ISSN 0255-7193

CLAY RESEARCH

Vol. 39, No. 1

June 2020

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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Print + online access	Rs. 1,800.00	\$ 350.00
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Print	Rs. 1,200.00	\$ 200.00

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Clay Research, Vol. 39, No. 1, pp. 1-8 (2020)

Dielectric Properties of Kaolin Material with Different Concentrations of NaOH

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Abstract–*Kaolin powder ($Al_2O_3.2SiO_2.H_2O$) with average grain size of 350 5ßm was mixed with five different concentrations (2, 3, 5, 8, 16) M of NaOH solutions. The capacitance and reactance of prepared samples were measured using LCR meter. At frequencies smaller than 1000 Hz, the addition of sodium hydroxide to kaolin resulted in a significant increase of capacitance, while the sample at concentration 3M showed significant stimulation in the capacitance and reactance. At high frequency, the sample at concentration 2 M was the most stimulating samples. At the 20 Hz and at the few concentrations of sodium hydroxide, the 3 M sample showed significant stimulation in the capacitance value. It found that the concentrations of the electrolytic solution create electrostatic forces that affect the prepared sample leading to an increase in dielectric constant and decreasing reactance which can be candidate for supercapacitor applications.*

Keywords: Dielectric Properties, Electrolytic Solution, Kaolin, Reactance, Supercapacitor.

Ceramic is brittle and high thermal capacity material. It has good properties like strength, high resistivity, thermal, chemical, and consists of oxides types, addition some types consist of H_2O molecular in insert structure, named metallic clay, as kaolinite. Others types of ceramic don't consist of H_2O molecular, named nonmetallic clay, as sand (Eda, 2007; Mayer, 2007)

The kaolin material is considered raw material, which has the ability to the formation with high absorption. The kaolin properties often consider white color and gradient to gray and then yellow color, that depends on ratio iron, silica and alumina oxides existing in kaolin molecular and little quantity of secondary material as organic materials. The kaolin inserted in fabrication bricks, cement and also, in more material construction of buildings (Njoya *et al.* 2016).

The kaolin usually exists in nature as a form of argillaceous rocks and sedimentary layers successive, also, sedimentary in igneous rocks (due to baring process), and often exists near the earth's surface. The appearance of kaolin depends on the percentage of oxides that make up it and are shown in the Table 1, while the pure kaolinite $((OH)_4(AL_2Si_2O_5)$ is a mineral extract of kaolin. The kaolinite molecule consists of two layers $(Si_2O_5)^{2-}$ and $Al_2(OH)_4^{2+}$, which is the electrical identity of it. The O^{2-} ion in $Si_2O_5^{2-}$ is connected to the OH ion available in $Al_2(OH)_4^{2+}$ to consist of the mid-planeanion, so that strong and medium bonds are generated like ionic and covalent in kaolinite molecule, and weak bond (van der Waals) between nearest sheets (Callister and Rethwisch, 2014).

Arulanandan and Mitchell (1968) measured dielectric constant of clay satiated in water using the wide range of frequencies. He showed the highest dielectric constant recorded at the lowest frequency. Kaya (2001) compared and studied

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DOI: 10.5958/0974-4509.2020.00001.7

Table 1. *The composition of the kaolin (Adapted from Yahaya at al., 2017).*

Sample Chemical composition (weight %)							
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	P_2O_5
57.633	37.766	0.860	0.596	0.346	1.801	0.605	0.311

electric conduction of the kaolin and bentonite in water solution with ammonium acetate, and he showed the electrical conductivity of bentoniteis higher than from kaolin samples because of existence the conductive ions in bentonite more from the kaolin. D'ujanga *et al.*, 2002) measured the polarization effect with pore sizes for different kaolin powder sintered at 1200°C. They showed the polarization increasing proportionally with that samples which have the highest porosity from that has the lowest porosity. Maki *et al.* (2011)prepared samples from Alumina (α-Al_2O_3) with different ratios of MgO (0.1, 0.2, 0.3, 0.5) and sintered at 1500°C whereas grain size was 635m. The result is shown that the best dielectric constant was at ratio 0.5 of MgO. Hasaani *et al.* (2015) fabricated supercapacitor for energy storage from raw clay, carbon powder, and zinc oxide. They found that the current density was about 24 A m^{-2}, and proving the raw clay has a high characteristic of diffusion.

The ceramic consist from oxides types, addition, some types consist of H_2O molecular in insert structure, named metallic clay, as kaolinite. And there others types don't consist of H_2O molecular, named nonmetallic clay, as sand (Carterand Norton, 2007). A large part of the modern preparing method of ceramic makes it superior to competing materials such as alloys, composites, and polymers. High strength and resistivity are the most properties of ceramics, performance for electrical industrial applications. These performances of ceramics are very sensitive to the compaction pressure, particle size, sintering temperature and time. It is useful when studying the clay structure knowing the electrical properties of the clay-water-electrolyte process, or using as part from fabrication of supercapcitor from nano clay (Oraon *et al.*, 2015). Chen *et al.*, 2019 and Reinosa *et al.*, 2019) proved that if the cement material is kept on polarization after removing electric field, it becomes solid

Knowledge of the change in the electrical properties of kaolin during treated with mineral hydroxide is important for preparing electro-ceramic materials. The electrolytic solutions, in general, are assisting in increasing polarization process to materials. Therefore, using kaolin with dilute electrolyte NaOH, the physical and chemical influence occurs between Na^+ ion existed in the electrolyte solution with ion OH^- that presenting in kaolin molecule. This lead to increase ionic conjunctions resulting that the statistic forces between the molecules have increased, that driven to increase the relative dielectric, and then, could use in energy storage. According to, the study of the polarization ability and electric properties of kaolin molecules via using the LCR device test at addition difference concentrations of electrolyte solution by constant quantities has been adopted.

One of the significant causes of failure that occurs in warehouse floors is largely related to the abundance of alkaline materials that come from leaked alkaline water. The alkaline water leaking between the ceramic tiles results in a contraction or expansion in the clay materials below the tiles, which negatively affects the integrity of the tiles and leads to high losses in the costs of flooring reconstruction in every time. This problem led to the current research in order to know the best concentration of alkaline water that interacts with clay materials, in order to take the treatment reasons for this problem.

Materials and Methods

1.5 ml of NaOH solutions with varying concentrations were mixed with a kaolin powder ($Al_2O_3.2SiO_2.H_2O$) with an average grain size of 350 μm. All samples weigh is 7.5 g. The samples were compressed, and then 2.5 g of sample was placed in a mold which was 1 cm diameter under 1 tan pressure of 1minute interval. The samples were cut to equal thickness (5 cm) thick and then polished to be ready to test the RLC.

Results and Discussion

The capacitance of kaolin with different concentration of NaOH is shown in Fig. 1. There is a significant increase in amplitude capacitance values at low frequencies (<1000 Hz) after adding electrolyte of sodium hydroxide to kaolin and any ratio as shown in Fig. 1 (a). The kaolin used is composed of aluminum oxide, iron oxides and others, so sodium ion enters between these oxides, increasing the polarization resulting from the separated of these oxides from each other. The abundance of sodium ion makes the material more flexible, causing spacing of the particle sheets apart, thus increasing the resulting polarization. Therefore, any external field leads to polarization, which increases the resistance to the insulation and decrease capacity reactance of capacitance.The lowest capacity resistancehas highest polarization and highest energy storage. At high frequencies and at high concentrations, ions converge due to the increase in ionic abundance, leading to the breakdown of the insulation and the capacitance of the system decreases with an increase in ionic strength as shown in Fig. 1 (b). For frequencies with values greater than 1000 Hz, the addition of sodium hydroxide to kaolin resulted in less capacity than kaolin without treatment except in 2 molar ratio. The capacitance was greater for each frequency range. At high frequencies, the polarization induced by sodium ion between kaolin oxides does not correspond to the external frequency, it is much delayed and thus less capacity, thisis observed in Fig.1. The highest capacitor can regard in sample 2 Mover high applicable frequencies.

