-interlayered-manganate and chromate clays) recovered after the reaction and for 12 hrs (Table 2).



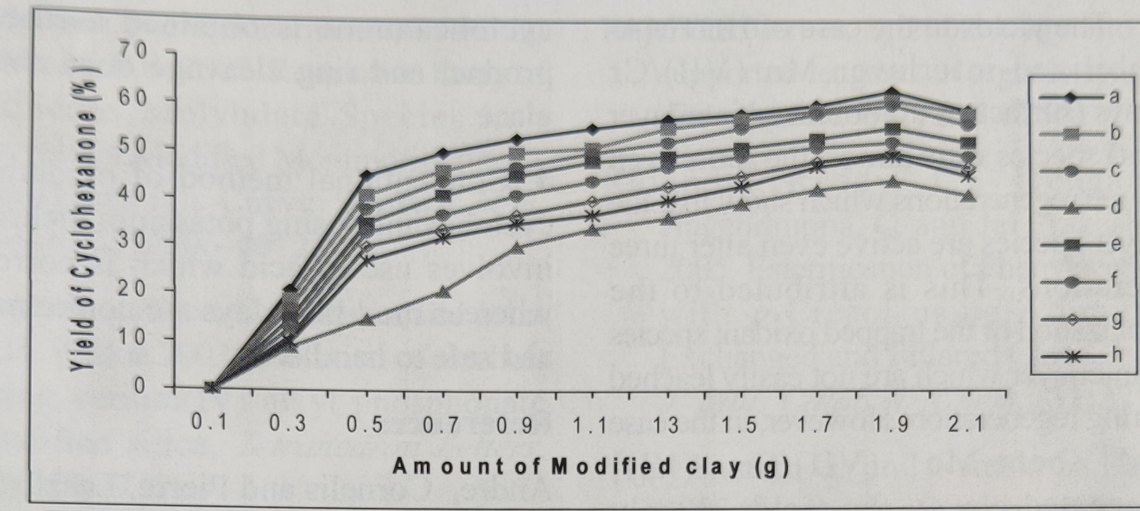
A-HDTMA-MnO$_4^-$- clay; b-Al^{3+}-bent- MnO$_4^-$- clay; c-Cr^{3+}- bent- MnO$_4^-$- clay; d-Fe^{3+}- bent- MnO$_4^-$- clay;e-Cu^{2+}- bent- MnO$_4^-$- clay;f-Ni^{2+} bent- MnO$_4^-$- clay; g-Mn^{2+}- bent- MnO$_4^-$- clay; h-Zn^{2+}- bent- MnO$_4^-$- clay;

Fig 2.1a. *A graph of reaction period against yield of cyclohexanone in presence of [M^{n+}-bent-Mn(VII)] and HDTMA-immobilized- interlayer-Mn(VII)clays.*



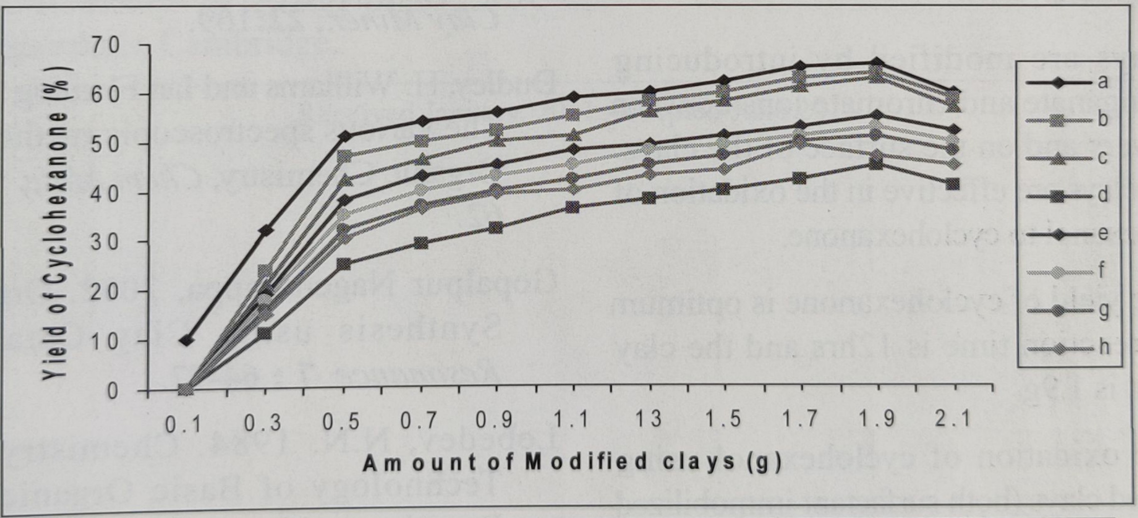
A-HDTMA-Cr$_2$O$_7^{2-}$- clay;b-Al^{3+}-bent- Cr$_2$O$_7^{2-}$ - clay;c-Cr^{3+}- bent- Cr$_2$O$_7^{2-}$ - clay; d-Fe^{3+}- bent- Cr$_2$O$_7^{2-}$ - clay; e-Cu^{2+}- bent- Cr$_2$O$_7^{2-}$ - clay;f-Ni^{2+} bent- Cr$_2$O$_7^{2-}$ - clay; g-Mn^{2+}- bent- Cr$_2$O$_7^{2-}$ - clay;h-Zn^{2+}- bent- Cr$_2$O$_7^{2-}$ - clay;

Fig 2.1b. *A graph of reaction period against yield of cyclohexanone in presence of [M^{n+}-bent-Cr(VI)] and HDTMA-immobilized-interlayer-Cr(VI)clays*



A-MnO_4^-- clay; b-Al^{3+}-bent- MnO_4^-- clay; c-Cr^{3+}- bent- MnO_4^-- clay; d-Fe^{3+}- bent- MnO_4^-- clay;e-Cu^{2+}- bent- MnO_4^-- clay; f-Ni^{2+} bent- MnO_4^-- clay; g-Mn^{2+}- bent- MnO_4^-- clay; h-Zn^{2+}- bent- MnO_4^-- clay;

Fig 2.2a. *A graph of amount of M^{n+}-bent-Mn(VII) and HDTMA-immobilized-interlayer-Mn(VII)clays against yield of cyclohexanone.*



A-$Cr_2O_7^{2-}$- clay; b-Al^{3+}-bent- $Cr_2O_7^{2-}$ - clay;c-Cr^{3+}- bent- $Cr_2O_7^{2-}$ - clay; d-Fe^{3+}- bent- $Cr_2O_7^{2-}$ - clay; e-Cu^{2+}- bent- $Cr_2O_7^{2-}$ - clay; f-Ni^{2+} bent- $Cr_2O_7^{2-}$ - clay; g-Mn^{2+}- bent- $Cr_2O_7^{2-}$ - clay; h-Zn^{2+}- bent- $Cr_2O_7^{2-}$ - clay;

Fig 2.2b. *A graph of amount of M^{n+}-bent-Cr(VI) and HDTMA-immobilized-interlayer-Cr(VI)clays against yield of cyclohexanone.*

The yields in the case of HDTMA-Immobilized-interlayer Mn (VII)/Cr (VI)clays (surfactant immobilized interlayer oxidant) species were almost the same even after three regenerations which show that the interlayer species are active even after three regenerations. This is attributed to the immobilization of the trapped oxidant species in the interlayer which are not easily leached out during regeneration. However, in the case of M^{n+}-bent-Mn (VII)/Cr (VI)] (impregnated clays), the yields sharply decreased with every regeneration it is attributed to the easy accessibility of the impregnated oxidant species, presumably present on the external surface, to the washing solution during regeneration.

Conclusions

1. Clays are modified by introducing permanganate and chromate ions between the layers and on the surface of the clays. These clays are effective in the oxidation of cyclohexanol to cyclohexanone.

2. The yield of cyclohexanone is optimum when reaction time is 12hrs and the clay amount is 1.9g.

3. The oxidation of cyclohexanol using modified clays (both surfactant immobilized and impregnated) have advantage over conventional method. With the traditional methods, the reaction cannot be stopped at the intermediate stage of cyclohexanone formation. Whereas, using modified clay, cyclohexanone is obtained as the sole product and ring cleavage does not take place.

4. Conventional method of oxidation of cyclohexanol using potassium dichromate involves use of acid which is corrosive, whereas modified clays are non- corrosive and safe to handle.

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Received January, 2011 Accepted June 2011

Clay Research, Vol. 30, No. 1 pp. 15-27 (2011)

Seat of Charge in Clay Smectites of Some Vertisol Maharashtra

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Abstract: *In view of scanty information about the position of charge in smectites for soils of Maharashtra in particular, and India in general an attempt has been made to locate seat of charge of some Vertisol clays by determining the reduced cation exchange capacity (CEC_R) of smectitic clays. Six benchmark Vertisols from Maharashtra namely, Linga (P1), Loni (P2), Asra (P3), Paral (P4), Kalwan (P5) and Nimone (P6) from Nagpur, Yavatmal, Amravati, Akola, Nashik and Ahmednagar districts, respectively were chosen for the study. Fine clays were separated from the soils and their original CECs (CEC_{UT}) were determined by exchange with neutral normal $MgCl_2$ followed by $CaCl_2$ and $BaCl_2$. Greene-Kelly test was performed by treating these clays with 3N LiCl. The Li-clays were also treated with the above metal chlorides in the same order to get the reduced CECs.*

Methods were formulated to calculate the actual CEC. The tetrahedral CEC decreased with increasing depth of soil for Linga, Asra, Kalwan and Nimone, whereas opposite trend was observed for Loni and Paral. The octahedral charge increased with depth for all except for Asra and Paral. The study indicated that cation exchange capacity determination appeared to be an accurate and less time-consuming approach to measure charge reduction. It can be used to locate seat of charge and also to study changes in the proportion of tetrahedral and octahedral charge during the pedogenetic processes of soil formation.

Vertisols are dominated by smectitic group of clay minerals (Pal and Deshpande, 1987; Bhattacharyya *et al*., 1993; Ray *et al*., 2003; Deshmukh, 2009; Bhople, 2010). Natural smectites have various chemical compositions having non-equivalent substitutions of central atoms in the octahedral and/or tetrahedral to generate a net negative charge on the layer that is balanced by hydrated exchangeable cations e.g. Ca^{2+}, Mg^{2+}, Na^+, etc. Ideally the charge in the layer silicate minerals should be either in the tetrahedral sheet or octahedral sheet, but it is usually observed that the charge is distributed over both the sheets (Foster, 1960; Schultz, 1969; Malla and Douglas, 1987).

Vertisols are dominated by smectitic group of clay minerals. These clays hold a number of cations like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, etc. Natural smectites have various chemical compositions having non-equivalent substitutions of central atoms in the octahedral and/or tetrahedral to generate a net negative charge on the layer that is balanced by hydrated exchangeable cations e.g. Ca^{2+}, Mg^{2+}, Na^{+}, etc. The negative charge on smectite layers is recognized as one of the most important characteristics of 2:1 phyllosilicates (Komadel et al., 2005).The exchange of cations has been explained on the basis of the electrokinetic theory of ion exchange. According to this theory, the adsorbed cations forming the outer shell of the ionic double layer are supposed to be in a state of oscillation, when suspended in water, forming a diffuse double layer. Due to these oscillations, some of the cations move away from the surface of clay micelle. In the presence of solution of an electrolyte, cations of the added electrolyte slip in between the inner negative layer and outer oscillating positive ion. The electrolyte cation is then adsorbed on the micelle and the surface cation remains in solution. Thus exchange of cation takes place (Grim, 1953).

Cation exchange capacity (CEC) usually expressed in milliequivalents per 100g of soil. Its SI unit cmol(p+)kg^{-1} soil/clay is a measure of the quantity of readily exchangeable cations, neutralizing negative charge in the soil. These charges may be viewed as being balanced by either (i) an excess of ion of opposite charge or a deficit of ions of like charge, or (ii) the excess of ions of opposite charge over those of like charge (Bolt et al., 1976). The negative charges in soil constituents are derived from isomorphous substitution within the structure of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of acidic functional groups in organic compounds, amorphous materials and the preferential adsorption of certain ions on the particle surfaces (Rhoades and Krueger, 1968).

Hofmann and Klemen (1950) examined reference smectites to determine relationship between Li-uptake, cation exchange capacity and octahedral layer charge after Li-saturation and heating at 250°C. They also observed a loss of exchangeable Li and reduction of layer charge when Li saturated montmorillonite was heated at low temperatures (200-300°C). The mechanism of charge reduction advocated by Hofmann and Klemen (1950) by Greene-Kelly (1953) invoked migration of Li ions into the vacant octahedral sites until the octahedral charge imbalance was neutralized. Thus, a lower limit to total charge was set by tetrahedral substitution plus terminal edge sites. Jaynes and Bigham (1987) reported that direct measurement of exchangeable Li after heating led to over estimation of charge reduction due to entrapment of Li in collapsed interlayers. Tettenhorst (1962) was of the view that Li moves into the hexagonal cavities of the Si-O network but not into the octahedral sheet. Lim and Jackson (1986) reported that non-exchangeable Li in excess of reduction of cation exchange capacity ranged from 4 to 21 meq/100g in a series of standard smectites.

Brindley and Erten (1971) determined the CEC of Wyoming montmorillonite ("Volclay") after Li-treatment by measuring Li-displaced with ammonium acetate. They found no leveling of CEC at a value corresponding to tetrahedral layer charge. Farmer and Russell (1967) reported that charge reduction and Li-retention in heated Li-montmorillonites could be partially reversed by treatment with NH_3. Calvet and Prost (1971) opined from the interpretations of IR data and suggested that Li remaining in the hexagonal cavities is in a transitional state prior to movement into the octahedral sheet. Relationship between Li uptake, charge reduction, and octahedral charge has also been disputed. They also observed that total charge reduction to be equal to the octahedral charge. An attempt has been made to locate seat and distribution of charge of some Vertisol clays of Maharashtra by using cation exchange capacity method of fine clays with the aid of mechanism of charge reduction advocated by Hofmann and Klemen.

Materials and Methods

Six Benchmark Vertisols from Maharashtra namely Linga (P1), Loni (P2), Asra (P3), Paral (P4), Kalwan (P5) and Nimone (P6) from Nagpur, Yavatmal, Amravati, Akola, Nashik and Ahemadnagar districts respectively were chosen for the study.

Cation exchange capacity of clays

The method used by Jaynes and Bigham (1987) was followed for the determination of reduced CEC of the lithium saturated and heated at 250°C (Li-250) clay samples. The reduced CEC would give the values of tetrahedral CEC (as the octahedral sites have been blocked by Li). Samples were saturated with 3N LiCl (AR, Merck) solution (pH 7.0), mixed uniformly and kept overnight. The treatment was repeated 3 more times. Subsequently the excess salt was removed by washings first with 50 per cent methanol and then with pure methanol until the EC was between 40-55 mhos cm^{-1}. A centrifuge was used for these treatments. The Li-saturated samples were then transferred into previously dried and weighed silica crucibles with minimum amount of water. Later they were kept in a furnace at 250°C for 16 hours and their weights recorded, so as to express the data on an oven-dry basis (110°C) or at 250°C. The CEC of these samples were determined by exchange with $MgCl_2$. This CEC is the tetrahedral CEC

(CEC_T). The original fine clays were also treated with $MgCl_2$ to get their CEC. The octahedral CEC (CEC_O) may be computed from the difference between untreated CEC (CEC_{UT}) and CEC due to tetrahedral charge (CEC_T) as follows:

$$CEC_O = CEC_{UT} - CEC_T$$

Results and Discussion

Cation exchange capacities of original untreated fine clays

The fine clays were staturated with 1N $MgCl_2$ (AR Merck, Germany) and then exchange with 1N $CaCl_2$ (AR Merck, Germany). The extracted solution which is statured with Mg^{2+} ions is the magnesium exchange capacity ($MgEC_{UT}$) of the original untreated samples.

The total CECs of original untreated fine clays with respect to Mg^{2+} ion ($MgEC_{UT}$) ranged from 93.1 to 107.5 cmol (p^+) kg^{-1} for P1, 90.0 to 118.4 cmol (p^+) kg^{-1} for P2, 75.5 to 113.2 cmol (p^+) kg^{-1} for P3, 69.9 to 79.6 cmol (p^+) kg^{-1} for P4, 67.2 to 76.0 cmol (p^+) kg^{-1} for P5 and 66.4 to 80.0 cmol (p^+) kg^{-1} for P6 respectively (Table 1). Pedons 1, 2 and 3 showed higher CEC values. In pedons 4, 5 and 6 whereas no definite trend was observed. For soil smectites similar values also reported by Jaynes and Bigham (1987) and Kapse (2007).