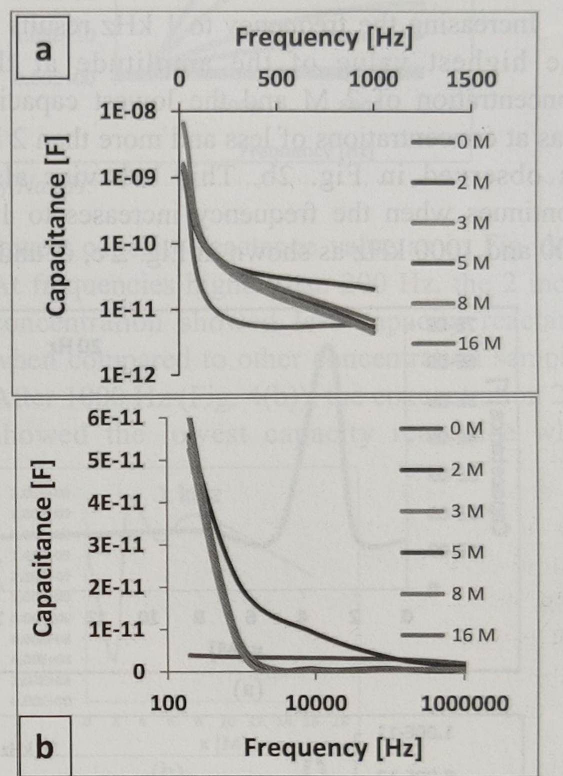


Fig. 1. *The capacitance of kaolin with different concentration of NaOH.*

It's shown in Fig. 2 (a), at 20 Hz, it's noticed that the lowest values of the capacitance were at concentrations 2 and 5 M while the highest value of the capacitance was at 3 M. At the 20 Hz and at the few concentrations of sodium hydroxide, the 3 M sample showed significant stimulation in the capacitance value. This was directed to the proportionality between the energy of the incident wave with the concentration of sodium ions and the spaces between the kaolin particles. At concentrations of less than 3 M, sodium ions are separated from each other, where the space between them causes a significant impediment to the transmission of the wave, causing a lack of capacity values. When the concentration increased to greater than 3 M, the convergence of sodium ions resulted in the generation of an electric field opposite to the applied electric field, causing a clear decrease in the capacitance values as shown in Fig. 2 (a).

Increasing the frequency to 1 kHz results in the highest value of the amplitude at the concentration of 2 M and the lowest capacity was at concentrations of less and more than 2 M as observed in Fig. 2b. This behavior also continues when the frequency increases to 10, 100 and 1000 kHz as shown in Fig. 2 c, d, and e respectively. At high frequencies, the 2 M sample was the most stimulating of all other samples. The results showed that at this value of 2 M, the ratio between the energy of the indecent wave and the spaces formed by the concentration of sodium ions was consistent, leading to a significant increase in the capacitance value. This ratio (2 M) continued to dominate the other ratios of the whole frequency range as in the Figs. 3 (c-e).

Figure 3 shows the capacity reactance change with the frequency of the mixed kaolin with

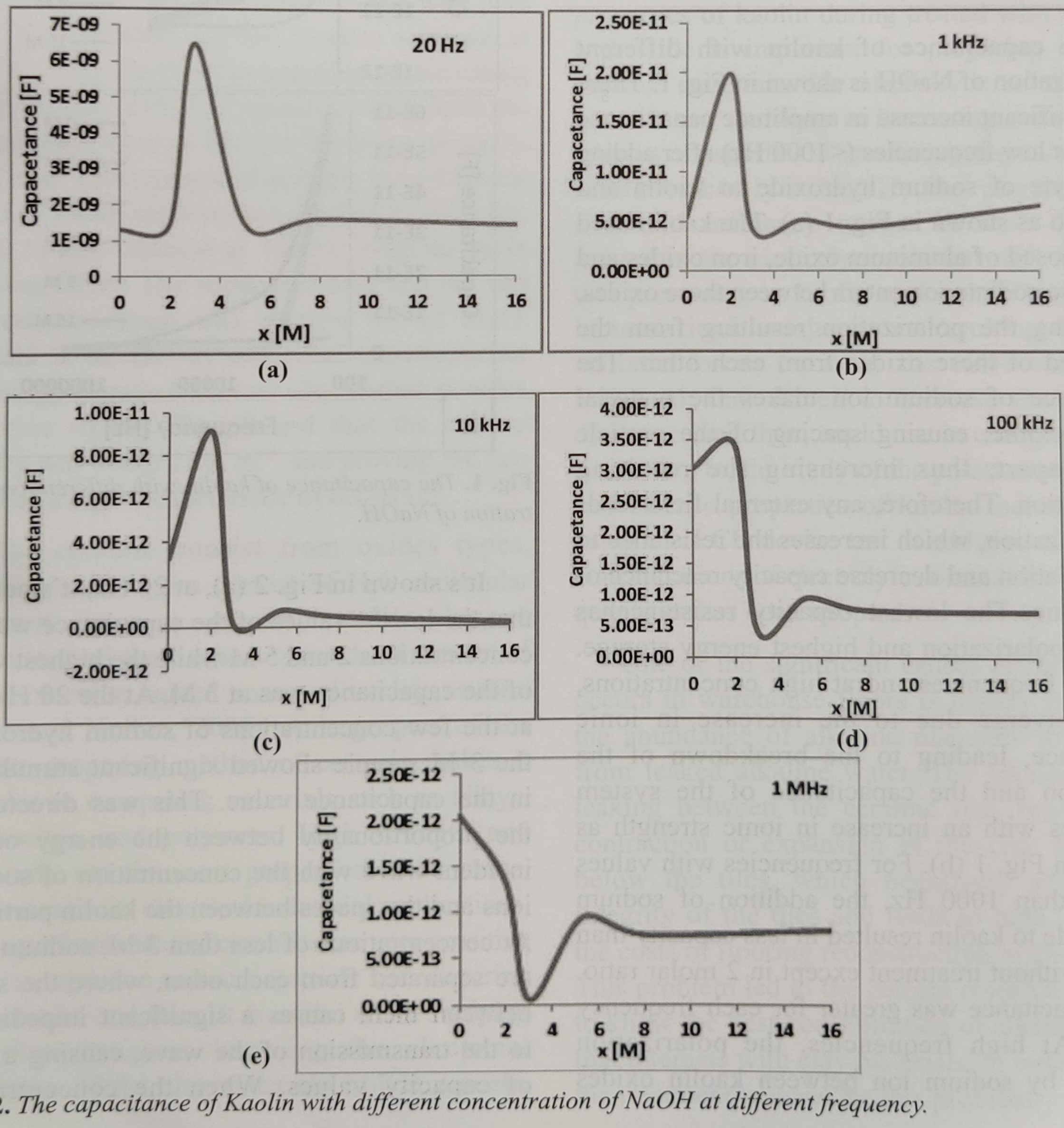


Fig. 2. *The capacitance of Kaolin with different concentration of NaOH at different frequency.*

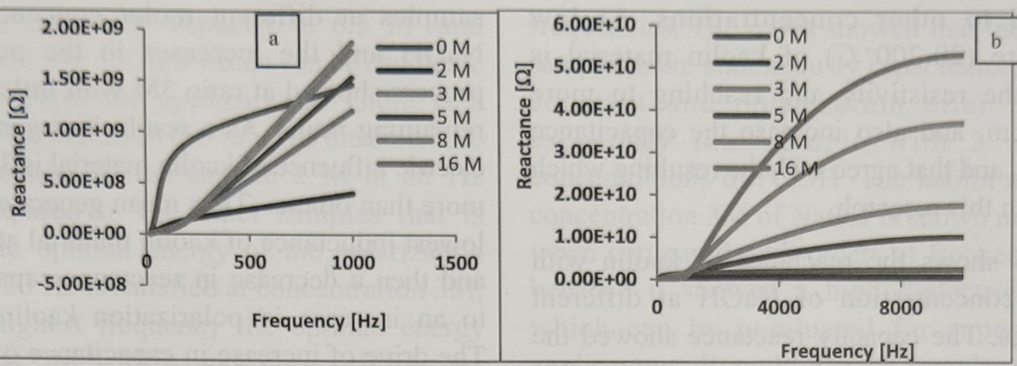


Fig. 3. *The reactance of Kaolin with different concentration of NaOH.*

sodium hydroxide and different concentrations. By defining capacity reactance as resistance to the capacity of capacitance, we find that at low frequencies (less than 1000 Hz), kaolin without addition is the highest capacity reactance value while the highest concentration (3M) has the lowest capacity reactance value as in Fig. 3(a). At frequencies higher than 200 Hz, the 2 molar concentration showed less capacity reactance when compared to other concentration samples. After 1000 Hz (Fig. 4(b)), the concentration 2 M showed the lowest capacity reactance when

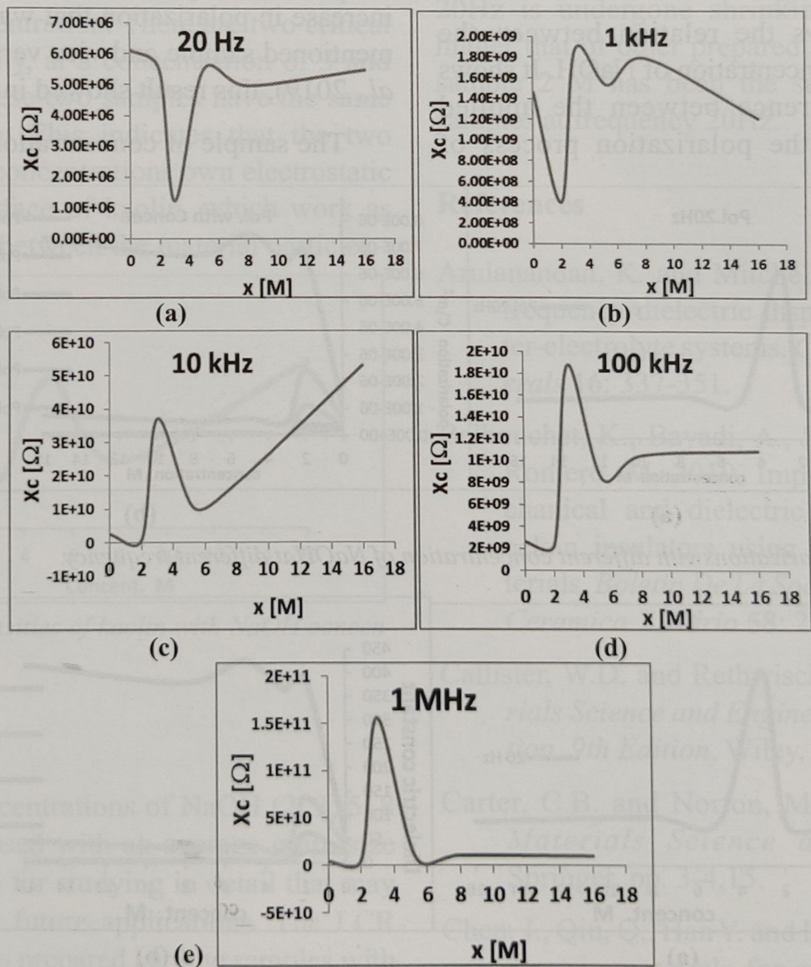


Fig. 4. *The reactance of kaolin with different concentration of NaOH at different frequency*

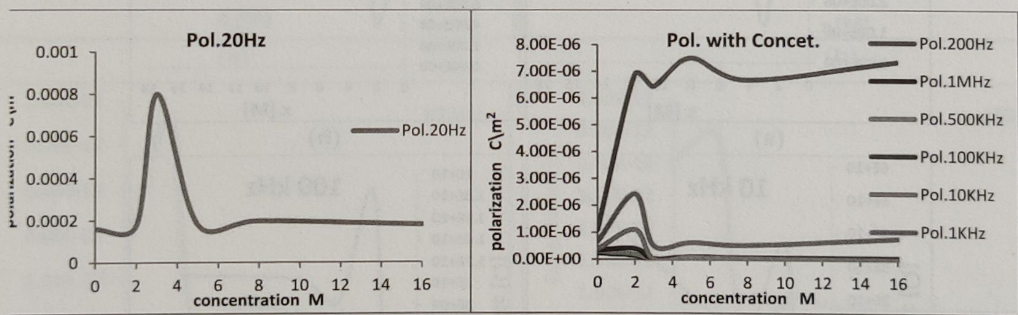
compared to other concentrations. At low temperature (20-200° C) of kaolin material is increase the resistivity and reaching to more 1×10^{8} Ω.cm, and also increase the capacitance value [15], and that agree with the resulting which recorded in this research.

Fig. 4 shows the reactance of kaolin with different concentration of NaOH at different frequencies. The capacity reactance showed the lowest value of the sample at concentration 3M at 20Hz, while sample at 2M has been the lowest value for each frequency range greater than 20 Hz as shown in Fig. 4. Therefore, there existsa balance between, concentrations of the electrolytic solution and electrostatic forces are driving the prepared sample to increase in electric permittivity and low reactance.

Fig. 5 displays the relation between the polarization and concentration of NaOH. It shows also a high difference between the applied frequencies with the polarization process of samples at different molar concentrations of NaOH and the increases in the polarization process showed at ratio 3M with little change at remaining ratios. As a result, it is generated the electric influence of kaolin material is 3 M sample more than others. Thus mean generate obtaining lowest inductance of kaolin material at ratio 3M, and then a decrease in reactance capacity leads to an increase in polarization kaolin material. The drive of increase in capacitance of material, and the lowest value of energy loss related to resistance electric material influence, resulted in the highest inductance of material.

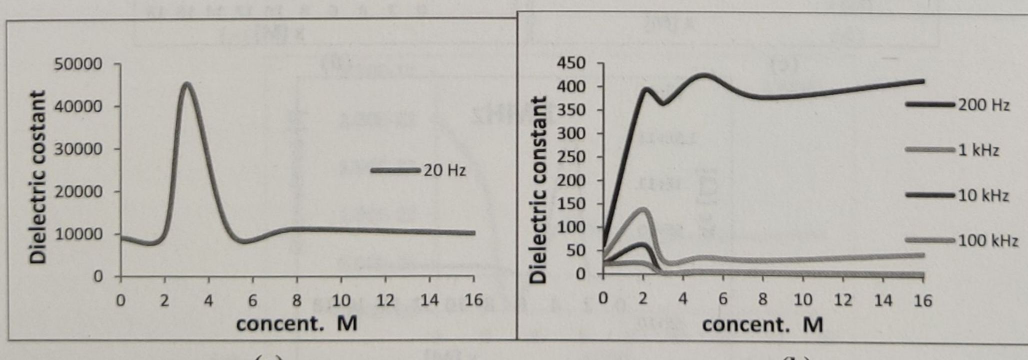
Dielectric constant with concentration of NaOH at different Frequency is shown in Fig. 5. The increase in the dielectric constant at concentration 2 M can be attributed to the increase in polarization that was observed in the mentioned sample and vice versa (Belhouchet *et al.,* 2019), this result showed in Fig. 5 b.

The sample of concentration 3M has density



(a) (b)

Fig. 5. *Polarizationswith different concentration of NaOHat different frequency.*



(a) (b)

Fig. 6. *Dielectric constant with concentration of NaOH at different Frequency*

(1.79 g m^{-3}), electric capacity is 6.5 nF and average grain size 350 μm which can be candidate for a supercapacitor applications. There is a significant difference in the value of the dielectric constant relative to the sample 2 M at 20 Hz when compared to the other samples that is indicated to optimal energy of the polarization process at 20 Hz is satisfied at concentration 3M, while at highest frequency the optimal energy has been at 2M with a wide range difference. Therefore, we could choose the prepared samples to employ in methods energy storage, for example: in the fabrication of composite piezoelectric, in the composite capacitors as fabrication supercapacitor or generating light electric force using in other fields.