Reduced CECs of the fine clays

Hofmann and Klemen (1950) effect is characterized by a loss of exchangeable Li and a reduction of layer charge when Li-saturated montmorillonite was heated at low temperatures (200º-300ºC). The mechanism of charge reduction advocated by Hofmann and Klemen and later by Greene-Kelly (1953) involved migration of Li ions into vacant octahedral sites until the octahedral charge imbalance was neutralized. The blocked octahedral layer position has thus no contribution towards CEC. After Lithium treatment, the CEC as well as charge are likely to reduce. Lithium saturation and heating caused the colour of dioctahedral minerals to darken. The colour of the samples under study changed from nearly off white to dark grayish brown.

As expected, all the six pedons showed reduction in CEC following Li-saturation and heating at 250°C (Lim and Jackson, 1986). The CEC measured after Greene-Kelly test is the reduced CEC (CEC_R) or the CEC contributed by the tetrahedral layer (CEC_T). The difference between the CEC of the original undtred samples and the CEC_T would give the CEC contributed by octahedral layer (CEC_O). The reduced Li exchange capacity ($LiEC_R$) values obtained by exchanging Li^+ ions with Mg^{++} ions (Fig 3.8) of P1 to P6 ranges from 31.0 to 127.0 cmol(p+)kg^{-1}. Similarly the $MgEC_R$ (= $MgEC_T$) values obtained by exchanging

Mg^{2+} ions by Ca^{2+} ions for P1 to P6 ranges from 39.2 to 96.3 cmol(p+)kg^{-1}. The $CaEC_R$ values obtained by exchanging Ca^{2+} ions by Ba^{2+} ions for P1 to P6 varies from 26.8 to 76.0 cmol(p+)kg^{-1}. Barring only two horizons, one from Kalwan and another from Nimone soils, the $LiEC_R$ values are higher than the $MgEC_R$ values (Table 1). This may be due to entrapment of Li in the interlayer region in a manner similar to K fixation observed in K-saturated and heated clay smectites and vermiculites (i.e. collapsed interlayers). Lithium fixation probably affected the results of Brindley and Erten (1971) who also reported charge reduction in montmorillonite (on the basis of exchangeable Li) that exceeded the octahedral charge. By washing the samples with diluted $MgCl_2$, the collapsed interlayers were effectively re-expanded and the entrapped Li was released, thereby giving irregular results (Jaynes and Bigham, 1987). The Mg^{2+} ions were exchanged by Ca^{2+} ions as the latter is a better exchanger than the former because clays saturated with highly hydrated cations are themselves more highly hydrated and are more difficult to coagulate than clays saturated with less hydrated cations (Weigner, 1935). Thus the zeta potential of Ca^{2+} ion is less than Mg^{2+} ion thus favouring better exchange of the latter. Further when Ca^{2+} ions are exchanged by Ba^{2+} which replaces the Ca^{2+} ions with ease (being less hydrated) resulting in higher values of $CaEC_R$. Differences between the reduced values $LiEC_R$ and $MgEC_R$ for each sample can be attributed to Lithium entrapped in the interlayer region in a manner similar to the K-fixation observed in heated, k-saturated smectites (i.e. collapsed interlayers). The collapsed interlayers were effectively re-expanded and entrapped Li which was released by extended washing with dilute $MgCl_2$ solution. The $MgEC_R$ values seem to be more stable indicator and appears to give a reliable picture and reasonably quantitative indicator for exchange studies done with clays. Similar results were also obtained by Jaynes and Bigham (1987). Consequently, the difference between total CEC (untreated) and $MgEC_R$ (reduced) (Table 1) is hence forth used as a measure of net charge reduction following Li-saturation and heating.

Distribution of corrected CECs of the fine clays

It appears that tetrahedral charge is over estimated which may be due to the fact that the CEC contri buted by vermiculite and chloride may have been included with tetrahedral charge. Some previous workers (Kapse, 2007 and Ray et al., 2009) have worked out a relationship between the content of vermiculite (V) and chlorite (Ch) from XRD analysis and the non-exchangeable Lithium CEC ($LiEC_{NE}$) obtained by treating mild acid to the Lithium treated and heated followed by Mg treated fine clays. Thus it was envisaged to deduct the contribution of V+Ch (towards total

Table 1. *Untreated and Li-treated CECs (reduced CECs) of fine clays*

Horizon	Depth (cm)	$LiEC_R$	$MgEC_{UT}$ Total CEC	$MgEC_R$ Tetrehedral CEC	$MgEC_O$ Octahedral CEC	$CaEC_{UT}$	$CaEC_R$	Li-trapped in the interlayer =(LiECR-MgECR)
		←			$cmol(p+)kg^{-1}$			→
P1:Linga Series, Nagpur (Typic Haplustert)								
Ap	0-16	84.6	99.0	83.3	15.6	80.3	76.0	1.3
Bw1	16-44	87.0	93.1	76.3	16.8	65.0	56.6	10.7
Bw2	44-69	77.3	97.2	69.6	27.6	69.4	60.9	7.7
Bss1	69-102	78.6	99.6	69.5	30.1	74.1	60.8	9.1
Bss2	102-128	81.1	107.5	62.4	45.1	80.5	59.3	18.7
Bss3	128-150+	81.9	99.9	64.8	35.1	82.5	62.7	17.1
P2: Loni Series, Yavatmal (Typic Haplustert)								
Ap	0-14	104.4	90.0	75.2	14.8	71.9	55.4	29.2
Bw1	14-36	113.6	95.2	63.9	31.3	75.3	48.9	49.8
Bw2	36-65	127.0	114.0	69.8	44.2	88.5	42.5	57.3
Bss1	65-99	114.3	118.4	96.3	22.1	91.5	60.1	18.0
Bss2	99-144	127.0	101.5	56.4	45.2	84.0	32.6	70.6
Bss3	144-160	105.9	116.9	76.1	40.8	88.8	47.7	29.8
P3: Asra Series, Amravati (Sodic Haplustert)								
Ap	0-14	87.4	100.1	64.1	36.0	81.5	63.6	23.3
Bw1	14-40	73.2	94.2	64.9	29.4	77.2	51.7	8.3
Bw2	40-59	110.0	87.3	74.6	12.8	70.0	51.0	35.4
Bss1	59-91	102.6	75.5	70.4	5.1	61.2	56.9	32.2
Bss2	91-125	90.4	113.2	69.6	43.5	91.0	63.9	20.7
Bss3	125-150	118.4	78.3	57.9	20.4	83.1	57.3	60.5
P4: Paral Series, Akola (Sodic Haplustert)								
Ap	0-9	96.7	69.9	60.6	9.3	54.6	33.6	36.1
Bw1	9-35	130.1	77.5	57.9	19.5	69.7	42.0	72.2
Bss1	35-69	118.1	79.6	63.2	16.5	56.7	32.4	55.0
Bss2	69-105	121.1	79.5	63.9	15.7	60.4	51.9	57.3
Bss3	105-132	86.3	76.3	71.3	5.1	67.2	62.0	15.1
Bss4	132-150	120.2	72.8	70.0	2.8	63.0	33.6	50.2

contd...

P5: Kalwan Series, Nashik (Sodic Haplustert)								
Ap	0-20	90.7	72.2	62.0	10.2	46.8	34.4	28.7
Bw1	20-48	110.4	77.5	75.6	1.9	47.3	37.6	34.8
Bss1	48-70	89.8	76.0	62.6	13.5	60.2	55.6	27.2
Bss2	70-88	68.3	73.6	55.7	17.9	54.3	49.0	12.7
Bw2	88-133	67.5	72.3	50.7	21.7	41.4	34.3	16.9
Bw3	133-154	18.9	67.2	39.2	28.0	30.9	26.8	-20.3
P6: Nimone Series, Ahemadnagar (Sodic Haplustert)								
Ap	0-13	31.0	66.4	65.6	0.8	49.7	42.7	-34.6
Bw1	13-38	71.6	80.0	59.1	21.0	70.0	48.6	12.5
Bw2	38-55	74.5	79.2	54.5	24.7	63.6	49.1	20.0
Bss1	55-94	76.3	79.1	54.4	24.7	59.9	41.0	21.9
Bss2	94-128	92.0	67.7	52.0	15.7	70.5	36.4	40.0
Bw/Bc	128-150+	87.4	68.5	47.8	20.8	59.5	28.6	39.7

$LiEC_R$ = reduced lithium exchange capacity ; $MgEC_{UT}$ = Total or untreated magnesium exchange capacity; $MgEC_R$ = Tetrahedral or reduced magnesium exchange capacity; $MgEC_O$ = Octahedral magnesium exchange capacity; $CaEC_{UT}$ = Total or untreated calcium exchange capacity; $CaEC_R$ = Tetrahedral or reduced calcium exchange capacity

CEC) from the tetrahedral CEC to obtain a better relation between the octahedral and tetrahedral CEC values (Table 1, Fig. 1). This is expected to give a better representation of the tetrahedral charge and is henceforth mentioned as corrected tetrahedral CEC ($MgEC_{CT}$). The distribution of corrected total (or untreated), tetrahedral and octahedral CEC of fine clays is shown in figure 2 for all six pedons. Similarly the proportion of weighted mean of tetrahedral and octahedral (corrected) CECs are about 65% and 35%, respectively for P1, 63% and 37% for P2, 69% and 31% for P3, 81% and 19% for P4, 74% and 26% for P5 and for P6 69% and 31%, (Fig. 2, a to f). After correction the proportion of octahedral CEC value has increased compared to the uncorrected one, though the tetrahedral CEC value continued to dominate the interlayer exchange complex. The tetrahedral CECs (MgE_{CT}) decreased down the depth (Table 2) for pedons 1, 3, 5 and 6 whereas opposite trend was observed for pedons 2 and 4. The octahedral CEC ($MgEC_O$) on the other hand showed an increase in trend except in pedon 4 as both the data are complementary to each other (Kapse, 2007). When CEC values were corrected the percent octahedral CEC increased with depth except for pedons 3 and 4 (Table 2).

Table 2. *Untreated (Total), tetrahedral and octahedral CEC and corresponding corrected CEC of fine clays*

Hori-zon	Depth (cm)	Mg EC_{UT}	Mg EC_T	Mg EC_O	Vermi-culite (%)	Chlorite (%)	Contribution of V and Ch in CEC			Corrected Total CEC	Corrected tet CEC	CEC_{CT} (%)	CEC_{CO} (%)
							V	CH	V+Ch	i= (a-h) ($MgEC_{CUT}$)	j= (b-h) ($MgEC_{CT}$)		
		cmol (p+)kg^{-1}					cmol (p+)kg^{-1}						
		a	b	c	d	e	f	g	h	i	j	k	l
P1:Linga Series, Nagpur (Typic Haplustert)													
Ap	0-16	99.0	83.3	15.6	9	5	14	2	15.5	83.5	67.8	81	19
Bwl	16-44	93.1	76.3	16.8	11	3	17	1.2	17.7	75.4	58.6	78	22
Bw2	44-69	97.2	69.6	27.6	11	2	17	0.8	17.3	79.9	52.3	65	35
Bss1	69-102	99.6	69.5	30.1	9	4	14	1.6	15.1	84.5	54.4	64	36
Bss2	102-128	107.5	62.4	45.1	9	3	14	1.2	14.7	92.8	47.7	51	49
Bss3	128-150+	99.9	64.8	35.1	10	3	15	1.2	16.2	83.7	48.6	58	42
P2:Loni Series, Yavatmal (Typic Haplustert)													
Ap	0-14	90.0	75.2	14.8	14	0	21	0	21	69.0	54.2	79	21
Bwl	14-36	95.2	63.9	31.3	15	0	23	0	22.5	72.7	41.4	57	43
Bw2	36-65	114.0	69.8	44.2	6	0	9	0	9	105.0	60.8	58	42
Bss1	65-99	118.4	96.3	22.1	5	0	7.5	0	7.5	110.9	88.8	80	20
Bss2	99-144	101.5	56.4	45.2	9	0	14	0	13.5	88.0	42.9	49	51
Bss3	144-160	116.9	76.1	40.8	7	0	11	0	10.5	106.4	65.6	62	38
P3:Asra Series, Amravati (Sodic Haplustert)													
Ap	0-14	100.1	64.1	36.0	5	0	7.5	0	7.5	92.6	56.6	61	39
Bwl	14-40	94.2	64.9	29.4	9	0	14	0	13.5	80.7	51.4	64	36
Bw2	40-59	87.3	74.6	12.8	12	0	18	0	18	69.3	56.6	82	18
Bss1	59-91	75.5	70.4	5.1	6	0	9	0	9	66.5	61.4	92	8

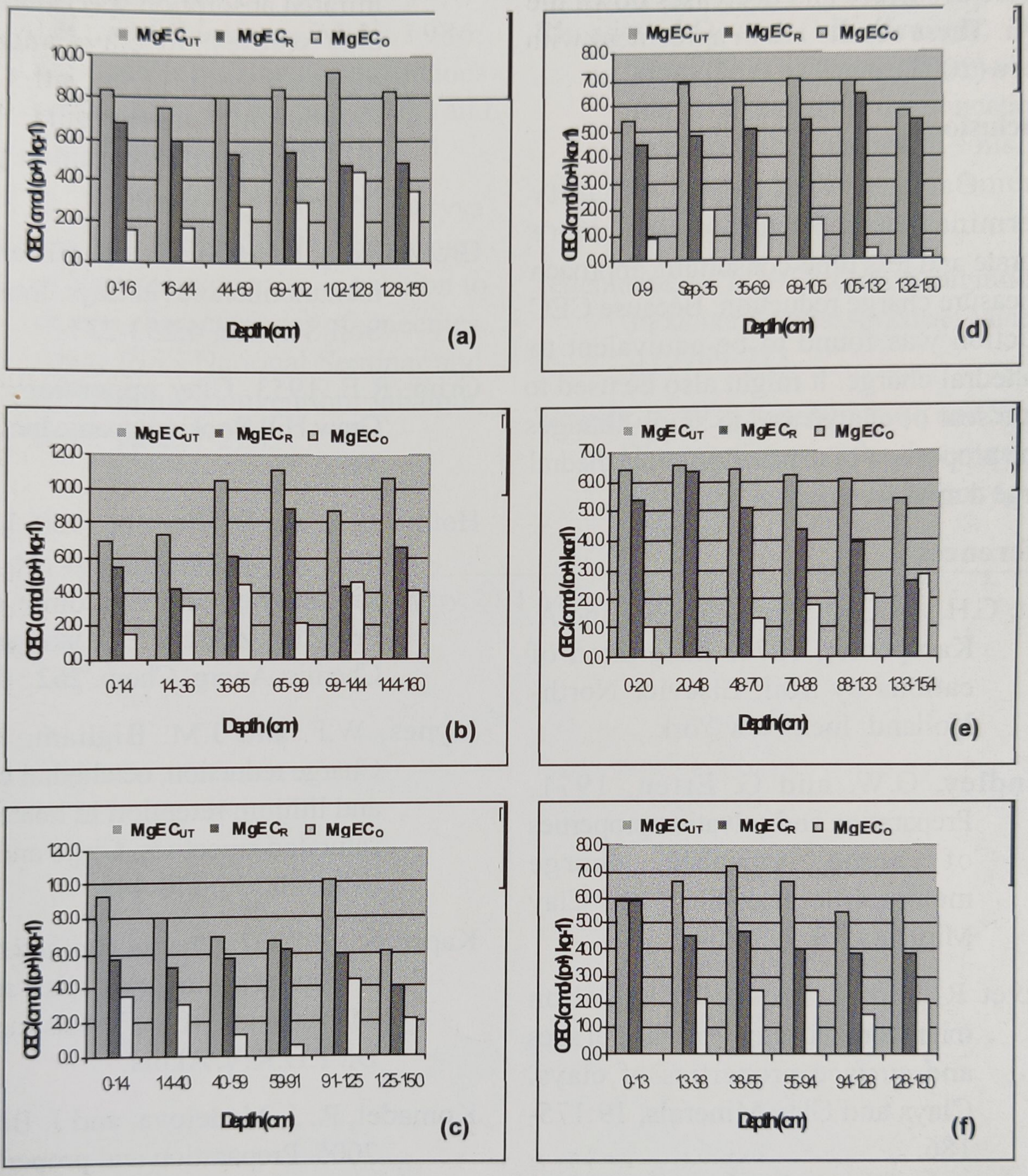

Fig.1: *Distribution of corrected total CEC (CEC$_{UT}$), tetrahedral CEC (CEC$_{CT}$) and octahedral CEC (CEC$_{CO}$) of fine clays for (a) Linga (b) Loni (c) Asra (d) Paral (e) Kalwan (f) Nimone soil fine clays*

This data shows that the tetrahedral charge is more at surface and decreases down the depth. These results are in agreement with Kapse (2007) and Ray et al. (2002).