Fig. 7 shows the bulk density of all samples with NaOH concentration. There are two critical depressions density, at a concentration of 3 and 8 M, although these two samples have the same weight of kaolin. This indicates that the two samples at these concentrations own electrostatic forces on the surface of kaolin, which work as an impulse force between the material particles.

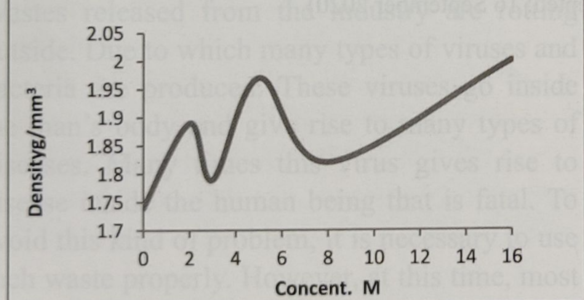


Fig.7. *The bulk densities of kaolin with NaOH concentration.*

Conclusions

Different concentrations of NaOH (2, 3, 5, 8 and 16) M was used with an average grain size 350 μm of kaolin for studying in detail that may be used in many future applications. The LCR meter was used on prepared kaoline samples with different NaOH concentrations under various frequencies. The result showed that the prepared samples have anomalously capacitance, dielectric constant and polarization after treatment especially that sample with 2 and 3 M concentrations of NaOH. The kaolin material at concentration 3M of NaOH is shown more active when compared with others at frequency 20 Hz because it showed a high dielectric constant which can be nominated for supercapacitor applications. It could choose samples according to the current result (sample 3 and 2 M at frequency 20Hz) for employing in methods energy storage, for example: in the fabrication of composite piezoelectric, in the composite capacitors as fabrication supercapacitor or generating light electric force using in other fields. It is found that the sample 3 M at frequency 20Hz is undergone shrinking and expanding higher that of other prepared samples, while the sample 2 M has been the superiority of other samples at frequency 20Hz.

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(Received: 7 March 2020; Accepted: 16 September 2020)

Clay Research, Vol. 39, No. 1, pp. 9-15 (2020)

Microstructure, Mechanical and Thermal Behaviour of Al-Clay Composite Material Developed by Stir Casting Technique

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Abstract–*Present study deals with the development of aluminium based composite reinforced with clay particles with an average size of 50μm. Stir casting technique has been employed to develop the composite material. The weight percentage of clay varied from 2.5 % to 17.5 %. Microstructure and Mechanical Behaviour of clay reinforced aluminium based composite were identified. Microstructure image of Al/12.5 % composite showed fair distribution as compared to other selected composition. Interfacial reaction layer developed between the clay and aluminium alloy has been also observed to identify the bond strength between the reinforcement material and matrix material. Interfacial reaction layer between the clay and aluminium alloy showed proper wettability between the reinforcement and the matrix material. Results showed that tensile strength and hardness were improved significantly by adding 12.5 wt. % of clay in aluminium alloy. However, ductility of the composite material continuously decreased by adding the clay in the aluminium alloy. Thermal expansion behaviour of the composite material has been also identified to observe the effect of clay addition in the aluminium alloy.*

Keywords: Clay; composite; hardness interfacial reaction layer; microstructure; tensile strength.

Today, it is a very difficult task to use the waste generated by the industry in a good way. Wastes released from the industry are rotting outside. Due to which many types of viruses and bacteria are produced. These viruses go inside the man's body and give rise to many types of diseases. Many times this virus gives rise to disease inside the human being that is fatal. To avoid this kind of problem, it is necessary to use such waste properly. However, at this time, most industries either re-use their waste or throw it to the right place so that there is no environmental pollution (Pierson, 1996). Today, many such waste materials are being used to make the aluminium based composite. Waste material like fly ash, eggshell, bagasse, red mud, rice husk ash etc. were used to make an aluminium based composite material. However, many of these waste materials cause pollution in the environment (Paris, 2011). Therefore, by using them, the environmental pollution generated by them was reduced and at the same time, they were made composite. Today, waste material is a good replacement of ceramic particles. However, ceramic particles such as SiC, Al_2O_3, B_4C, graphite and Si_3N_4 etc. addition (Nazari, 2011) in the aluminium alloy also improved the mechanical properties of the composite, but overall cost as well as density also increased simultaneously. It has been seen that the waste material also helps in increasing the good mechanical property of aluminium in the form of reinforcement (Cao, 2012).

Aluminium and aluminium alloys are being used in many products today. Aluminium is used because its density is very low relative to the

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DOI: 10.5958/0974-4509.2020.00002.9

rest of the material. Also, there are many aluminium alloys whose specific strength is also very good (Souza, 2014). Because of which they are used in aircraft industries and automobile sector. Although there are many aluminium alloys whose density is low but the specific strength is also not very good. The composite material is created to increase the mechanical property of the matrix material (Wan, 2003). To make a composite material, either adds one reinforcement particle, or two. Sometimes more than two reinforcement needs to be added. When single reinforcement is added to the matrix material, it is called monolithic composite (Tekeli, S. 2006). But when two or more than two are mixed, it is called hybrid composite. Many times by adding single reinforcement, the property of the matrix is obtained. But many times by adding single reinforcement, the property of the matrix is not achieved. In this case, two or more reinforcements are added to the matrix (Yang, 2013). Automobile sectors, as well as aircraft industries, preferred high specific strength material. Wear resistance of the material also a very important factor. Usually, the aluminium based composite material used in the aircraft industries and automobile sectors due to its lightweight and good mechanical properties such as hardness and tensile strength (Li, 2011). However, measure limitation of the aluminium alloy is soft property. Hence, reinforcement particles such as SiC, Al_2O_3, B_4C, graphite, Si_3N_4, SiO_2, Fe_2O_3, TiO_2, Na_2O, TiC, TiB_2, eggshell, rice husk ash, fly-ash, red mud etc. are added in the aluminium alloy to enhance tribo-mechanical behaviour of aluminium alloy (Okonkwo, 2012). However, there are various waste reinforcement particles used with the aluminium alloy in the development of composite (Sudarshan, 2008). Clay is another waste product obtained from the industries. It contains a combination of various hard phases such as Al_2O_3, SiO_2 and Fe_2O_3. Presence of these hard phases in clay makes it making it potential reinforcement particles in the development of aluminium based composite material. Incorporation of clay as waste material in the aluminium alloy may improve the hardness, tensile strength and wear resistance of the material (Toro, 2007).

The main properties of materials are tensile strength and hardness. These two properties are very important for the application of the same material (Severa, 2010). Several attempts have been made to increase the tensile strength and hardness property of the materials (Chen, 2010). The properties of materials have been enhanced by refining the grain structure of materials in many previous research. Many researchers refine the grain structure by re-melting the materials and providing an electromagnetic stirrer to refine the grain structure. Sometimes heat treatment of materials is also done to increase their properties. However, in most cases, their mechanical properties are enhanced by adding reinforcements to materials.

From the archival literature, it was observed that very few researchers used clay as reinforcement material with aluminium alloy and identifies thermal behaviour of composite. However, some researchers develop aluminium based composite material but did not observe the thermal property of composite. Keeping this fact in the mind, in the present study, along with mechanical behaviour, the thermal behaviour of Al-clay composite has been also observed.

Materials and Methods

Matrix Material

In the present study, pure aluminium alloy (aluminium about 99%) has been considered for matrix material. Aluminium alloy was taken as matrix material due to its lightweight. However, its strength and hardness are relatively low as compared to Iron. But, the density of the Iron is higher than aluminium. Hence, it (Iron) is not preferred in automobile sectors and aircraft industries. Hence, in the present study by incorporation of clay in aluminium alloy, an attempt was made to enhance the mechanical properties of the aluminium base matrix material. The aluminium material is used to make various parts in many manufacturing industries. Aluminium and aluminium based composite are used to make many parts in automobile industries. Similarly, it is also used in many other industries (Sudarshan, 2008). However, there are many types of aluminium. There are many alloys in which their mechanical properties are good. However, there are also many alloys whose mechanical properties are not good. In such a situation it becomes difficult to use them. But, if their mechanical properties are increased without increasing their cost, then this material can prove very useful. In this study, the mechanical properties of aluminium have been tried to increase without increasing its cost.