Conclusion

Cation exchange capacity determination appeared to be a more accurate and less time-consuming approach to measure charge reduction. Because CEC reduction was found to be equivalent to octahedral charge. It might also be used to locate seat of charge and to study changes in the proportion of tetrahedral to octahedral charge during weathering.

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Received February, 2011 Accepted June 2011

Clay Research, Vol. 30, No. 1 pp. 29-41 (2011)

Changes in Potassium Forms, Clay and Silt Mineralogy Brought About by Intensive Cropping

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Abstract: *Potassium management in Indian agriculture has been traditionally overlooked because of high fertilizer cost and anomalous crop response to potassium fertilizers in majority of Indian soils. Suspecting that this could have an adverse effect on potassium nutrition of crops and affect soil health and Indian agriculture, a study was undertaken to simulate short term heavy removal of potassium by repeated harvesting of Panicum maximum (Jacq.) grown with or without fertilization on three major soil groups of India viz., Inceptisol, Alfisol and Vertisol. Fertilization increased cumulative crop yield and potassium uptake in Alfisol followed by Inceptisol and Vertisol. The quantity of water soluble, exchangeable, non exchangeable K decreased during the crop growing cycle both in the fertilized and unfertilized treatments in all the soils. Exchangeable K in the Inceptisol and non exchangeable K in the Vertisol decreased more significantly in the fertilized plots as compared to control. A decrease in 10 Å peak and consequent increase in vermiculite / montmorillonite-interstratified minerals in Inceptisol and kaolinite in Alfisol suggests degradation of mica whereas transformation of vermiculite to montmorillonite-interstatified minerals was taking place in the clay fraction of the soils under study. A general decrease of 10 Å peak was also observed in the silt fraction of Inceptisol and Alfisol suggesting degradation of micas. Thus intensive cropping without K fertilization will lead to all forms of potassium depletion and subsequent degradation of clay and silt minerals that may constraint profitable crop production in the post green revolution era.*

Key words: Potassium depletion, intensive cropping, clay mineralogy, silt mineralogy

Potassium (K) is the third major essential nutrient required for plant growth and plays an essential role in enzyme activation, protein synthesis and photosynthesis. Potassium management in Indian agriculture has traditionally been an overlooked issue as can be judged from the highly imbalanced nutrient use ratios in the country. Intensive cropping with relatively high rates of N and P application and practically no K application has been a decade old practice. This is partly because potassic fertilizer is a costly input in Indian agriculture as there is no reserve of K-bearing minerals in India for production of commercial K-fertilizers and the whole consumption of K-fertilizers are imported, which leads to a huge amount of foreign exchange (Pandian and Datta, 2009). Moreover, the major soils of India (alluvial, ferruginous and black soils) are endowed with fine-grained micas which are known as natural K suppliers to plants and consequently, crop response to K fertilizer application has been anomalous (Pal *et al.,* 2001).

Potassium in soil is present in water-soluble (solution K), exchangeable, non-exchangeable and structural or mineral forms. The amount of readily available K for plant uptake depends on the dynamic equilibrium and kinetic reactions between the different forms of soil K that affect the level of soil solution K at any particular time (Sparks, 1987). The rate and direction of reactions between solution and exchangeable forms of K determine whether applied K will be leached into lower horizons, taken up by plants, converted into unavailable forms, or released into available forms (Sparks, 2000). Clay content, clay mineralogy of soil, and the nature of crops grown, determine the fate of K in soil. Under intensive cropping in the absence of potassium fertilization, the levels of exchangeable and solution K are decreased by crop uptake and release of non-exchangeable K to the exchangeable form occurs. Although it is believed that mineral K is slowly available to plants depending on the forms of soil K and the weather ability of K bearing minerals in soil (Sparks and Huang, 1985), we suspected that continuous and heavy removal of K by crop uptake could speed up the otherwise slow transfer of potassium from primary minerals to the exchangeable and slowly available forms, leading to soil degradation. The study was conducted to find out whether short term heavy removal of K from soils could leads to changes in forms of soil K and clay and silt mineralogy leading to soil degradation.

Materials and Methods

Experimental soils

Soil samples were collected from three different identified locations representing three major soil orders of India viz., Inceptisol, Alfisol and Vertisol. Inceptisol was collected from Delhi, Alfisol from Bangalore and Vertisol from Nagpur. The rationality of sampling laid on the basis that Inceptisols, Alfisols and Vertisols collectively cover more than sixty per cent of the geographical area of the country.

Methods

Physical and chemical properties of soil samples and various forms of soil potassium were determined as follows. pH, EC, CEC, calcium carbonate, specific surface area, mechanical analysis, organic carbon, water soluble K, exchangeable K and non-exchangeable K and total K were determined following methods of Jackson (1973) and Page et al. (1982). Mineral K was obtained by subtracting water-soluble K, exchangeable K and non-exchangeable K from total K.

K depletion experiment

A pot experiment was conducted in glazed pots with 2.5 kg soil with or without fertilization. Fertilization was done through a nutrient solution containing all the macro and micro nutrients except potassium. Nutrient solution was added once in every week during the first and second cuts and thereafter once in two weeks. Control plots received only distilled water. Guinea grass (*Panicum maximum* Jacq.) was sown so as to have 50 healthy plants per pot and was grown for 12 months. Nine harvest of the plant was carried out at 40 days interval. After the fourth, sixth and eighth cutting, plants were harvested along with the roots and fresh seeds planted. *Panicum maximum* was chosen as the test plant because of it high dry matter production and K uptake. Aerial and root biomass and its K content were evaluated after each cut. Aerial biomass was harvested 1 cm over soil level, dried at 70°C, and ground to pass a 0.5-mm sieve. The K content of plant material was determined by digesting (0.5 g) sample in a HNO_3-H_2SO_4-$HClO_4$ mixture (9:2:1) and the resulting solution K was determined by a flame photo meter. At sowing time and after each harvest, the soils were sampled, air-dried, sieved (0.5 mm), and analyzed for K distribution in the different fractions and changes in clay mineralogy.

Mineralogy study

Mineralogical changes due to K depletion by continuous and exhaustive cropping were studied by X-ray diffraction analysis. Briefly, soils were dispersed and fractionated to separate silt (2-20 µm) and clay (< 0.2 µm) after removal of salts, organic matter and oxides by treatment with sodium acetate, hydrogen peroxide and citrate-dithionate-bicarbonate respectively (Jackson, 1956). Identification of the silt and clay minerals was done from the X-ray diffractograms of the fraction treated with (i) Mg-saturated air dried, (ii) Mg-saturated glycerol solvated, (iii) K-saturated air dried, (iv) K saturated and heated to 550 °C. Semi-quantification of minerals in the coarse clay and fine clay was done following the procedure of Gjems (1967).

Results and Discussions

Soil properties and potassium status

Table 1 shows the details of the soils and the various forms of K in the Inceptisol, Alfisol and Vertisol under study. The clay content in the Vertisol was almost double than in the Alfisol and four times than in the Inceptisol. However the Inceptisol had higher silt fraction than Alfisol and Vertisol. The organic carbon content of the Vertisol (0.49%) was much higher than the Alfisol (0.14%) or Inceptisol (0.28%) and consequently the Vertisol had much higher cation exchange capacity (46.3 Cmol kg^{1}) than the Inceptisol (15.9 Cmol kg^{-1}) or Alfisol (10.3 Cmol kg^{1}). The Alfisol had no calcium carbonate and high surface area as compared to the Inceptisol and Vertisol.

The Inceptisol and Vertisol had similar water soluble (10 mg kg^{1} soil) and exchangeable K content (164 and 184 mg kg^{-1} soil respectively), but the Vertisol had much higher exchangeable K content (242 mg kg^{-1} soil) but lower water soluble K content (6 mg kg^{-1} soil). However the share of water soluble and exchangeable K in the total soil K pool was the lowest in Inceptisol (1.3%) followed by Vertisol (3.7%) and Alfisol (5.6%). The non exchangeable K content was highest in Inceptisol, followed by Alfisol and Vertisol. The non exchangeable K content constituted 4.8% of the total K in Vertisol, 7.1% in Inceptisol and 15.4% in Alfisol. The ratio of non exchangeable to exchangeable K content was however the lowest in Vertisol (1.4), followed by Alfisol (2.9), and highest in Inceptisol (6). Lattice K constituted about 91% of total soil K in Inceptisol and Vertisol and 79% in Alfisol. The total soil potassium was however almost 2.6 and 3.1 times higher in the Inceptisol as compared to Vertisol and Alfisol.

Yield and K uptake

Fertilization increased cumulative (nine cuts) crop yield with respect to control treatment in all the soils (Table 2). Higher crop yield was however obtained in the Inceptisol as compared to the Alfisol and Vertisol, which had similar yield. Potassium uptake in the control plots was always greater than fertilized plots because of greater biomass yield produced upon fertilization. The cumulative amount of K uptake in the absence of fertilization in Alfisol was almost 1.6 (Inceptisol) to 3 (Vertisol) times higher, whereas when grown under fertilization the values were 1.3 and 2 respectively. The lower values of K removal in unfertilized control was because of low yields and lesser K removal by the crop. The higher cumulative K uptake was because of higher exchangeable K content in Alfisol as compared to Inceptisol or Vertisol.

Changes in K fractions

In all the soils, the quantity of water soluble, exchangeable, non exchangeable K decreased during the crop growing cycle

Table 1. *Initial soil properties and K fractions*

Soil Properties	Soils		
	Inceptisol	Alfisol	Vertisol
pH	7.5	7.2	8.3
E.C. (dS m^{-1})	0.61	0.22	0.13
Organic C (%)	0.28	0.14	0.49
SSA (m^2 g^{-1})	11	35	29
$CaCO_3$ (%)	0.4	Nil	9.6
CEC (Cmol kg^{-1})	15.9	10.3	46.3
Sand (%)	53	46	20
Silt (%)	32	20	18
Clay (%)	15	34	62
Potassium fractions (mg kg^{-1} soil)			
Water soluble (WS)	10	6	10
Exchangeable (Exch)	164	242	184
Non-Exchangeable (Non Exch)	984	689	254
Lattice	12702	3524	4831
Total	13863	4461	5278

Table 2. *Cumulative (after 9 cuts) yield of the above ground biomass of Panicum maximum Total yield (g pot $^{-1}$)*

Inceptisol	Alfisol	Vertisol	
Control	1.79 *a*	1.55 *b*	1.50 *b*
Fertilized	5.08 *a*	4.51 *b*	4.57*b*

Different letters in a row indicate significant differences among treatments (Tukey, P<0.001)

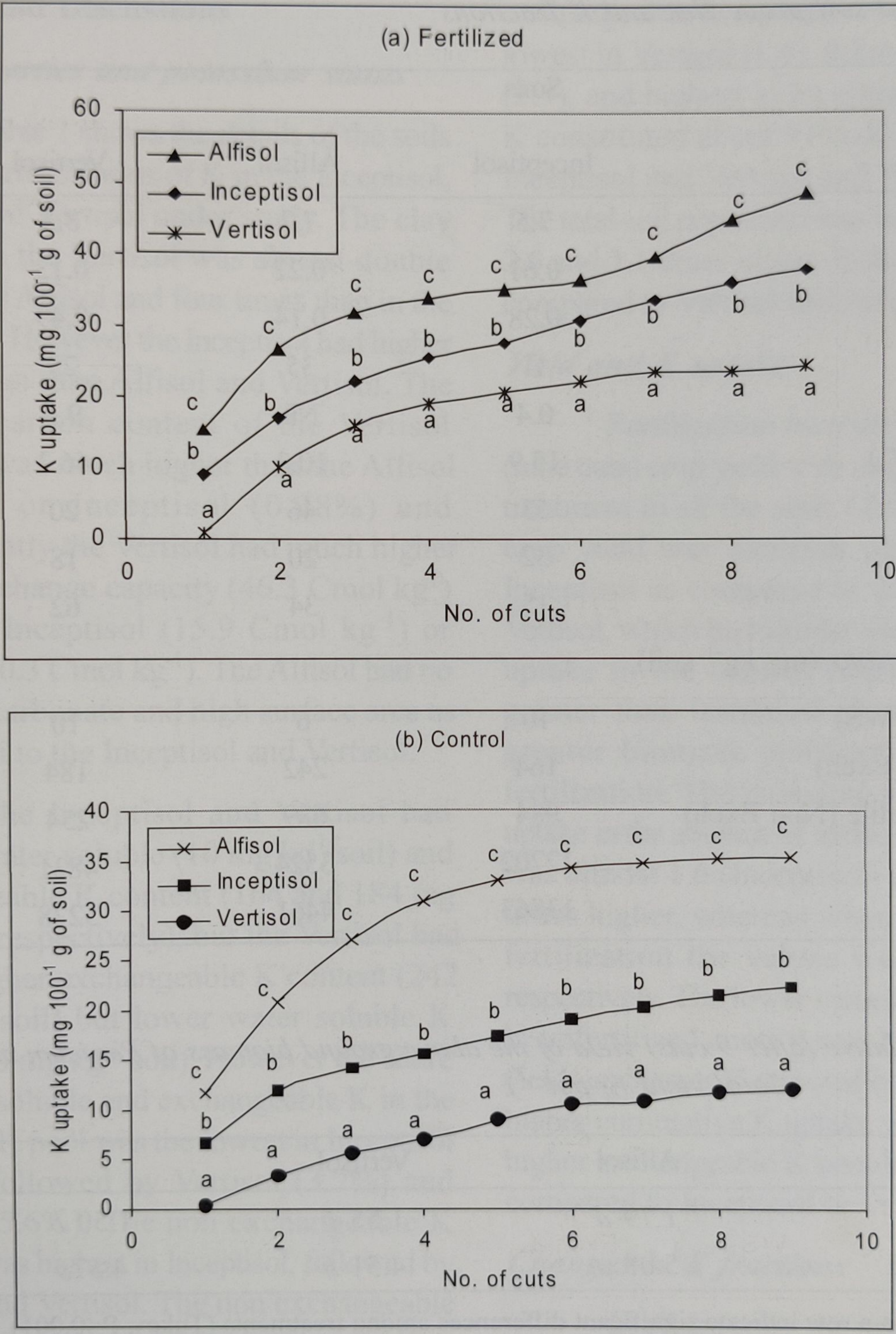


Fig 1. Cumulative K uptake by *Panicum maximum* Jacq. grown under exhaustive cropping with (a) or without fertilization (b).

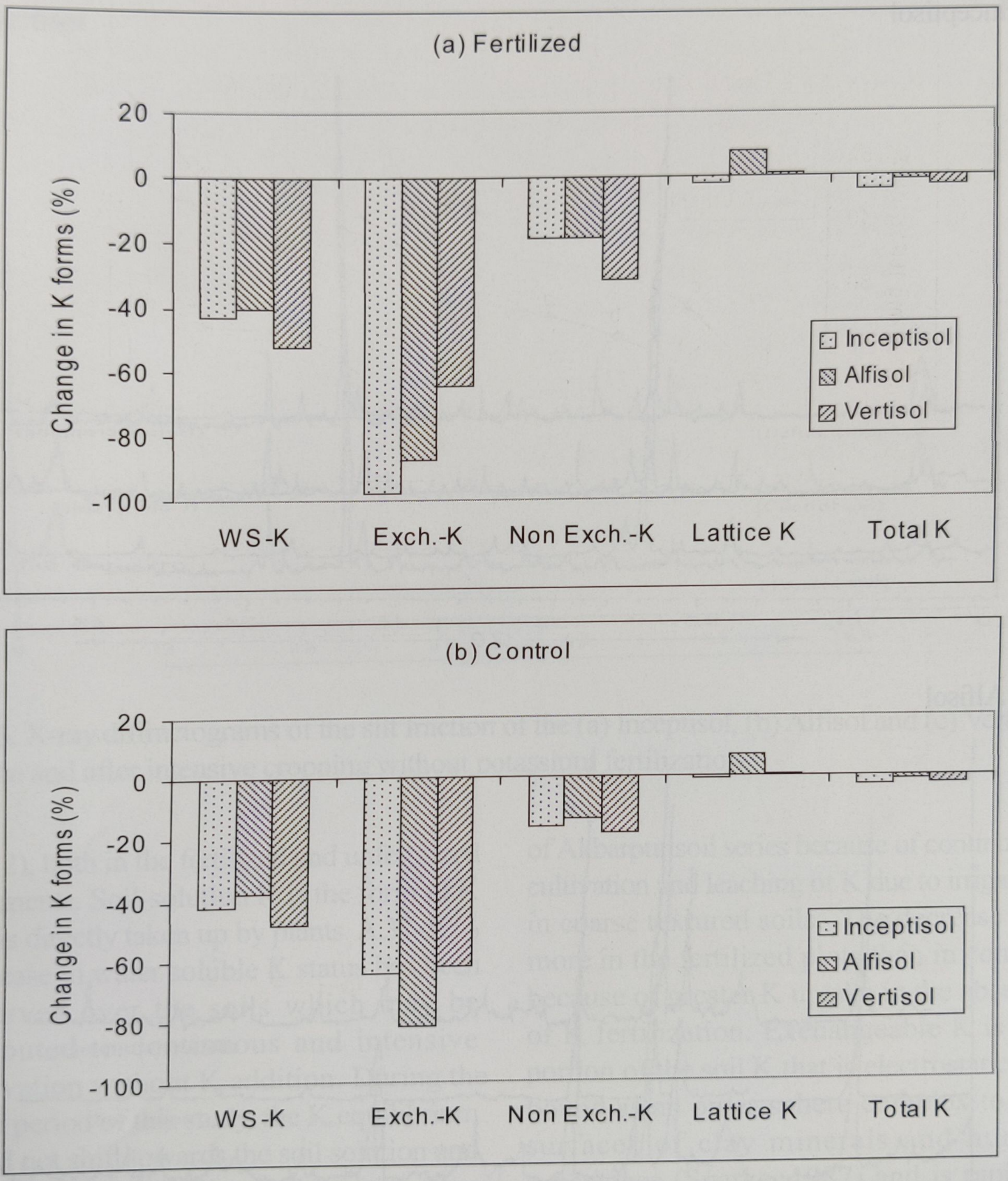
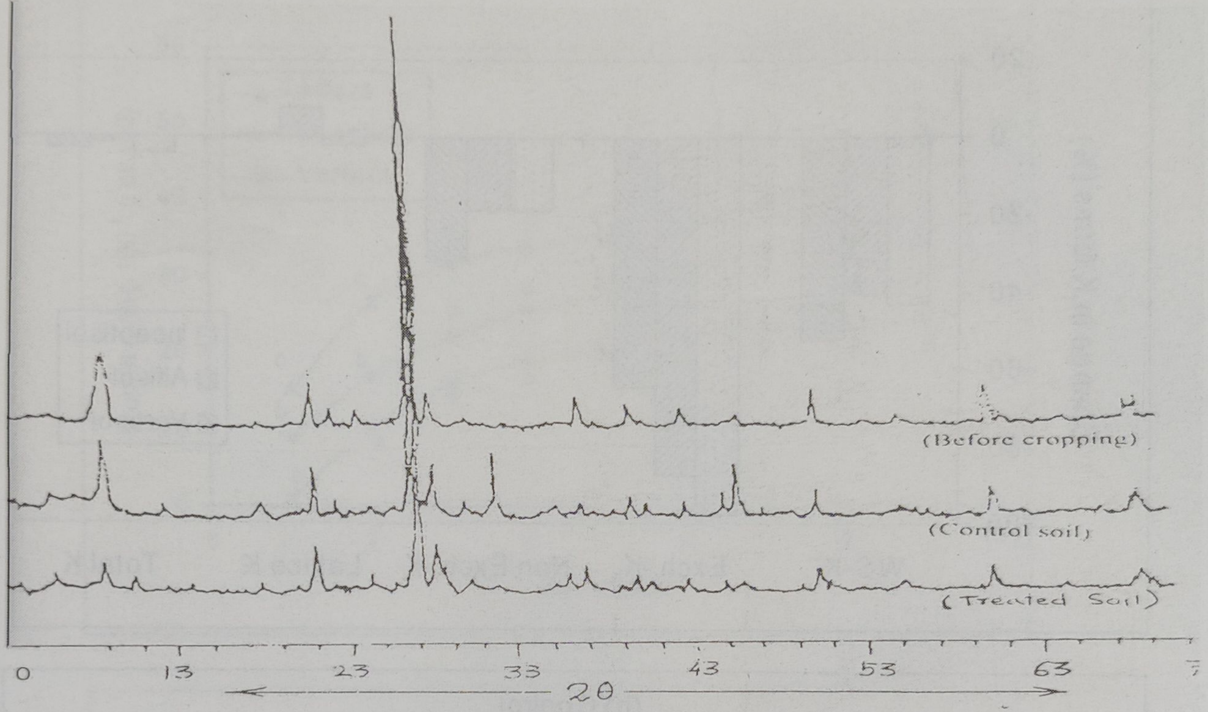
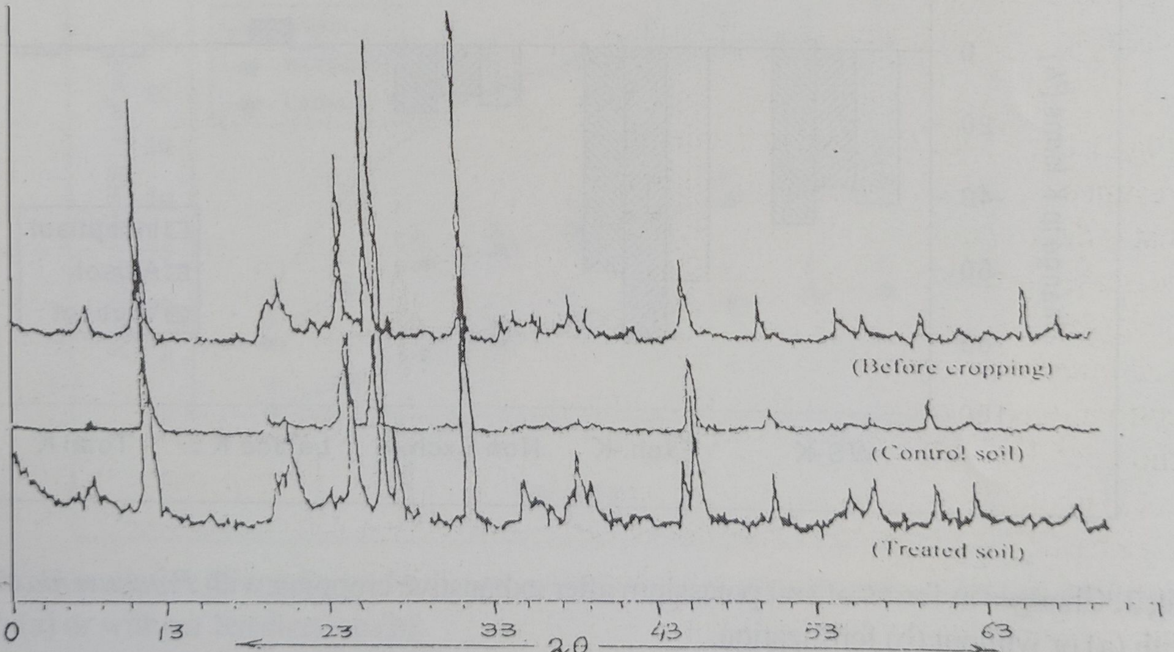


Fig 2. Changes in forms of soil potassium after exhaustive cropping with *Panicum maximum* with (a) or without (b) fertilization.

(a) Inceptisol



(b) Alfisol



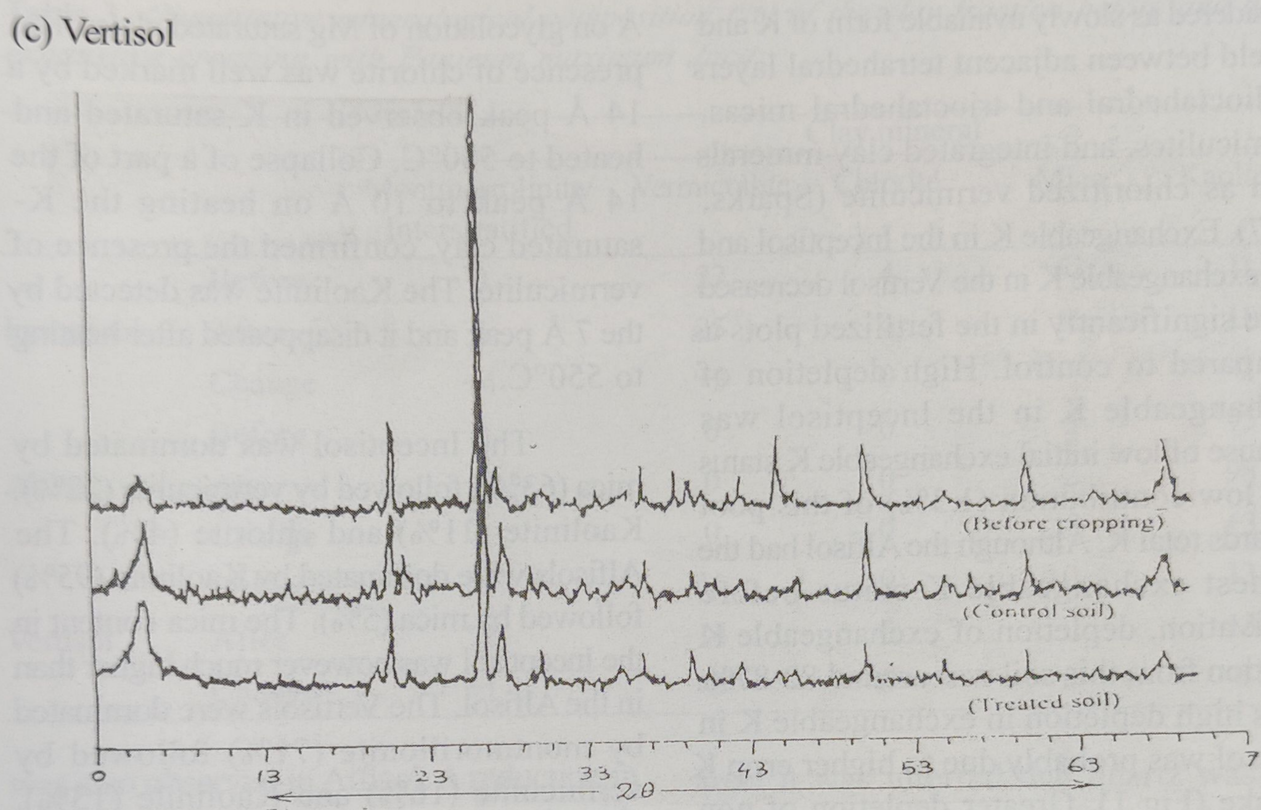

(c) Vertisol

Fig 3. X-ray diffractograms of the silt fraction of the (a) Inceptisol, (b) Alfisol and (c) Vertisol before and after intensive cropping without potassium fertilization.

(Fig 2), both in the fertilized and unfertilized treatments. Soil-solution K is the form of K that is directly taken up by plants. A 37-52% decrease in water soluble K status has been observed over the soils which may be attributed to continuous and intensive cultivation without K addition. During the short period of this study, the K equilibrium could not shift towards the soil solution and K release did not maintain the initial water soluble K status. Bansal et al. (2002) reported decrease in water soluble K status of Akbarpur soil series because of continuous cultivation and leaching of K due to irrigation in coarse textured soils. The decrease was more in the fertilized plots than in control, because of greater K uptake in the absence of K fertilization. Exchangeable K is the portion of the soil K that is electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and humic substances (Sparks, 1987) and is rapidly exchanged with other cations. The non-exchangeable form of K is generally considered as slowly available form of K and is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and integrated clay minerals such as chloritized vermiculite (Sparks, 1987). Exchangeable K in the Inceptisol and non exchangeable K in the Vertisol decreased more significantly in the fertilized plots as compared to control. High depletion of exchangeable K in the Inceptisol was because of low initial exchangeable K status and low contribution (1.3%) of this pool towards total K. Although the Alfisol had the highest exchangeable K status before cultivation, depletion of exchangeable K fraction from this soil was around 82-87%. This high depletion in exchangeable K in Alfisol was probably due to higher crop K uptake (Fig 1). Greater depletion of non exchangeable K in the Vertisol was due to the lowest initial non exchangeable K content in this soil and dominance of montmorillonite group of minerals.

Changes in clay mineralogy

The mineralogical compositions of the clay fractions of soils obtained from X-ray diffraction analysis are given in table 3. The soil clays exhibited the dominance of mica in Inceptisol (63%) and to a much lesser extent in Alfisols (5%) by the strong 10 Å diffraction maxima that remained unaffected by various treatments. The dominance of smectite in Vertisols (71%) was clear from the shifting of a part of 14 Å peak to 17.8 Å on glycolation of Mg saturated clays. The presence of chlorite was well marked by a 14 Å peak observed in K saturated and heated to 550°C. Collapse of a part of the 14 Å peak to 10 Å on heating the K-saturated clay, confirmed the presence of vermiculite. The Kaolinite was detected by the 7 Å peak and it disappeared after heating to 550°C.

The Inceptisol was dominated by mica (63%), followed by vermiculite (22%), Kaolinite (11%) and chlorite (4%). The Alfisols were dominated by Kaolinite (95%) followed by mica (5%). The mica content in the Inceptisol was however much higher than in the Alfisol. The Vertisols were dominated by montmorillonite (71%) followed by vermiculite (16%) and Kaolinite (13%). Roushani (2010) reported dominance of Illite followed by Smectite, Vermiculite and Kaolinite in Inceptisols of Delhi and a predominance of Kaolinite followed by Illite in Alfisols of India.

Continuous cropping without potassium addition in Inceptisol resulted in a decrease in 10 Å peak and corresponding increase in vermiculite and mica-vermiculite / interstratified minerals suggesting that transformation of Illite was taking place. Increase in the quantity of vermiculite and interstratified mineral shows that the process of mica degradation due to K removal is in progress. A decrease in the quantity of mica and consequent increase in Kaolinite content

Table 3. *Quantitative mineralogical composition (%) of the clay fraction before and after exhaustive cropping with Panicum maximum Jacq.*

		Clay mineral				
		Montmorrolinite/ Interstratified	Vermicullite	Chlorite	Mica	Kaolinite
Inceptisol	Before	0	22	4	63	11
	After	4	25	4	56	11
	Change	+4	+3	0	-7	0
Alfisol	Before	0	0	0	5	95
	After	0	0	0	2	98
	Change	0	0	0	-3	+3
Vertisol	Before	71	16	0	0	13
	After	72	14	0	0	13
	Change	+1	-2	0	0	0

was also observed in Alfisol. A reduction in the quantity of vermiculite content with increase in the montmorillonite content has been observed in the Vertisol suggesting that transformation of vermiculite was taking place. Roushani (2010) also reported a decrease in intensity of 10 ú peak resulting in degradation of illite due to permanent removal of potassium ions by plants from inter-layers of clay lattice which proved the formation of vermiculite, chlorite and smectite from Illite degeneration.

Changes in silt mineralogy

The X-ray diffractogram of the silt fraction of the Inceptisol showed presence of quartz, feldspar, mica, vermiculite and mixed layer minerals. From the relative peak area, it was inferred that quartz was the dominant mineral in the silt fraction. Presence of a 14 Å peak indicate presence of chlorite in the soils before and after cropping. The 10 Å peak of the silt fraction before cropping showed a larger width, but after intensive cultivation without K fertilization the sharp 10 Å peak showed a smaller width which shows weathering of mica due to K uptake.

The silt fraction of the Alfisol mainly consisted of quartz. Peaks at 3.57 Å and 1.53 Å before and after cropping showed the presence of chlorite. A sharp peak at 3.24 Å showed the presence of K feldspar mineral. Apatite and other mixed layer minerals were also observed. The peak at

10.25 Å before cropping was reduced after cropping which shows some transformation of mica.

In the Vertisol, quartz, feldspar, vermiculite and chlorite were the dominant minerals in the silt fraction. The peak at 3.19 Å after exhaustive cropping showed the presence of plagioclase feldspar. The small peak at 14 Å before cropping was transformed into a sharp peak after exhaustive cropping which suggests the formation of vermiculite.

Conclusion

The results of this study clearly indicate that intensive cultivation without potassium fertilization resulted in depletion of water soluble, exchangeable and non exchangeable K reserves of the Inceptisol, Alfisol and Vertisol under study. A decrease in 10 Å peak and consequent increase in vermiculite / montmorillonite-interstratified minerals in Inceptisol and kaolinite in Alfisol suggests degradation of mica whereas transformation of vermiculite to montmorillonite-interstatified minerals was taking place in the clay fraction of the soils under study. A general decrease of 10 Å peak was also observed in the silt fraction of Inceptisol and Alfisol suggesting degradation of micas. Thus intensive cropping without K fertilization will lead to degradation of clay and silt minerals and constraint profitable crop production in the post green revolution era.