Reinforcement Material

Clay is the combination of SiO_2, Al_2O_3, MgO and organic matter. It is grained natural rock. Table 1 shows the chemical composition of clay. It can be seen that there are various hard phases present in the clay. These hard phases are mainly responsible for enhancing the mechanical properties of composite (Agbeleyea, 2017).

Table 1. *The chemical composition of clay* (Agbeleyea, 2017)

S. No.	Composition	Weight percentage
1	SiO_2	About 45.6%
2	Al_2O_3	About 33.7%
3	Fe_2O_3	About 0.45%
4	MnO	About 0.01%
5	MgO	About 0.05%
6	Na_2O	About 0.05%
7	CaO	About 0.04%
8	K_2O	About 0.63%
9	BaO	About 0.01%
10	SO_3	About 0.03%
11	LOI	About 4.55%

Fabrication of Composite

Various casting technique is used to make composite materials. The stir casting technique is often used to make the aluminium based composite. The main reason for using stir casting technique is its simple casting structure. The construction of stir casting technique is very simple, due to which it is easy to make the composite. In the stir casting technique, an external stirrer is used to mix the reinforcement with the matrix. Whereas, an electric furnace or muffle furnace is used to melt the matrix material. Aluminium based composite material reinforced with clay as reinforcement material has been developed by stir casting technique (Dwivedi, 2020). Aluminium was melted in muffle furnace by setting the temperature of furnace 700°C. Reinforcement particles (clay) were preheated before mixing in the melt aluminium alloy. Preheated clay particles were mixed with the help of stirrer as shown in Figure 1. The composite material was allowed to cool inside the furnace.

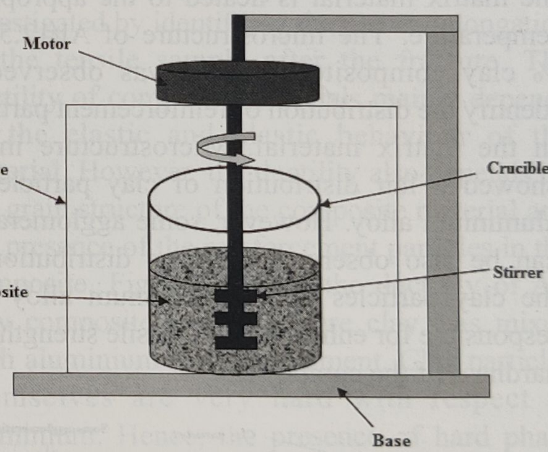

Fig. 1. *Stir casting set-up*

Materials and Methods

Microstructure Analysis

The role of the microstructure of composite is very important for its various properties. Many factors affect the microstructure of a composite. Factors that affect the microstructure of a composite are; reinforcement density, reinforcement preheat temperature, type of stirrer, melting temperature of the matrix material, solidification rate of composite etc. Many times it has been observed that when the density of reinforcement is higher than the matrix material then the reinforcement settles down as soon as it is added to the molten aluminium. Due to which it is difficult to mix well reinforcement particles with the matrix. In the same way, sometimes the density of reinforcement particles is low with respect to the matrix material. Due to its low density, it floats on the surface of the molten matrix material. As a result, it becomes difficult to combine them into the matrix. Many times if the reinforcement is not preheated properly then the reinforcement materials do not create good wettability with the matrix material, and the microstructure is affected. The design of the stirrer also plays an important role in mixing reinforcement. The microstructure of composite is also very often dependent on the melt temperature of the matrix material. Therefore, the matrix material is heated to the appropriate temperature. The microstructure of Al/12.5 wt. % clay composite material was observed to identify the distribution of reinforcement particles in the matrix material. Microstructure image showed a fair distribution of clay particles in aluminium alloy. However, some agglomeration can be also observed. Uniform distribution of the clay particles in the aluminium alloy was responsible for enhancing the tensile strength and hardness of the composite.

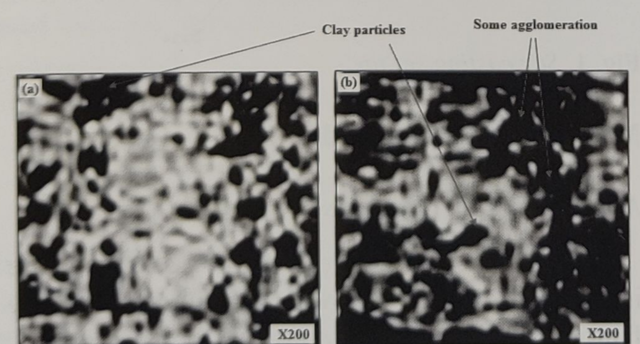

Fig. 2. *Microstructure image of Al/12.5 wt. % clay composite*

Interfacial reaction layer

Interfacial reaction layer between the clay particle and aluminium alloy has been observed to identify the bonding between the reinforcement particles and matrix material. Figure 3 shows the interfacial reaction layer developed between the reinforcement particles and matrix material. Proper interfacial reaction layer can be observed between the clay particles and aluminium alloy. Proper interfacial reaction layer improved bond strength between the clay particles and aluminium alloy. Improved bond strength enhanced the hardness and tensile strength of composite material.

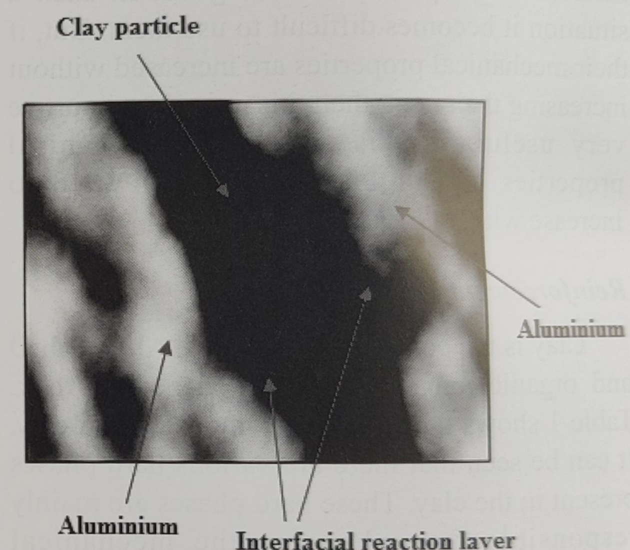

Fig. 3. *Interfacial reaction layer developed between the aluminium alloy and clay particle*

Tensile Strength Analysis

Tensile strength is the most important property of any material. By tensile strength, it is found that if the gradual load is being applied on the material then how many loads the material can sustain itself without failure. However, when it comes to ductile material, its failure is assumed at the yield point itself. Whereas, in the case of brittle material the failure of the material is considered at the fracture point. Tensile strength of Al-clay composite material has been observed. Figure 4 shows the tensile strength of Al-clay composite material. From the present study, it can be observed by the tensile strength of composite material increased by adding the clay weight percent in aluminium alloy up to 12.5 %. Tensile strength began to decrease beyond 12.5%. Maximum tensile strength was found to be 130.32 MPa for composition Al/12.5 wt. % clay composite material. Presence of hard phase (Dwivedi and Saxena, 2020) in clay such as SiO_2, Al_2O_3 and MgO were responsible for enhancing the tensile strength of composite material.