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Received March, 2011 Accepted July 2011

Clay Research, Vol. 30, No. 1 pp. 43-59 (2011)

Adsorption and Desorption of Bt protein (Cry 1Ab) on Clay Minerals and Amorphous Aluminosilicates

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Abstract: *Studies on adsorption and desorption of Bt protein (Cry 1Ab) were carried out with clay minerals saturated with Zn, Cu and Co and also on synthetic amorphous aluminosilicates with different Si/Al molar ratios. Bt-protein adsorption was higher in montmorillonites; clays saturated with zinc and amorphous aluminosilicates with Si/Al=0 compared to others. The Langmuir adsorption isotherm fitted well in almost all the cases while the Freundlich isotherm failed to explain the fitness in some of the samples. Montmorillonites showed highest bonding energy and adsorption maxima and lowest free energy suggesting that the adsorption reaction was fast and spontaneous. With respect to desorption (10.0-31.6% in different reacting surfaces) of adsorbed Bt-protein, highest desorption was seen in from clay minerals saturated with Co and amorphous aluminosilicates with Si/Al ratio=2 compared to rest of the reacting surfaces.*

Key words: Bt-protein, adsorption, amorphous aluminosilicates, Langmuir, Freundlich

Introduction

Many agronomically important crops have been genetically engineered to express certain Cry genes from *Bacillus thuringiensis* (Bt) and produce larvicidal toxin to kill Lepidoptera and Coleopteran pests. The incorporation into plants of genes from Bt that encode the production of insecticidal toxins eliminates many concerns associated with the use of chemical pesticides, as the toxin continuously produced in these plants (Kumar and Sharma, 1994; Stotzky, 2004; Liu, 2009).

However, if production exceeds consumption and inactivation in insect larvae, degradation by the microbiota and abiotic inactivation, the toxin could accumulate in the environment to concentrations that may (i) constitute a hazard to non-target organisms (Addison, 1993; James *et al.* 1993; Losey *et al.* 1999; Hilbeck *et al.* 1999) and other animal classes, and (ii) result in the selection and environment of toxin resistant target insects (Tabashnik, 1994; Bauer, 1995; Tabashnik *et al.* 1997). Accumulation is enhanced when the toxin bound on surface-active particles in the environment (e.g., clay and humic substance) and thereby, is rendered less accessible for microbial degradation (Saxena and Stotzky, 2000; Fu *et al.* 2007).

Bt toxins (proteins) from engineered crops may reach the soils through three possible modes *i.e.,* decomposing plant debris after harvest (Tapp and Stotzky, 1998; Stotzky, 2000), toxin pollen falling to the ground during tasseling (Losey *et al.* 1999), and exudates from roots (Saxena*et al.* 1999, 2002). Therefore, their fate and persistence in soil ecosystem assumes a special significance. The insecticidal proteins after getting entry to the soils may be inactivated or removed from the soil environment by (i) consumption by insect larvae, (ii) degradation and mineralization by microorganisms, or (iii) natural sunlight.

The toxins from *B. thuringiensis* subsp. Kurstski (Cry protein) and subsp. Tenebrionis (Cry111 protein) bound rapidly on montmorillonites homoionic to K, Na, Ca, Mg, La, or Al; on kaolinite homoionic to Na or Ca; on montmorillonite and kaolinite coated with two types of polymeric oxyhydroxides of Fe; and on the clay fractions separated from various soils (Fusi *et al.* 1989; Crecchio and Stotzky, 2001; Zhou *et al.* 2006; Wang *et al.* 2008; Helassa *et al.* 2009). Some intercalation of montmorillonite occurred with both toxins, although the toxins did not completely penetrate the clay. Similar results were obtained with the toxin from *B.thuringiensis* subsp. There is no information available related to the adsorption-desorption of Bt-protein on the synthetic amorphous aluminosilicates (AAS) with varying Si/Al ratios, which are always present in the soils. Therefore the present study was undertaken to investigate the sorption and desorption of Bt-protein on clay minerals saturated with cations and AAS of varying Si/Al molar ratios.

Material and Methods

Clay Minerals

For the present study, montmorillonite in the form of bentonite was obtained from Rajasthan Minerals (contained 5-10% kaolinite as impurities), kaolinite from Starke and Company (contained 13 and 9% of mica and bentonite) and attapulgite from Tandur mines near Hyderabad. To ensure complete dispersion the minerals were made free of salt by washing with distilled water several times. Clays (<2µm) were separated following Stokes law after peptizing 2% suspension of montmorillonite with electric stirrer and that of kaolinite and attapulgite by sodium bicarbonate and bringing the pH to 8.5 (Jackson, 1976). These minerals were made homoionic with Cu, Co and Zn. For this the clays were equilibrated with desired salt solution at a specific pH for one hour (10 ml/g) and centrifuged to remove the supernatant. The process was repeated four times and the clays were washed free of salt with distilled water and ethyl alcohol (pH at which salt was taken).

Synthesis of Amorphous Aluminosilicates

Amorphous aluminosilicates were prepared by modified procedure of Wada *et al.* (1979) in 5-litre batches as standardized in our laboratory (Basak, 1996). In each batch an appropriate volume of freshly prepared and standardized 0.1 M aluminium chloride solution were added to 2x10^{-3} monomeric orthosilisic acid solution obtained by hydrolysis of an ethanol solution of tetraethyl orthosilicate with water to get Si/Al molar ratios of 0.0, 0.5, 1.0, and 2.0.

The contents were stirred rapidly on magnetic stirrer while titrating with standardized 0.1M NaOH at an average rate of 0.5 cm^3 per minute to give an OH/Al molar ratio of 3. After about 2 hrs standing, the solution was heated for 5 days at 95-100ÚC under a reflux condenser on sand bath. The material precipitated or remaining suspended in the solution, was flocculated by addition of saturated NaCl solution and was collected by centrifugation. The material was dialyzed using deionized water until the chloride reaction with $AgNO_3$ become negative and then freeze dried.

Amorphous aluminosilicates of Si/Al molar ratio zero i.e. only amorphous aluminium hydroxide was prepared by neutralizing 0.1M $AlCl_3$ solution. Solution of $AlCl_3$ was stirred rapidly on magnetic stirrer and titrated with standardized 0.1 M NaOH very slowly to give pH 7.0 to the solution. The precipitate was centrifuged quickly, dialyzed and freeze dried. The detailed characterization of amorphous aluminosilicates has been reported elsewhere (Basak, 1996).

Preparation, Purification and Characterization of Bt-protein

Insecticidal crystal protein (ICP) was prepared from over expressing *E. coli.* For this a single colony of *E. coli* strain was inoculated into 400 ml of Luria Bertani (LB) medium for 24 - 48 hrs with ampicilin (100 µg/ml) at 32 to 37ÚC. This procedure requires that cells be growing rapidly at early or mid log phase and subsequently harvested, centrifugated at 7000 rpm for 10 minute. All subsequent centrifugations were done at this speed and duration. The pellet was resuspended in 100 ml lysis buffer (50 mM Tris, pH 8.0; 50 mM EPTA and 15% sucrose) with addition of 0.5 mg/ml lysozyme and kept on shaker with slow shaking for 2 hours to overnight and centrifuged, resuspended in 50 ml of crystal wash-I (0.5 M NaCl, 2% Triten X 100). The sample was sonicated and subsequent addition of 100 ml crystal wash-I to the sample, centrifuged and resuspended the pellet in 100 ml crystal wash-I using glass rod to break the pellet. Again centrifuged wash-II (0.5 M NaCl) and 3 more time with sterile distilled water and stored the crystal in distilled water at 40°C. Centrifuged the final sample and resuspended the pellet in 5-10 ml of solubilization buffer (50 mM sodium carbonate and 10 mM DTT, pH 8-9) and incubated the sample at 37°C for 3-4 hours on shaker, subsequently centrifuged the sample at 10,000 rpm for 10 minutes and transferred the supernatant to a clean tube and this is referred to as protoxin.

For Bt-protein analysis approximately 5 µg of buffer extractable protein was subjected to sodium dodecyl sulphate (SDS) 10% poly acrylamide gel electrophoresis (PAGE) according to a standard protocol (Sambrook *et al.* 1989). The purified Cry1Ab protein was also measured spectrophotometrically (Lowry *et al.* 1951).

Adsorption and Desorption Studies

Bt-protein (50-450 µg) was added to suspension of clay minerals pre-saturated Zn, Cu and Co and synthetic amorphous aluminosilicates of different Si/Al molar ratios (1000 µg) in double distilled water to a total volume of 1 ml. The contents were shaken in centrifuge tubes (2 ml volume) at 80 rev min^{-1} on a motorized wheel at 37°C for one hour. At the end of equilibrium time of contact, the contents were centrifuged at 10,000 g, supernatant collected and Bt-protein concentration determined (Lowry *et al.* 1951). The difference between the amount of the Bt-protein added and the amount of the Bt-protein detected in the supernatant was used to calculate the amount adsorbed at equilibrium. The data was subjected for plotting the equilibrium adsorption isotherms (amount adsorbed *vs* equilibrium concentration). For the adsorption isotherms, two most commonly used equations i.e., Freundlich and Langmuir were employed.

At equilibration adsorption, the samples were washed three times, each with one ml of double distilled water. The amount of Bt-protein in the supernatants was determined by Lowry method and the amount desorbed was calculated by difference method.

Results

Adsorption Isotherms

After agitation of varying amounts of Bt-protein (50-450µg/ml) with a constant amount of clay minerals and AAS (1000µg), the concentration of equilibrium solution (µg/ml) were compared to initial concentration in order to calculate the quantities adsorbed (µg/g) by AAS and montmorillonite, kaolinite and attapulgites saturated with Cu, Co and Zn. The adsorption data of Bt-protein on minerals saturated with Zn, Cu and Co is presented graphically (Fig. 1) and tabular form (Table 1-3). Bt-protein adsorption was highest on montmorillonites (54.92-95.64%) as compared to attapulgite (57.88-72.52%)

Table 1. *Equilibrium Bt-protein concentration (µg ml^{-1}) and percentage of Bt-protein adsorbed on attapulgite*

Attapulgite saturated with	Concentration (µg ml^{-1})					
	50	100	200	250	300	350
Zn	21.14 (57.72)	42.12 (57.88)	84.13 (57.94)	101.12 (59.55)	113.12 (62.29)	114.09 (67.40)
Cu	20.13 (59.74)	33.12 (66.88)	76.08 (61.96)	89.12 (64.35)	102.19 (65.94)	103.20 (70.51)
Co	18.09 (63.82)	30.79 (69.21)	72.02 (63.99)	86.21 (65.52)	95.29 (68.24)	96.18 (72.52)

Figure in parenthesis shows percentage adsorbed

Table 2. *Equilibrium Bt-protein concentration (µg ml^{-1}) and percentage of Bt-protein adsorbed on montmorillonite*

Montmorillonite saturated with	Concentration (µg ml^{-1})						
	50	100	200	300	350	400	450
Zn	2.18 (95.64)	7.87 (92.13)	54.87 (72.57)	97.88 (67.37)	120.85 (65.47)	132.87 (66.78)	180.88 (59.80)
Cu	4.17 (91.66)	10.88 (89.12)	59.88 (70.06)	102.01 (66.00)	127.24 (63.65)	138.89 (65.28)	187.88 (58.25)
Co	6.88 (86.24)	13.1 (86.90)	63.19 (68.41)	107.14 (64.29)	133.81 (61.77)	154.99 (61.25)	202.88 (54.92)

Figure in parenthesis shows percentage adsorbed

and kaolinites (15.01-90.12%) saturated with cations (Table 2). The shape of curves with respect of minerals was observed to be S-type. On attapulgites, the maximum Bt-protein adsorption was with Zn saturation (114.09 µg/1000 µg of clay) followed by copper (103.20 µg/1000 µg clay) and cobalt (96.18 µg/1000 µg clay) (Fig. 1). The trend was identical for both kaolinite and montmorillonites; however the magnitude was quite different. The general order of Bt-protein adsorption on montmorillonite and kaolinite is given as Zn-montmorillonite > Cu-montmorillonite > Co-montmorillonite

Fig. 1. *Bt-protein sorption on clay minerals saturated with Cu, Zn and Co*

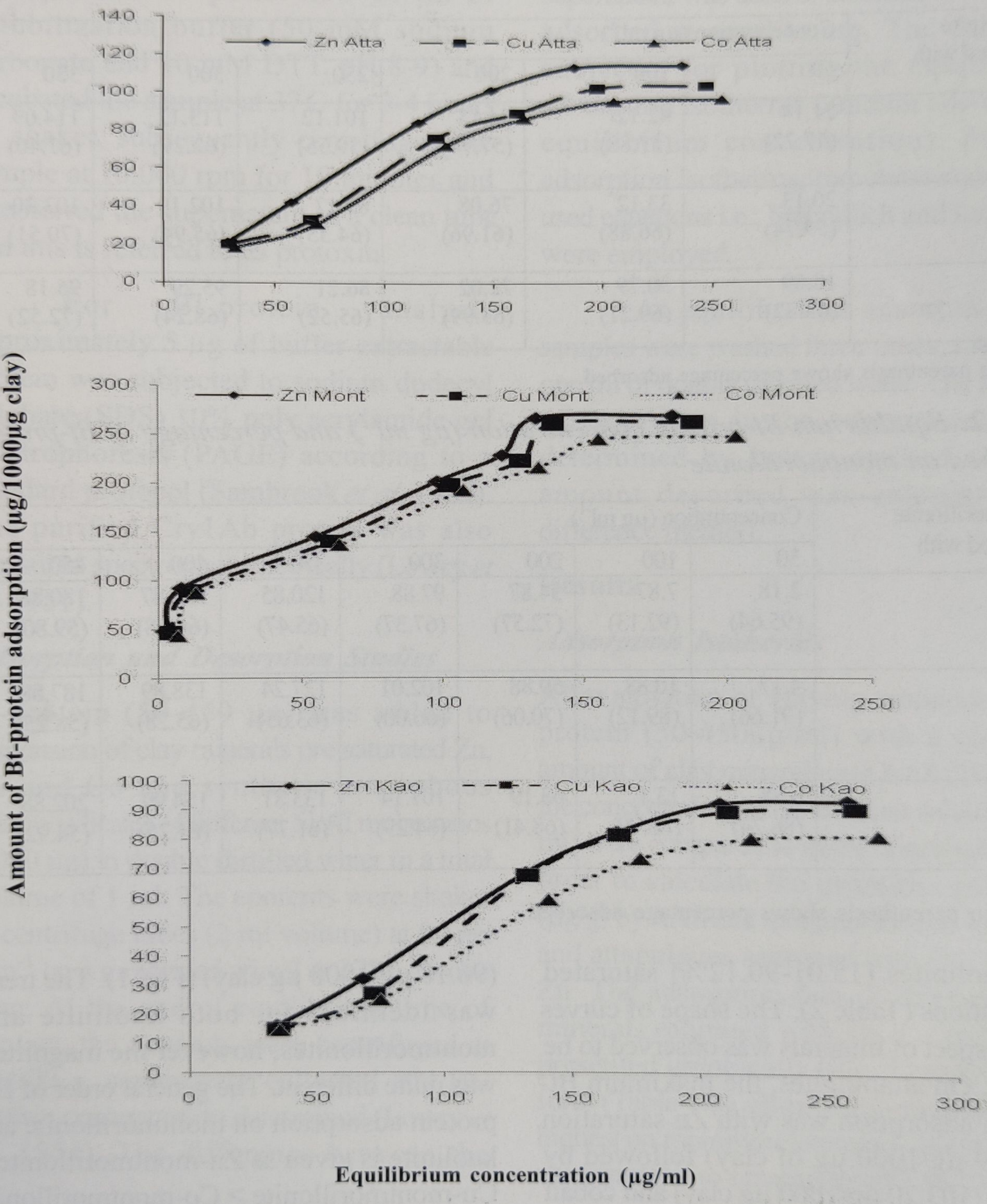

Table 3. *Equilibrium Bt-protein concentration (μg ml^{-1}) and percentage of Bt-protein adsorbed on kaolinite*

Kaolinite saturated with	Concentration (μg ml^{-1})					
	50	100	200	250	300	350
Zn	33.86 (32.28)	67.90 (32.10)	131.88 (34.06)	167.86 (32.86)	207.88 (30.71)	256.95 (26.59)
Cu	34.99 (15.01)	72.85 (27.15)	132.86 (67.14)	168.88 (81.12)	210.86 (89.14)	259.88 (90.12)
Co	35.21 (29.58)	74.88 (25.12)	140.92 (29.54)	176.88 (29.25)	219.89 (26.70)	268.80 (23.20)

Figure in parenthesis shows percentage adsorbed

Table 4. *Equilibrium Bt-protein concentration (μg ml^{-1}) and percentage of Bt-protein adsorbed on synthetic amorphous aluminosilicates with different Si/Al molar ratios*

Synthetic amorphous aluminosilicates	Concentration (μg ml^{-1})				
	50	100	150	200	250
Si/Al=0.0	38.28 (23.44)	81.08 (18.92)	128.38 (14.41)	177.37 (11.37)	227.19 (9.12)
Si/Al=0.5	39.92 (20.16)	82.06 (17.94)	129.08 (13.95)	179.65 (10.68)	228.58 (8.57)
Si/Al=1.0	39.06 (19.88)	82.99 (17.01)	129.81 (13.46)	178.96 (10.52)	228.68 (8.53)
Si/Al=2.0	40.99 (18.02)	84.14 (16.86)	130.06 (13.29)	179.07 (10.47)	228.97 (8.41)

Figure in parenthesis shows percentage adsorbed

(269.12 > 262.12 > 247.12 µg/1000 µg of clay) and Zn-kaolinite > Cu-kaolinite > Co-kaolinite (93.05 > 90.12 > 81.20 µg/1000 µg clay).

Equilibrium Bt-protein concentration (µg/ml) and percentage adsorption on synthetic amorphous aluminosilicates is given in table 4. Bt-protein adsorption was maximum on the synthetic amorphous aluminosilicates with Si/Al molar ratio zero (22.81 µg/1000 µg AAS) followed by Si/Al = 0.5 (24.42 µg/1000 µg AAS), Si/Al = 1 (21.32 µg/1000 µg AAS) and Si/Al = 2 (21.03 µg/1000 µg AAS). The results clearly indicated that as the Si/Al molar ratio increases, Bt-protein adsorption decreased. The equilibrium adsorption isotherms were of L-type, showing a plateau with the concentrations of Bt-protein added.

The adsorption parameters like K_F, 1/n and free energy were calculated using the Freundlich equation, $C_A = K_F Ce^{1/n}$ or $\log C_A = \log K_F + 1/n \log C_E$, where C_A is the equilibrium concentration (µg/g) of Bt-protein adsorbed on clay minerals, K_F is the Freundlich coefficient, C_E is the equilibrium concentration (µg/ml) of the Bt-protein in the liquid phase and 1/n is the Freundlich exponent (Sundaram, 1996). Values of K_F and 1/n were estimated by linear regression after log-log transformation. Attapulgite saturated with zinc showed maximum selectivity coefficient (1.2067) as compared to copper (1.0734) and cobalt (0.8210), while the 1/n value was highest in Co-attapulgite (0.8897) followed by Zn-attapulgite (0.8614) and Cu-attapulgite (0.8539) (Table 5). The free energy was minimum in Zn-attapulgite (-0.1113) as compared to Cu-attapulgite (-0.0419) and Co-attapulgite (0.1170). The data indicates that the Bt-protein strongly adsorbed in Zn-attapulgite, while the efficiency of adsorption was lowest in that system. The selectivity coefficient was observed to be highest in Zn-montmorillonite (37.307) followed by Cu-montmorillonite (26.509) and Co-montmorillonite (20.244), but the trend was just reverse for 1/n values. It indicates that the free energy was lowest in Zn-montmorillonite (-2.143), thereby the reaction of Bt-protein on the material was fast and spontaneous. Freundlich equation could not be fitted well to the kaolinites.

In amorphous aluminosilicates the selectivity coefficient (K) was found to be maximum in sample with Si/Al=0, which was followed by Si/Al = 0.5, Si/Al = 1.0 and Si/Al = 2.0 (Table 6). The trend was quite reverse for 1/n value, while the free energy was minimum in Si/Al molar ratio zero, highest in Si/Al=2 and Si/Al = 0.5, Si/Al = 1.0 samples lying in between.

The adsorption data obtained for pure clay minerals and synthetic amorphous aluminosilicates were also fitted into the Langmuir equation:

$$C_E/C_A = 1/K_1K_2 + C_E/K_1$$

Table 5. *Adsorption parameter and regression equation of Bt-protein for pure clay minerals in Freundlich isotherm model*

Clay mineral	1/n (Slope)	K_F	Regression equation	? G (Free energy)	R^2
Attapulgite					
Zn-attapulgite	0.8614	1.2067	Y= 0.8614x + 0.0816	-0.1113	0.98
Cu-attapulgite	0.8539	1.0734	Y=0.8539x + 0.0308	-0.0419	0.96
Co-attapulgite	0.8897	0.8210	Y= 0.8897x – 0.0858	+0.1170	0.96
Montmorillonite					
Zn-montmorillonite	0.3785	37.307	Y= 0.3785x + 1.5718	-2.143	0.98
Cu-montmorillonite	0.4408	26.509	Y=0.4408x + 1.4234	-1.9415	0.97
Co-montmorillonite	0.4785	20.244	Y= 0.4785x + 1.3063	-1.7817	0.96
Kaolinite					
Zn-Kaolinite	0.9207	0.6670	Y= 0.9207x - 0.1755	+0.2390	0.98
Cu-kaolinite	0.9835	0.4570	Y=0.9835x - 0.3398	+0.4634	0.96
Co-kaolinite	0.9239	0.5380	Y=0.9239x – 0.2688	+0.3666	0.97

Table 6. *Adsorption parameter and regression equation of Bt-protein for synthetic amorphous aluminosilicates in Freundlich isotherm model*

Synthetic amorphous aluminosilicates	1/n (Slope)	K_F	Regression equation	? G (Free energy)	R^2
Si/Al =0.0	0.3775	3.2255	Y=0.3775x + 0.5086	-0.6937	0.90
Si/Al =0.5	0.4302	2.3094	Y= 0.4302x + 0.3635	-0.4958	0.87
Si/Al =1.0	0.4370	2.1993	Y= 0.4370x + 0.3423	-0.4668	0.90
Si/Al =2.0	0.4955	1.6132	Y= 0.4955x + 0.2077	-0.2833	0.88

where, C_E = equilibrium concentration, C_A = amount of Bt-protein adsorbed per unit of adsorbent, K_1 is adsorption maxima and K_2 is bonding energy constant, C_E/C_A vs C_E was plotted, with a slope of $1/K_1$ and intercept of $1/K_1K_2$ (Sundaram, 1996). K1 and K2 were calculated from slope and intercept. Attapulgite saturated with Zn fitted relatively well in Langmuir isotherm, however, Cu- and Co attapulgites could not be fitted well in this adsorption isotherm (Table 7). The R^2 value varied from 0.41 to 0.76 and other adsorption parameters are listed in Table 7. Amongst cations, the Zn-montmorillonite showed highest bonding energy, while the Cu- or Co-montmorillonite had similar adsorption maxima (303.03). Free energy was lowest in Zn montmorillonite (-4.769) suggesting the reaction was fast and spontaneous. R^2 value varied from 0.93 to 0.96 and the adsorption parameter and regression equation of Bt-protein on montmorillonite is presented in Table 7. Kaolinites saturated with different cations could not be fitted well in Langmuir equation (Table 7).

Adsorption parameter and regression equations for Bt-protein adsorption on synthetic amorphous aluminosilicates having different Si/Al molar ratio in Langmuir isotherm are presented in Table 8. The sample with Si/Al=0 showed highest bonding energy (17.616) while the highest adsorption maxima (27.932) was observed in synthetic aluminosilicates with Si/Al ratio of 2.0. Free energy was also lowest in Si/Al=0 (-1.699) followed by Si/Al = 0.5 (-1.569), Si/Al = 1.0 (-1.523) and Si/Al = 2.0 (-1.448)

Table 7. *Adsorption parameter and regression equation of Bt-protein for pure clay minerals in Langmuir isotherm model*

Clay mineral	K (Bonding energy)	S_{max} (Adsorption maxima)	Regression equation	? G (Free energy)	R^2
			Attapulgite		
Zn-attapulgite	280.01	322.580	Y= 0.0031x + 1.152	-3.337	0.76
Cu-attapulgite	240.50	357.142	Y=0.0028x + 1.485	-3.248	0.52
Co-attapulgite	224.78	384.615	Y= 0.0026x + 1.711	-3.208	0.41
			Montmorillonite		
Zn-montmorillonite	3135.58	294.11	Y= 0.0034x + 0.0938	4.769	0.96
Cu-montmorillonite	2395.49	303.03	Y=0.0033x +0.1265	-4.609	0.93
Co-montmorillonite	1888.04	303.03	Y= 0.0033x + 0.1605	-4.468	0.96
			Kaolinite		
Zn-Kaolinite	2826.05	1428.57	Y= -0.0007x + 0.5055	-4.7074	0.19
Cu-kaolinite	407.63	909.09	Y=0.0011x +2.2302	-3.560	0.07
Co-kaolinite	192.514	454.545	Y= 0.0022x + 2.3611	-3.116	0.26

Table 8. *Adsorption parameter and regression equation of Bt-protein for synthetic amorphous aluminosilicates in Langmuir isotherm model*

Synthetic amorphous aluminosilicates	K (Bonding energy)	S_{max} (Adsorption maxima)	Regression equation	? G (Free energy)	R^2
Si/Al =0.0	17.616	27.932	Y=0.0358x + 1.5856	-1.699	0.99
Si/Al =0.5	14.132	27.397	Y= 0.0365x + 1.9387	-1.569	0.97
Si/Al =1.0	13.088	27.472	Y= 0.0364x + 2.099	-1.523	0.98
Si/Al =2.0	11.531	28.818	Y= 0.0347x + 2.499	-1.448	0.96

Desorption of Bt-protein

By comparing attapulgite saturated with different cations, Co-attapulgite showed higher desorption of Bt-protein (31.5%) as compared to Cu attapulgite (25%) and lowest amount in Zn-attapulgite (22%). Among the montmorillonite saturated with different cations also, the similar trend was observed *i.e.,* highest desorption from Co-montmorillonite (10.5%) followed by Cu-montmorillonite (10.2%) and Zn-montmorillonite (10.0%). In kaolinite also the highest desorption was observed in Co-kaolinite (33.4%) followed by Cu-kaolinite (28.4%) and Zn-kaolinite (24.6%). The synthetic amorphous aluminosilicates with Si/Al molar ratio 2 (31.6%) showed maximum desorption of Bt-protein followed by Si/Al = 1 (29.6%), Si/Al = 0.5 (23.4%) and lowest being in Si/Al = 0 (22.2%).

Discussion

Bt-protein was rapidly adsorbed on montmorillonite, kaolinite and attapulgites saturated with Cu, Co and Zn, suggesting that the protein released from transgenic plant or microbial biomass would be free and susceptible to microbial degradation in soil if in the absence of reactive sites for its adsorption. The large amount of Bt-protein may be required to saturate pure clay minerals which are saturated with different cations. Amongst the clay minerals, the maximum adsorption of Bt-protein was observed in Zn montmorillonite. Bt-protein adsorption was not only governed by the type of clay minerals but also on the nature of the cation on the surface of pure minerals. The observed cationic sequence towards controlling Bt-protein adsorption on pure clay minerals was found to be highest in Zn followed by copper and cobalt. Harter and Stotzky (1971) and Fusi *et al.* (1989) reported that larger amount of proteins required to saturate montmorillonite than kaolinite which was probably a reflection of significantly higher specific surface area and cation exchange capacity of montmorillonite and agreed with observations made with other proteins. Tapp and Stotzky (1997) found that adsorption of Bt protein toxins (Btk and Btt) on clean clays was affected by the type of cation by which the clays were made homoionic and they also reported that adsorption of the toxins from Btk was greater on homoionic to monovalent than to polyvalent cations and decreased as the valence of the charge compensating cation increased. Anderson *et al.* (1981) reported that the adsorption of Bt-protein was not only depend on the type of clay minerals, saturating cation but also on pH and PI (isoelectric point) of the protoxin. At pH value near the PI, a net neutral protein would encounter minimal repulsive force. This can result in maximal collisions with charged clay surfaces and, hence, increased adsorption, as well as in the formation of ionic bonds between the net neutral or positively charged proteins and the net negatively charged surfaces of clays, at least in the initial phases of adsorption (Stotzky, 1986).

Bt-protein on clay minerals saturated with different cations was not in conformity with the Irving and William stability sequence. In the Irving and William stability sequence, Cu was stronger than Ni, Co, Zn, Fe, Mn, Mg, and Ca. But in the present investigation, Bt-protein adsorption was higher on all clay minerals saturated with Zn as compared to copper and cobalt. The classical Irving-William series formulated for stability of metal-organic complexation reaction was more applicable in intermediate pH medium (McBride, 1984).

The variation in the adsorption pattern on synthetic amorphous aluminosilicates with different Si/Al molar ratios was also greatly influenced by the high pH (8-9) at which the adsorption was carried out. At the high pH condition, the protein would develop negative change. In that condition protein might be adsorbed, if less negative charge surface was persist in the system. Therefore, the observed higher adsorption of Bt-Protein was on amorphous silicate with Si/Al molar ratio zero.

At the same pH, the PK_1 and PK_2 value of Si-OH has <2 or 6-7, while for Al-OH it was 5-7.5 or 8-10, respectively. So, at high pH still aluminium was having positive change, hence the adsorption of Bt-protein at high pH would still be higher on synthetic amorphous aluminosilicates with lesser Si/Al molar ratio (McBride, 1984). By comparing cations saturated on the montmorillonite, the selectivity coefficient was found to be highest in Zn-montmorillonite followed by Cu-montmorillonite and Co-montmorillonite while the trend for 1/n value was observed in reverse order. It indicates that the free energy was minimum in Zn-montmorillonite thereby the reaction of Bt-protein on the material was fast and spontaneous.

The regression equations and the different parameters derived showed that the Freundlich/Langmuir equations could not be a best fit in kaolinites saturated with different cations. The results indicated that the Langmuir equation was fitting well in montmorillonite due to highest specific surface area and cation exchange capacity and reaction between the Bt-protein adsorption on Zn-montmorillonite was also found to be fast and spontaneous due to lowest free energy as explained earlier.

Co-attapulgite showed higher desorption of Bt-protein as compared to Cu-attapulgite and lowest in Zn-attapulgite. Among the montmorillonites also, the similar trend was observed *i.e.,* highest desorption from Co-montmorillonite followed by Cu-montmorillonite and Zn-montmorillonite. In kaolinite also the highest desorption was observed in Co-kaolinite followed by Cu-kaolinite and Zn-kaolinite. The results indicate that the desorption of Bt-protein not only depend on the type and nature of clay minerals but also on the type of cations on the surface of clay minerals (Tapp et al. 1994; Venkateswarulu and Stotzky, 1992). Zn saturated clay mineral showed higher tendencies to bound Bt-protein tightly compared to other cations. The synthetic amorphous aluminosilicates of Si/Al molar ratio 2 showed maximum desorption of Bt-protein followed by Si/Al = 1and Si/Al = 0.5 and lowest being in Si/Al = 0. The results clearly indicate that the aluminum was mainly responsible for controlling adsorption and desorption of Bt-protein. With increase in Si/Al molar ratio, the adsorption was decreased, on the other hand, the equilibrium adsorbed Bt-protein was more desorbed from these Si/Al ratio materials.

In conclusion, Bt protein adsorption on clay minerals and AAS was quick and tenacious one and the minerals saturated with Zn showed higher adsorption compared to Cu and Co ions. Bt protein adsorption decreased progressively with increase in Si/Al molar ratios in the AAS. About 10.2-33.4% of adsorbed Bt protein on different surfaces may be liable for desorption, the maximum being from Co clays and AAS with Si/Al molar ratio of 2.

Acknowledgement

The authors express their thanks to the Head, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi for providing all the required facilities for the study.

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Received March, 2011 Accepted July 2011

Clay Research, Vol. 30, No. 1 pp. 61-71 (2011)

Geological and mineralogical formations on various abiotic edaphic stresses at Malegaon, Baramati, Maharashtra

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Abstract: *Field studies were conducted using Bore Logs and sample pits at different morphological features and elevations at NIAM Site, Malegaon, Baramati to understand the nature and alteration effects in different flows/rocks, nature of hydrothermal/ secondary mineral crystallization, type of soils/ paleosols formed and nature and extent of degradation for evaluating the possible role of edaphic stresses on agriculture in view of climate change effecting various soil process. Study indicated that due to average rainfall of 560 mm, the atmospheric drought will be a common experience. It was also observed that with impending increase in atmospheric temperatures due to climatic change, the rich calcium zeolites and calcite will weather faster and may accumulate on surface after sodium leaching which may lead to increased runoff due to soil sealing/ capping, thereby inhibits the plant phonological expression leading to desertification process. In the extreme eventuality of above process of separation of Ca and Na ions due to alteration of intensive leaching by reduced number of rainy days under retained average rainfall and high temperature due to climate change there may be a possibility of calcic and nitric horizons underlain within a profile leading to extreme degradation.*

Key words: Geological and mineralogical formations, Abiotic Stresses, Bore Log, Paleosols, Zeolite

The presence of zeolites as soil modifiers creates a unique pedo-chemical environment as these minerals have abilities to hydrate and dehydrate reversibly and to exchange some of their constituent cations (Bhattacharyya et al., 1999). The effects of Ca-zeolites as soil modifiers on soil hydraulic conductivity for defing the sodic soils were studied by Pal et. al., (2006). The presence of calcite also acts as soil modifiers as it releases Ca ions easily due to low hardness and solubility. Initiatives were taken at NIAM to documents the extent of modification in soil properties by these modifiers. The present study will provide an understanding the natural soil degradational process due to soil modifiers using field morphological and mineralogical associations on various edaphic stresses.