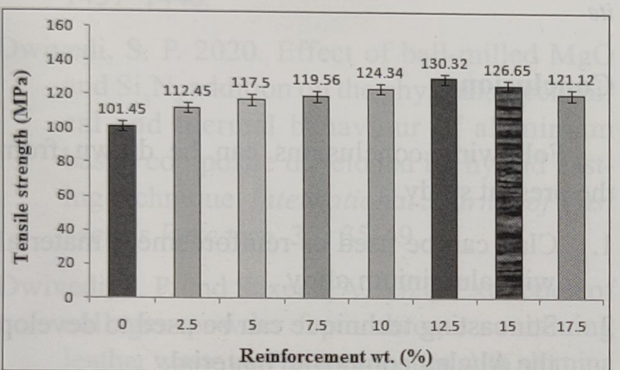

Fig. 4. *Tensile strength of Al-clay composite*

Hardness Analysis

Figure 4 shows the hardness of Al-clay composite material. Results showed that incorporation of clay particles in aluminium alloy, the hardness of the composite material improved. However, it was also observed that when the percentage of clay increased beyond 12.5%, hardness began to decrease. Maximum hardness was found to be 69 BHN for composition Al/12.5 % clay composite material. The hardness of the composite material improved due to the presence of alumina in clay particles. After casting, two types of factors are very important in increasing the hardness of the composite. The first factor is the refinement of the grain structure. The second factor is the amount of reinforcement particles added to matrix material after casting. Sometimes refinement of grain structure also helps a lot in increasing hardness. However, the weight % of reinforcement has the greatest effect in increasing the hardness of the composite. It has often been observed that increasing the weight percent of reinforcement increases the hardness of the composite. However, reinforcement gets collected in one place by increasing the weight percent of the reinforcement. Due to which the probability of generating porosity inside the composite is greatly increased. Due to which, the hardness of the composite declines.

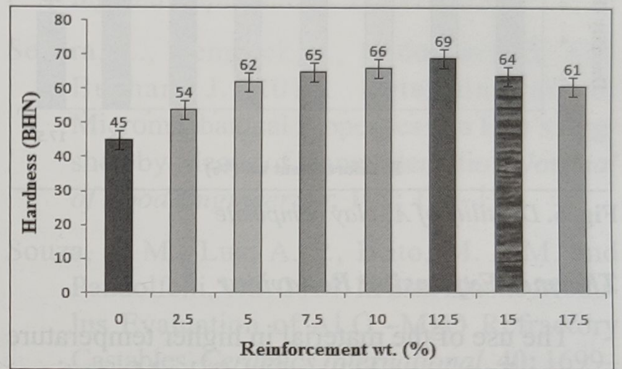

Fig. 5. *Hardness of Al-clay composite*

Ductility (Percent elongation)

Ductility of the composite material has been investigated by identifying the percent elongation in the tensile sample after the fracture. The ductility of composite materials mainly depends on the elastic and plastic behaviour of the material. However, the ductility also depends on the grain structure of the composite material and the presence of the reinforcement particles in the composite. Figure 6 shows the ductility of Al-clay composite material. Here clay was mixed with aluminium as reinforcement. Clay particles themselves are very hard with respect to aluminium. Hence, the presence of hard phase inside it proves to be quite useful as reinforcement particles. However, due to the presence of hard phase inside it, when added to aluminium it reduces the ductility of aluminium. Results showed that ductility of the composite material was decreased continuously by increasing the weight percentage of clay particles in the aluminium alloy. Addition of hard phases always resists the plastic deformation of the material. Clay particles contain various hard phases such as SiO_2, Al_2O_3 and MgO etc. These hard phases resist the plastic deformation of Al/clay composite material.

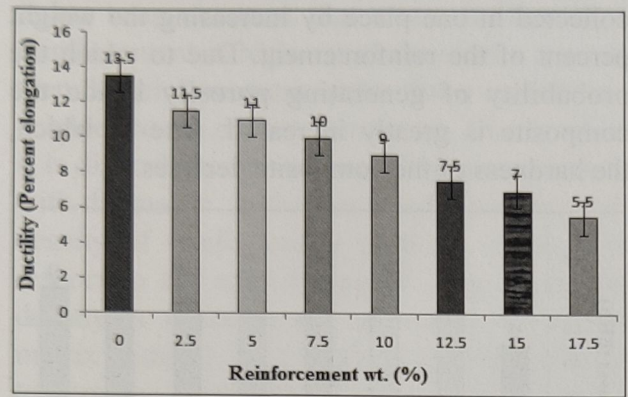

Fig. 6. *Ductility of Al-clay composite*

Thermal Expansion Behaviour

The use of the material in higher temperature surrounding is a challenging task. Many times when the aluminium-based alloy is used in high temperature, the material starts changing its dimension. Due to changes in the material dimension, it is no longer usable again. At the same time, the other parts that are attached to it also affect their dimension. Therefore, in today's time, whenever new material is made, it is necessary to know whether it can sustain at higher temperatures. When it comes to the aluminium-based alloy, the need to use it in more temperature increases. The main reason for this is its high specific strength. Keeping in mind all these things, thermal expansion of aluminium based composite has also been done in this study. The dimension of each sample was kept 21 mm x 10 mm x 10 mm (2100 mm^3) before putting the sample in the muffle furnace. The temperature of the muffle furnace was set 450 ^{0}C. All the samples were kept in the muffle furnace for 24 hours. Figure 7 shows the change in dimension after the thermal expansion test. Minimum dimension change has been observed for the composition Al/12.5 wt. % composite material. Hence, from this study, it can be concluded that Al/12.5 wt. % composite material showed the best properties among all the selected composition.

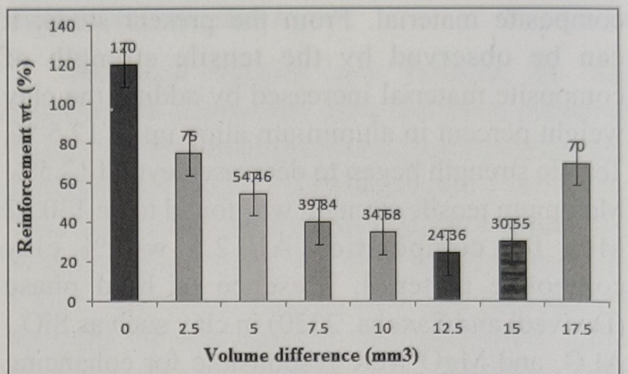

Fig. 7. *Thermal Expansion Behaviour of Al-clay composite*

Conclusions

Following conclusions can be drawn from the present study.

1. Clay can be used as reinforcement material with aluminium alloy.
2. Stir casting technique can be used to develop the Al/clay composite material.
3. The microstructure of Al/12.5 wt. % composite material showed a fair distribution of reinforcement particles in the matrix material.
4. Tensile strength and hardness of aluminium alloy improved 28.45 % and 53.33 % respectively by adding 12.5 % clay in the aluminium alloy. However, the ductility was continuously decreased by increasing the clay percentage.
5. Minimum dimension change has been observed for the composition Al/12.5 wt. % composite material.

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(Received: 29 March 2020; Accepted: 16 September 2020)

Clay Research, Vol. 39, No. 1, pp. 16-22 (2020)

Ground Water Potential Zones using Vertical Electrical Sounding (VES) Data in Osman Sagar and Himayath Sagar Reservoirs Catchment Area

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Abstract *– Out of many geophysical methods like Seismic methods, Electromagnetic methods, Magnetic method, Gravity method etc., resistivity method is familiar to identify the ground water potential zones in view of resistivity variations of rocks with presence or absence of water. Surface geoelectrical investigations were carried out in the Osman sagar and Himayath sagar reservoir catchment area and used in order to know the thicknesses of different layers below the near surface of the earth. A total of 77 soundings are collected spreading over the entire area. All these soundings are conducted using Schlumberger configuration with a maximum half-distance of current electrode separation (AB/2) equal to 100 m until the sounding curve attained "S" line which is an indication of establishment of contact with electrical basement points. From the result it is observed that the major aquifers are located in the northern half of the basin. More over the entire basin is covered by four principle layers namely soil layer, weathered layer, fractured layer and basement. The major aquifer layers are weathered and fractured layers whose thicknesses are varying from point to point.*

Keywords **:** Contour map; electrical restivity method; Groundwater potential zone; subsurface layer, VES.

Out of many geophysical methods like Seismic methods, Electromagnetic methods, Magnetic method, Gravity method etc., resistivity method is familiar to identify the ground water potential zones in view of resistivity variations of rocks with presence or absence of water. Surface geoelectrical investigations were carried out in the study area and used in order to know the thicknesses of different layers below the near surface of the earth. Those electrical methods in which current is applied by conduction to the ground through electrodes depend for their operation on the fact that any subsurface variation of conductivity alters the form of the current flow with in the earth and this affects the distribution of electric potential, the degree to which it is affected depending on the size, shape, location and electrical resistivity of subsurface layers or bodies (Zohdy *et al.,* 1974, Kearey and brooks 1988, Muralidharan, 1996, Andrade and Muralidharan, 2011, Das *et al.,* 2007). It is therefore possible to obtain the information about the subsurface layers or bodies. The usual practice is to pass the current into the ground by means of two electrodes and to measure the potential drop between a second pair placed in line between these. If the ground is uniform then from knowledge of the potential drop, current and electrode spacings, using the appropriate expression, the ground resistivity can be

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DOI: 10.5958/0974-4509.2020.00003.0

calculated. Where the resistivities of the ground through which the current flow is not uniform, the expression for uniform ground is still used but the calculated quantity is called "apparent resistivity". Deductions about the sub-surface can be made from an analysis of variation of apparent resistivity with changes in electrode position and spacing.

The passage of electrical current through rocks takes place, with the exception of clays and metallic ores, by way of the ground water contained in the pores and fissures, the rock matrix being non conductive. All other factors being constant an increase in the concentration of dissolved salts in the ground water leads to a decrease in resistivity. In a general way the resistivity is also controlled by the amount of water present. The more porous or fissured a rock, the lower the resistivity. Higher degree of saturation or greater amount of water presents in pore spaces and fissures also decreases the resistivity (Gowd 2004, Raffudin 2007, Chandra *et al.,* 2008, Coker *et al.,* 2009, Rajsanjeev, 2017).

Material and Methods

In the present paper the 1D Vertical Electrical Soundings (VES) data is collected from the Andhra Pradesh State Irrigation Development Corporation (APSIDC) and Centre for Water Resources, Jawaharlal Nehru Technological University Hyderabad (JNTUH) for the Osman Sagar and Himayath Sagar Reservoir catchment area. Major part of the area is covered with hard rock. A total of 77 soundings are collected spreading over the entire area shown in Fig. 6.1. All these soundings are conducted using Schlumberger configuration with a maximum half-distance of current electrode separation (AB/2) equal to 100 m until the sounding curve attained "S" line which is an indication of establishment of contact with electrical basement points is shown in Fig. 1.

Interpretation of VES Data

Apparent resistivities and half distance (AB/2) of the current electrode separation for each VES station are plotted on a bilogarithemic sheet taking AB/2 in meters on X-axis and apparent

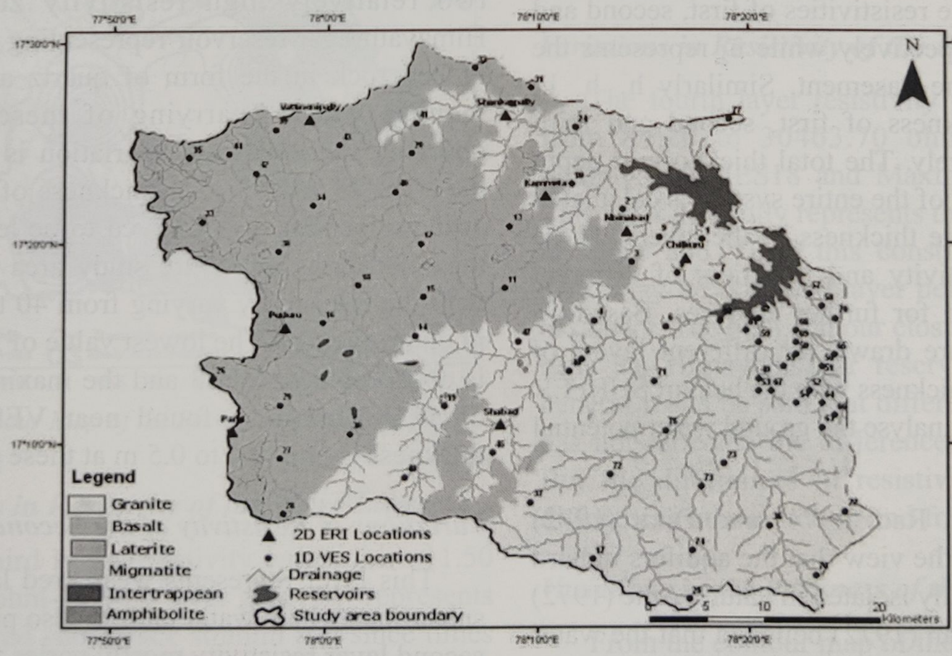

Fig. 1. *Location of base points*

resistivities ρ_a in ohm-m on Y axis. These 77 sounding curves are initially interpreted with the help of Orellana and Mooney's (1966) album of master curves for Schlumberger configuration. The album consist of 25 resistivity curves for a two layer system about 1000 resistivity curves for three layer system and about 400 curves for four layer system. The tracing sheet on which the S-shaped bilogarithemic field data plot of VES location No.1 for instance is drawn and placed on the master curves. The master curves that are as closure to the field data plot as possible is chosen.

The resistivities (ρ) and thickness (h) of all the subsurface layers in the system corresponding to the master curves are computed using the simple procedure indicated in Orellana and Mooney's manual. These curves were interpreted again with the help of RESIST software using the values obtained from curve matching technique and the values were resistivity and thickness accepted when the RMS error with in the tolerance limits.

At all the 77 VES locations the subsurface system contains 4 geo electric layers. The ρ_1, ρ_2, ρ_3 represents the resistivities of first, second and third layers respectively while $\tilde{n}_4$ represents the resistivity of the basement. Similarly h_1, h_2, h_3 represents thickness of first, second and third layers respectively. The total thickness or depth to the basement of the entire system is calculated by adding all the thickness of the layers. These values of resistivity and thickness of different layers are taken for further analyses. Based on this, contours are drawn for different layers of resistivity and thickness with the help of SURFER package tool to analyse the ground water potential of the zone.

Ramchandra Rao (1971) and Dixit (1972) have expressed the view that the aquifers in hard rocks are generally isolated in nature. Apte (1972) and Govindarajan (1972) believed that the water bearing properties of aquifers have a relation to the extent of weathering and the occurrence of fractures. Bhowmik and Renuka (1991) have explained that fractures in hard rock were the creation of tectonic disturbances. Hudson and Priest (1979) have observed an exponential distribution of fractures with depth. Zhdankus (1972) has made the observation that ground water existed mainly in upper weathered layer. The deeper this weathered layer, the greater is the amount of available water Sakthivadivel and Krishna Swamy (1972). Radhakrishna (1970) and Stevenson *et al.* (1975) have concluded that the surface weathered layer and underlying fractured granites constitute two district aquifers not connected with each other. Contradicting these facts, Briz-kishore and Bhimasankaram (1982) have found that there is hydraulic continuity and unity of ground water flow systems in weathered and fractured granites.

Results and Discussion

Variations in Resistivity of the First Layer

From the contour map of the first layer resistivity (Fig. 2) it is observed that there are two relatively high resistivity zones near Himayathsagar reservoir representing exposition of bed rock in the form of quartz and granite mounds where quarrying of these rocks is observed. The resistivity variation is sudden in the VES 71 and 72. The thickness of the layers at these locations is observed to be less. Except these locations the entire study area is covered with the Resistivity varying from 40 to 80 ohm-m on an average. The lowest value of 2.7 ohm-m is observed near VES3 and the maximum value of 1715 ohm-m is found near VES 71. The thickness is only 0.4 to 0.5 m at these places.