Material and Methods

The survey area at Malegaon, Baramati Taluka, Pune district, Maharashtra (18°09'01.12- 39.75-" N to 74°29'44.94"-30'13.51" E) is located in the semi-arid tract of the plains of Western Ghats with the elevation varied from 547 to 565m MSL. Bore Hole (BH1-17) and Geological Profile (GP1-13) were marked with black and red colures on the Map (Fig. 1).

Seventeen Bore Logs (5cm), twelve mini pits (1.5-2m) and one master pit (3m) and four soil profiles (12-24cm deep) were studied for their detail field morphological and mineralogical make up following standard methods using Drill

Core Machine. Soil horizons were described following Soil Survey Manual (Soil Survey Staff, 1951) and soils were classified according to Soil Survey Staff (1999).

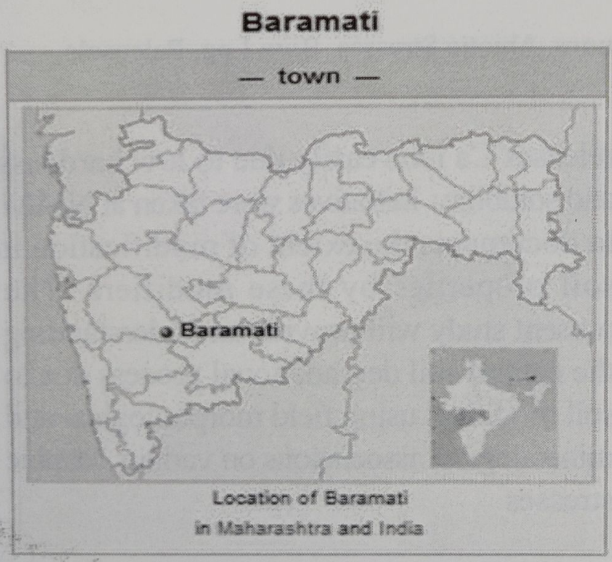

Fig.1. *Map of the NIAM site showing the location of Bore Hole (BH1-17), Geological Profile (GP1-13) and Soil Profile (P1-4)*

Results and Discussion

1. Field Morphological Observations

Field study on Bore Logs, mini pits and master pit show three episodes of volcanic activity at the sites which is indicated by vesicular (amygdular) and non-vesicular (ordinary) flows that occurred during Upper Cretaceous to Lower Eocene period (65-25 million years), Krishnan (1982). These flows (traps) are uniform in composition over much the greater part of the area and correspond to basalt. They are generally dark-grey to dark-greenish grey, but brownish to purplish tints are also met with.

1a. Vesicular (Amygdular) Flows

In vesicular flows upper part is full of vesicles, the middle fairly compact and bottom layer filled with secondary minerals which can be observed in several mini pits in the area (Figs. 2-4). At some places the vesicular horizons are overlain by altered zeolitic horizon mixed with soil matrix. These zeolites are friable and powdery in nature as shown in figures 5 & 6.

Fig. 2. *Highly vesicular top layer with fairly compact middle layer*

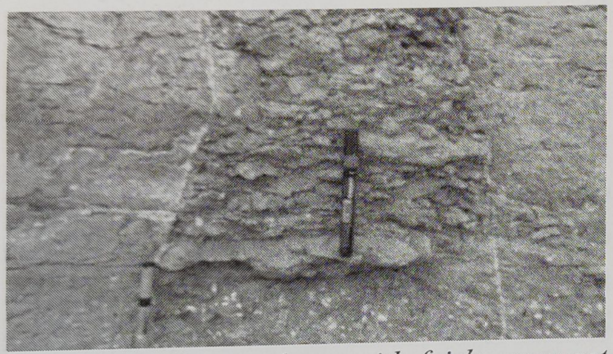

Fig.3. *Vesicular top layer with fairly, compact middle layer and lower layer with coarse grained and cavities are filled up with secondary minerals*

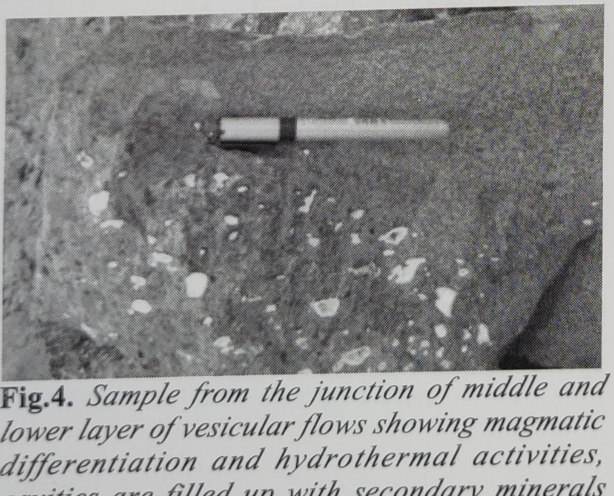

Fig.4. *Sample from the junction of middle and lower layer of vesicular flows showing magmatic differentiation and hydrothermal activities, cavities are filled up with secondary minerals (zeolites)*

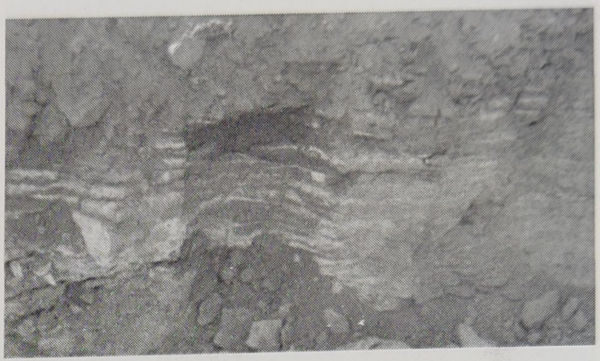

Fig.5. *Zeolitic horizon mixed with soil layer, a constant source of nutrient to the soil*

Fig.6. *Thick zeolitic horizon mixed with soil layer*

Besides several mini pits a representative master pit of vesicular flows upto depth of 2.5m has been studied which indicates 9 horizons of varying thickness. The micro-details of some of the important horizons which are self explanatory are shown in figures 7-9. The different horizons of master profile as shown in figure 10 indicate the nature of flow, their associations, mineralization of zeolites in the lower and upper horizons and their alterations to varying degrees.

Fig.7. *Weathered zeolitic horizon below soil layer with alternate horizons of red bolls.*

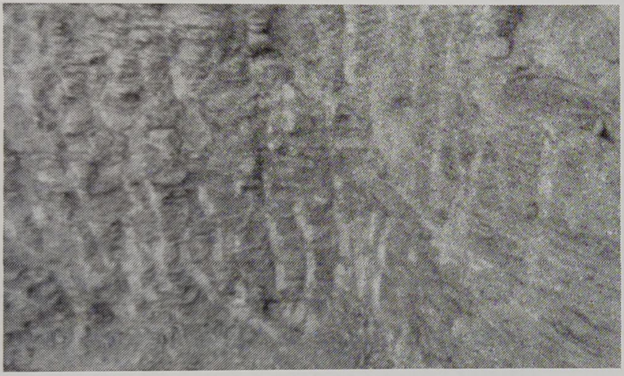

Fig.8. *Upper and Lower flows are separated by intertrappeans converted to clay (paleosols)*

Fig.9. *Lower most horizon of vesicular flow showing zeolite veins*

Field observations on master pit (side not shown in Fig.10) indicated that lower and upper flows are separated by the intertrappeans which are converted to paleosols (figure 8)

1b. Non-Vesicular (Ordinary) flows

In the ordinary flows the upper horizon is fine-grained which is exposed in greater part at site while the lower horizon is coarser with restricted distribution. A representative of such flow is shown in figure 11.

Seventeen bore wells upto the depth of 5m were studied at different sites of the NIAM to correlate the data with the excavated pits. It has been observed that five different combinations of flows have been reported viz. (i) Vesicular (Bore Log Nos. 8, 11, 14, 16 & 17) (ii) Nonvesicular (Bore Log Nos. 2 & 4) (iii) Vesicular-Nonvesicular (Bore Log Nos. 1, 5, 7, 10 & 15) (iv) Nonvesicular-Vesicular (Bore Log Nos. 3, 6 & 12) and (v) Vesicular-Nonvesicular-Vesicular (Bore Log Nos. 9 & 13). The most common and representative of each type of flow and a representative core samples from Bore Log No. 7 is shown in figure 12. The textural and lithological variations of bore logs were correlated with open pit profiles and it has been observed that the two findings are synchronous with each other.

Geological Profile	**Depth (cm)**	**Horizon**	**Description**
	0017		Soil Horizon
	27		Highly weathered zeolitic horizon mix with soil
	50		Red Bolls horizon with fine grained zeolitic intercalations
	65		Altered vesicular basalt with pockets of clay intercalations
	70		Red Bolls horizon with intercalations of zeolitic material
	83		Highly fractured vesicular basalt with zeolite crystals
	113		Altered vesicular basalt with zeolite
	156		Altered vesicular basalt
	231		Altered vesicular basalt with zeolite veins

Fig.10. *Geo-flow in the area (Vesicular basalt)*

1c. Weathering/Alteration

With lower contour height at backslopes the upper part of the trap has been weathered and lower horizon also shows the sign of alteration indicating the variations in weathering intensity.

This phenomenon is very common in both types of flows (Fig. 13).

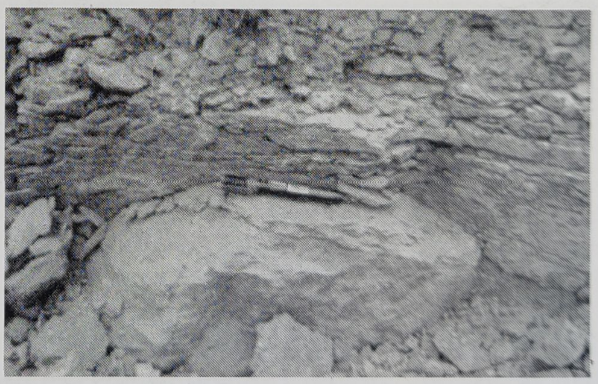

Fig.11. *Non-vesicular flow showing coarse grained in the lower part and fine grained basalt in the upper part with alteration effects*

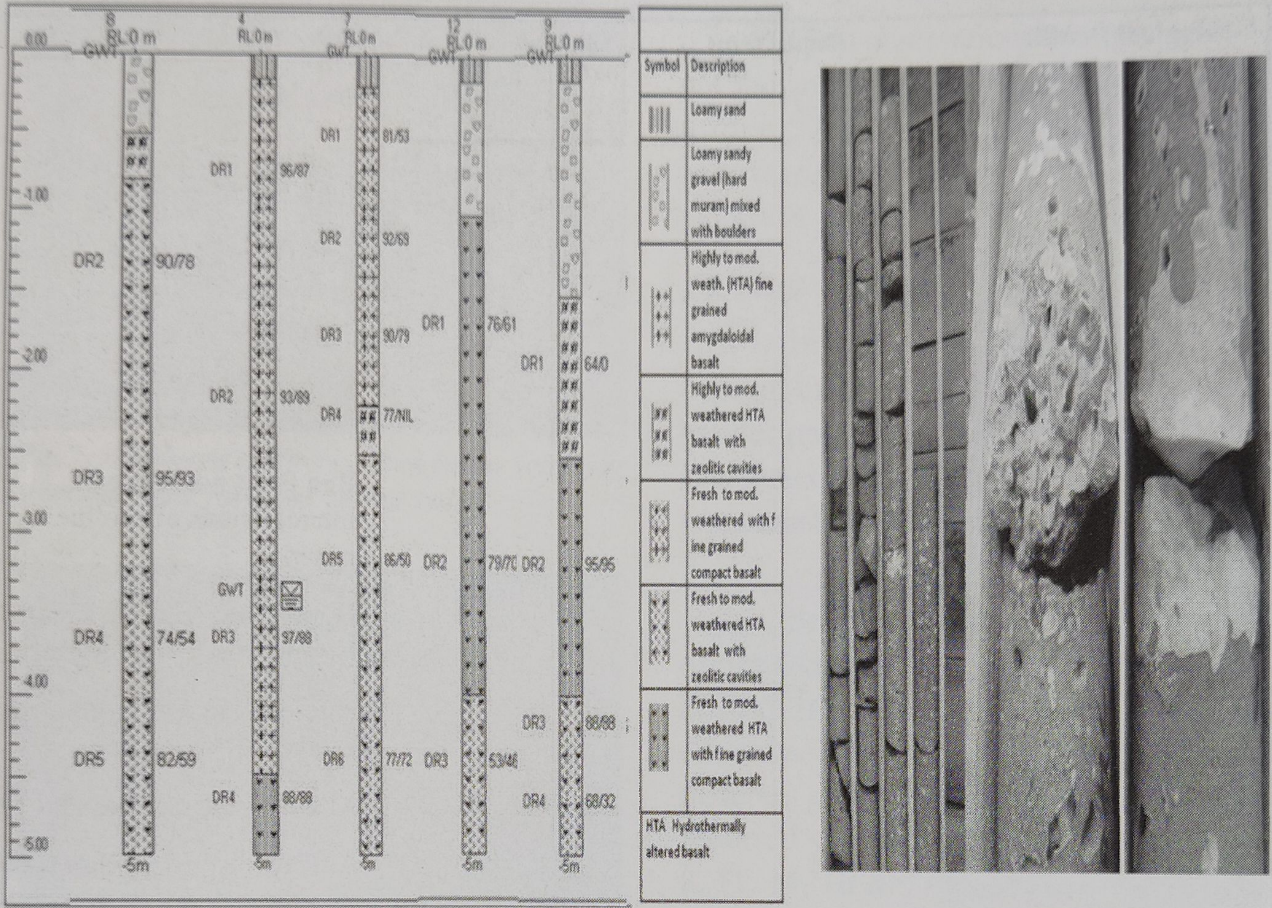

Fig.12. *Lithologs of five Representative flows (8- vesicular, 4-nonvesicular, 7- vesicular-nonvesicular, 12- nonvesicular -vesicular, 9-vesicular-nonvesicular-vesicular) with vesicular-nonvesicular core sample No.7.*

Fig.13. *Upper part of non-vesicular flow showing the differential dissolution and leaching and development of fractures and cracks in basalt*

From the study it has been established that Vesicular –Nonvesicular flows are alternate with each other and are separated by thin beds of intertrappeans which were converted and are preserved as paleosols (Fig. 14). These paleosols are indicator of climate change in the region.

Fig.14. *Vesicular (Amygdular) and non-vesicular (normal) flows are separated with thin beds of scoriae or inter-trappean beds, upper portion (vesicular flows) of the trap is showing weathering effects*

At some places weathering resulted in the development of skeletal box work structures, a very common features developed due to differential dissolution of material (Fig.15).

Fig.15. *Formation of skeletal box work structure during the weathering showing soft portion has been removed and harder portion forming the skeletal like structure, the profile is intercalated with soil matrix*

Due to hydrothermal alteration some of the rocks show differentiation in their colour as shown in figure 16.

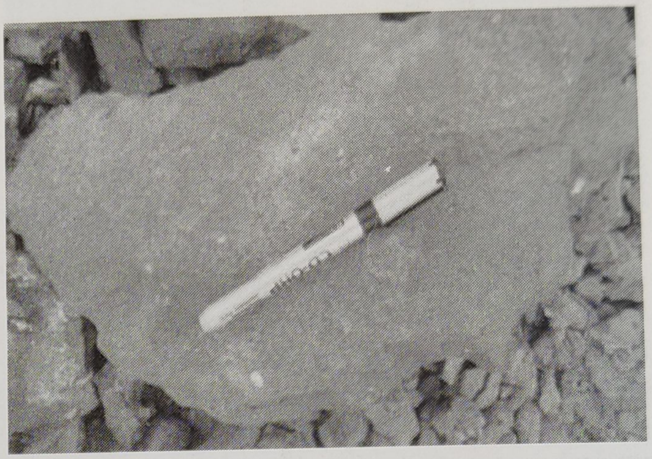

Fig.16. *Upper part of non-vehicular flow consisting of fine grained basalt, color gradation is due hydrothermal alteration*

1d. Soil formation

Field characteristics of soils were studied in a catenary sequence from higher to lower elevation (summit to backslopes) towards eastern side of the site as shown in figure 1. It was observed that the soils are shallow to very shallow (5-23 cm deep), brown to pale brown colour with texture of loamy sand, gravelly sandy loam to sandy clay loam and are associated with severe erosion, gravels and stones and rock out crops. These soils are classified as Loamy-skeletal, mixed, isohyperthermic (calcareous), Lithic Ustarthents and belong to the subgroups of Entisols. A typical soil profile is shown in figure 17.

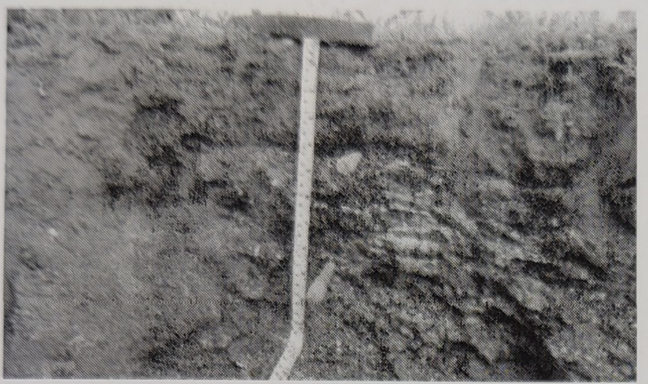

Fig.17. *Profile developed on shoulder slope, 23 cm deep, A horizon 8-10 cm underlain by C horizon of 12 cm (10-22cm) and followed by R horizon with gravelly sandy loam in texture*

Association of the soil with the underlying rock on the summit and side slope show the gradation from lower to upper horizon indicating the in-situ development whereas the soils developed on shoulder and back slope do not show any gradational relationship and indicate that these soils were transported. These observations were correlated with 12 excavated pits (upto rooting depth) at the site for evaluating the possible role of edaphic stresses on agriculture in view of climate change effecting various soil process.

2. Mineralogical Observations

The minerals of late hydrothermal activity or secondary minerals are often developed in the traps, either as fillings in the amygdular cavities or as products of alteration and replacement are zeolite (stilbite) and calcite. Amongst the zeolites, sheaf-like aggregates of different forms of stilbite are the most common and widely distributed (Figures 18-21), besides this divergent and radiating forms are also present (Figure 22). Development of rhombohedral calcite with well developed crystal faces is also present as shown in figure 23 & 24.

Fig. 18. *Nature of hydrothermal/ secondary mineral cryst- allization of zeolite in the cavities of basalt at depth of 1.5m below the ground.*

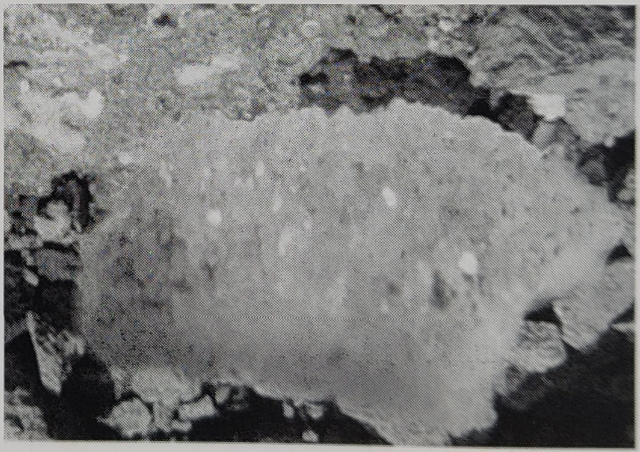

Fig.19. *Growth of sheaf-like aggregates of well developed zeolite crystals*

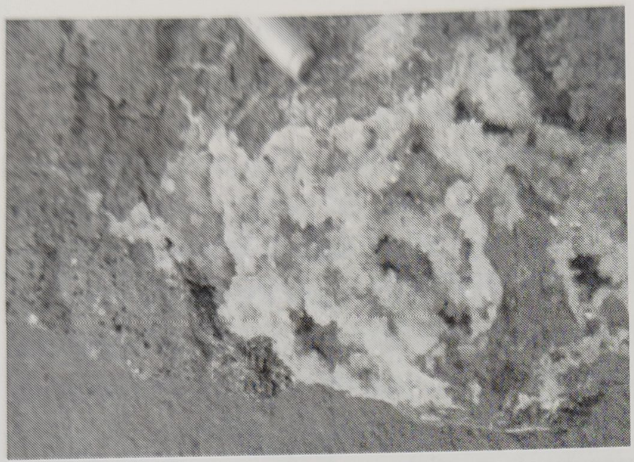

Fig.20. *Growth of sheaf-like aggregates of well - developed zeolite crystals*

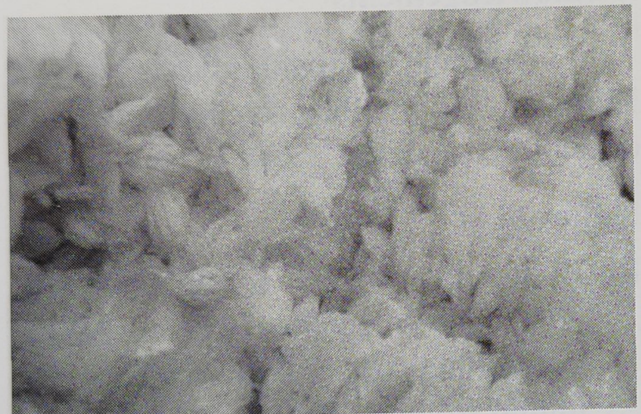

Fig.21. *Growth of sheaf-like aggregates of well developed zeolite crystals*

Fig. 22. Growth of well developed radiating crystals of stilbite (zeolite)

Fig. 23. *Development of Rhombohedral calcite crystals from carbonate gel over vesicular basalt*

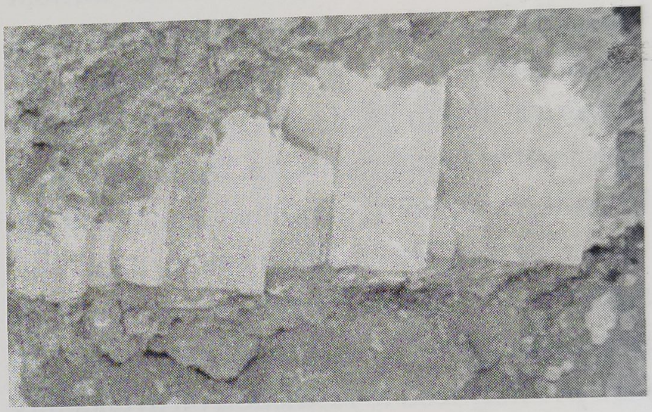

Fig. 24. *Rhombohedral calcite crystals occur as horizon*

From the study it has been observed that the soils are underlain by altered horizons mostly without the intercalation / development of soils and followed by hard rocks. In the north part of the site, hard rocks are exposed on the surface with/ without alteration. Under this situation of hard rocks, the rhizosphere depth is restricted to a maximum of 50 cm. Even this depth being gravelly, with A underlain by AC horizon at shallow depth the moisture retention of the soil, porosity, permeability and hydraulic conductivity are very much restricted. The topography of the site and the nature of parent rock just below the A horizon is not permitting to hold the water at the shoulder slopes and back slopes and therefore the area will experience a combination of edaphic stresses. The average rainfall being 560 mm, and restricted to SW monsoon, the atmospheric drought will be a common experience. These dry spells combined with shallow and gravelly rhizosphere make the plant experience moisture stress almost immediately without allowing the plant resort to adaptation or mitigation measures. However due to hard rock at shallow depth may lead to temporary water stagnation also. Even the secondary minerals zeolites in the vesicular trap are highly prone to alteration and are rich source of calcium to the soils and plants. The high calcium combined with high *p*H may lead to restriction on availability of secondary and micronutrients. Apart with impending increase in atmospheric temperatures due to climatic change, the rich calcium zeolites will weather faster and may accumulate on surface after sodium leaching. This may lead to increased runoff due to soil sealing/ capping, thereby inhibits the plant phonological expression leading to desertification process. In the extreme eventuality of above process of separation of Ca and Na ions due to alteration of intensive leaching by reduced no. of rainy days under retained average rainfall and high temperature due to climate change there may be a possibility of calcic and nitric horizons underlain within a profile leading to extreme degradation. In view of all it is desired that the present state of weathering may be retained by thick soil application on the surface. This may reverse the soil profile from non-supportive rhizosphere to enriched one. Eventually the vegetation will be a dominant factor reducing the ill effects of other parameters of degradation.

Acknowledgements

Authors are thankful to Er. Pravin More of this Institute for his technical assistance during the course of studies.

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Proceedings of the 16th Annual Convention and National Symposium on "Applications of Clay Science: Agriculture, Environment and Industry" held during 18-19 February, 2011 at NBSS & LUP, Nagpur

A brief report on the Convention is presented hereunder.

Inaugural session

The inaugural session was held on 18th February, 2011 at the Dr. S.P. Raychaudhari Auditorium of NBSS & LUP, Nagpur. Dr. Dipak Sarkar, Director, NBSS & LUP, Nagpur and Chairman Organizing Committee extended a warm welcome to the delegates, invitees, staff and students and dignitaries on dias *viz.* Dr. M. Velayutham, Former Director, NBSS&LUP, Nagpur, Dr. S.K.Ghosh, former President CMSI, Dr. D.K.Das, former Head, Division of Agril. Physics, IARI, New Delhi, Dr. D.K.Pal, President, CMSI and Dr. Tapas Bhattacharryya, Organizing Secretary. Dr. D.K.Pal, President Clay Minerals Society of India, briefed about the aims, objectives and activities of the CMSI and the steps initiated to make the CMSI a vibrant society. Dr. D.K.Das, Guest of Honour impressed the clay scientists to make accelerated use of information technology and nanotechnology in tackling different challenges faced in agriculture, environment and industry.

Dr. S.K. Ghosh in his address highlighted the research advancements in the area of clays and soil clay mineralogy, current trends and future prospects of its applications in agriculture, environment and industry. He highlighted the research work initiated by late Prof. J.N.Mukherjee on electrochemical properties of clays. Dr. Ghosh also cited latest research trends using nanoclays and nanoclay composites, their preparation, characterization and applications in biology and environmental studies.

Dr. M. Velayutham, in his address as the Chief Guest, emphasized on the necessity of adoption of a holistic approach with integration of basic knowledge, indigenous technologies, upcoming and advanced instrumentation techniques for the conservation, utilization and management of the natural resources and preserve them for the posterity. He exhorted the clay scientists to make best use of clays, nanoclays and their composites in less explored areas like development of sensors, slow release fertilizers, as environmental remediates etc.

Inaugural function formally came to a close with a vote of thanks by Tapas Bhattacharya, Organizing Secretary, the 16th Annual Convention and National Symposium of CMSI.

National Symposium

In the National Symposium there were seven technical sessions chaired by Dr. D.K. Das, Dr. Rajiv Sinha, Dr. D.K. Pal, Dr. S.K. Sanyal, Dr. Kunal Ghosh and Dr. S.K. Ghosh. In all 45 research papers were presented on diverse areas of clay research *viz.* geosciences, chemicals and fertilizers, nanoclays and their applications in ceramics, industry and soil quality, recent methods on characterization of soil clays, soil environment and physical quality, pedological aspects, clay-organic matter studies, ion exchange studies, soil mineralogy and development etc. All the papers were of high academic standards and the presentations were followed by lively interactions.

A critical and overall review of the national symposium was discussed in the plenary session. The recommendations which came out from the symposium are as follows:

- Clay mineral studies should be broad-based and shall not be confined to the agricultural crops. For example there is lot of scope to relate the clay mineral research with plantation crops, high value cash crops, etc.
- New areas of research viz., nano-technology needs to be encouraged. Efforts should be undertaken to establish nano-technology laboratories. Sufficient funds should be made available for this.
- At under-graduate and post-graduate level the students should be encouraged to take interest in subjects of clay research and nano-technology.

The general body meeting of the CMSI was held on February 18, 2011 at 5.30 P.M. and the proceedings of which has been shown separately.

Cultural Programme

Cultural programme depicting the cultural heritage, folk music and dance sequences of different parts of India was presented by professional artists of the Nagpur- based troupe on the evening of 18 February 2011.

Sd-
(K.M. Manjaiah)
Joint-Secretary

Proceedings of the 16th General Body meeting of the Clay Mineral Society of India held on 18 February 2011 at the Dr. S.P. Raychaudhari Auditorium of NBSS & LUP, Nagpur

Dr. D.K. Pal, President of the Clay Minerals Society of India (CMSI) chaired the meeting, which was attended by 42 members of the Society. Dr. Pal extended a formal welcome to all the delegates and members of the society and congratulated the organizers for nicely organizing the symposium. The business of the meeting was transacted as per the listed agenda. The proceedings of the 15th Annual General Body Meeting held on December 2, 2006 at Lake Hall, Kalyani, Bidan Chandra Krishi Viswavidyalaya, Nadia (Dist), West Bengal were considered and confirmed by the house. The house recommended that a letter should be sent to organizing secretary, 15th CMSI convention, Calcutta to get the audited statement, which was long awaited. During the period 2006-2011, 16 life members and 37 ordinary members, who sought admission to the CMSI, were admitted by the general body.

Dr. Nayan Ahmad, Treasurer presented the audited statement of the accounts for the year ended 31 March 2010 and budget estimates for 2010-2011. These were adopted by the house after some discussion and clarifications.

Regarding the issue of institution of Commemorative /memorial lecture, after detailed discussion it was decided to start a foundation lecture in the name of Dr. S. K. Mukherjee, the Founder President of the CMSI and to be named as “Dr. S.K. Mukherjee – CMSI Foundation Lecture”. A corpus fund of about one lakh may be generated for this activity. Further required initiative will be taken up by the Executive Council of the CMSI. On the agenda item for institution of Honorary Fellowships of the CMSI, there was no unanimity on this issue, instead the house recommended to initiate best student award/best poster awards to encourage young researchers.

Dr. K.M. Manjaiah, Joint Secretary presented the Report of the Society for the period from December 2006 – February 2011; it was adopted by the house.

Election of the Office bearers for the biennium 2011-12 was conducted as it was due. The following were the names elected /nominated as different office bearers of the society. It was also decided to have some international consulting editors for the Clay Research Journal.

President:	Dr. Dipak Sarkar
Vice presidents:	Dr. G.S.Sidhu Dr. K. M. Manjaiah
Secretary:	Dr. Nayan Ahmed
Joint secretary:	Dr. P. Chandran Dr. Kaushik Majumdar
Treasurer:	Dr. T.P. Ahmed Shabeer
Councilors:	
East zone:	Dr. M. Datta Dr. A.K. Sahoo
West zone:	Dr. A.L. Pharande Dr. Vilas Kharche
North zone:	Dr. C.S. Walia Dr. Pankaj Srivastava
South zone:	Dr. S.K. Ghosh Dastidar Dr. K.S. Anil Kumar
Central zone:	Dr. J. Prasad Dr. Tapan Adhikari
Editors, Clay Research:	Dr. S.C. Datta Dr. T. Bhattacharyya

The members nominated/elected were felicitated in the Annual General Body meeting.

Dr. D.K. Pal delivered the presidential address. He congratulated the newly elected members and urged to contribute their best for the upliftment of the CMSI and it activities. Dr. Pal highlighted the various issues of clay science education and research in the country. He emphasized that with the advent of sophisticated instrumentation techniques, clay science applications are enormous and its potential application in diverse areas like industry, soil-plant nutrition studies, pharmaceuticals, sensors, nanotechnology etc. should be pursued more rigorously.

The meeting came to close with a vote of thanks by Dr. K.M.Manjaiah, Joint Secretary, CMSI.

Sd-
(K.M. Manjaiah)
Joint-Secretary

INSTRUCTIONS FOR CONTRIBUTORS

CLAY RESEARCH is the official publication of THE 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, Mineralogical Abstracts, 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-110 012. E-mail: samar_1953@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 250 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 x 17 cm. Give the numbered legend on a separate sheet, not on the figure itself. Data available in the tables should not be uplicated 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.

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

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Clay Research

Vol. 30 **June 2011** **No. 1**

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Printed by : **M/s Sun Shine Art Press** (Mobile - 9873288898, 41412169)