Variations in Resistivity of the Second Layer

This layer represents weathered layer in the subsurface where water table is also present. The second layer resistivity mostly varies from 2.6 to 250 ohm-m except at three cases where it reads

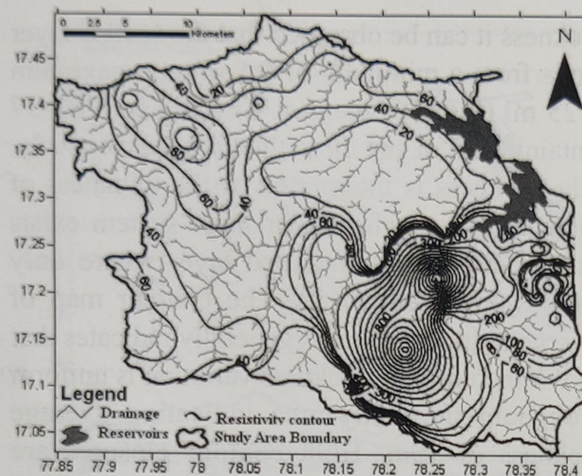

Fig. 2. *Contour Map of the First Layer Resistivity*

536.7 (VES 2), 603.2 (VES 30) and 11043.5 (VES 45). From the contour map of the second layer resistivity (Fig. 3) it can be observed that the high resistivity contour closures are observed near VES2, VES30 and VES45 near Osmansagar reservoir and centre south west of the Himayathsagar catchment which are vertical the extensions of basement of tenants mounds, earlier discussed under first stage.

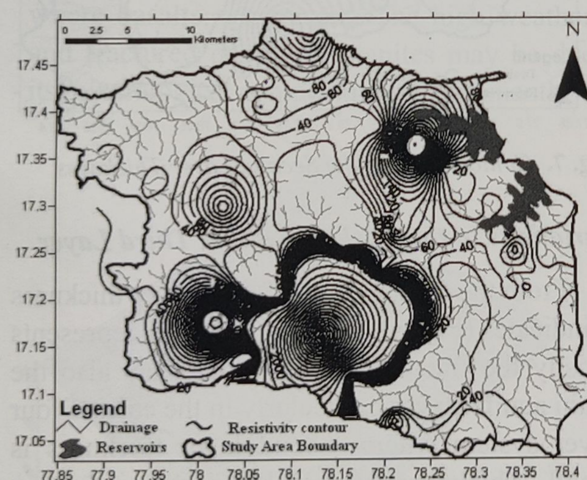

Fig. 3. *Contour Map of the Second Layer Resistivity*

Variations in Resistivity of the Third Layer

The third layer resistivity varies from 11.50 to 81256 ohm-m. This layer generally represents the fractured subsurface stratum and since times acts as the principal aquifer layer. Three high resistivity contour closures are observed in the contour map (Fig. 4). At the place of high resistive second layer, third layer also has high resistivity. Therefore there is less possibility of aquifer presence at these locations. These contour closures are due to the presence of high resistivity near VES1, VES30, VES31, VES32 and VES47. From this observation it can be found that at all these places the resistivity of third layer is very high representing substratum of the earlier granite mounds. In between these locations there may be some fractures in the layer.

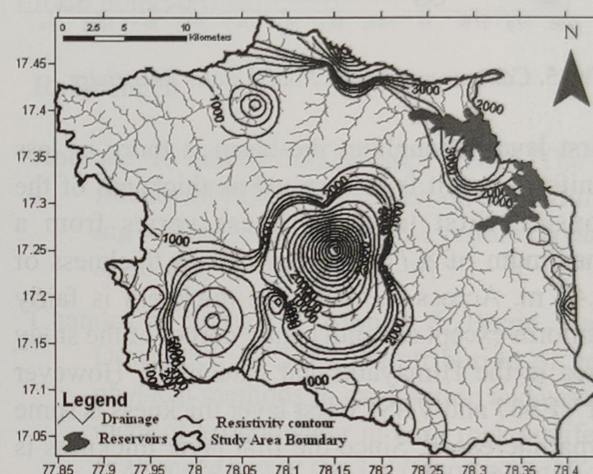

Fig. 4. *Contour map of the Third layer Resistivity*

Variations in Resistivity of the Fourth Layer

The fourth layer resistivity generally varies from 84.20 to 30463.70 ohm-m observing minimum at VES18 and Maximum at VES60. This layer generally represents the basement. But at VES6 and VES8 this constitutes the fourth layer may be fractured layer before meeting the basement. The high contour closures are observed near the Himayathsagar reservoir (Fig. 5). In general it can be said that differences in geology has not reflected the differences in resistivities. But the differences in resistivities are due to differences in weathering and fracturing.

Variations in the thickness of the First Layer

From the contour map of the thickness of the first layer (Fig. 6) it can be observed that the

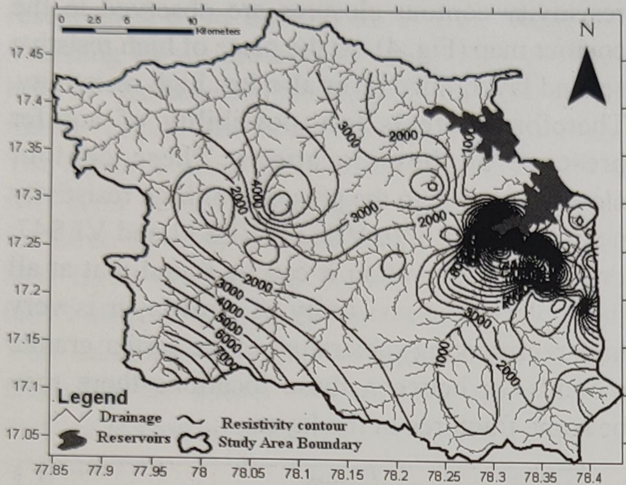

Fig. 5. *Contour map of the Fourth layer Resistivity*

first layer throughout the basin is more or less uniform and it is interpreted as thickness of the topsoil. First layer thickness varies from a maximum of 8.7 m to a minimum thickness of 0.40 m. Across the basin its thickness is fairly uniform except at south centre corner of the study area in the Himayathsagar catchment. However at VES37 and VES45 first layer thickness is some what increased. Since the first layer thickness is uniform throughout the basin, it is confirmed that the thickness does not have any bearing on the ground water potential of the study area.

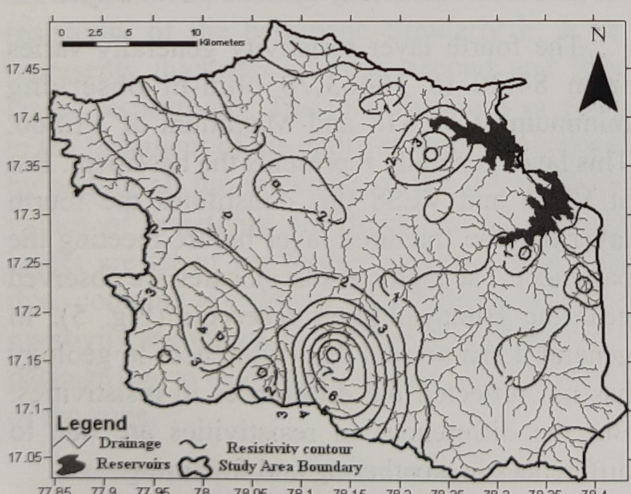

Fig. 6. *Contour map of the First layer Thickness*

Variations in the thickness of the Second Layer

From the contour map of the second layer thickness it can be observed that the second layer varies from a minimum of 0.5 m to a maximum of 25 m. (Fig. 7) except at VES20 and VES 37 containing 38 m and 64 m thickness respectively. This thickness is interpreted as the thickness of weathered layer where four layer system exists and weathered and fractured layer where only three layer system exists. The contour map of the second layer thickness generally indicates that the weathered layer thickness variation is uniform throughout the study area indicating average thickness of 10m. High contour closures are observed at VES12, VES20, VES37 and VES 66.

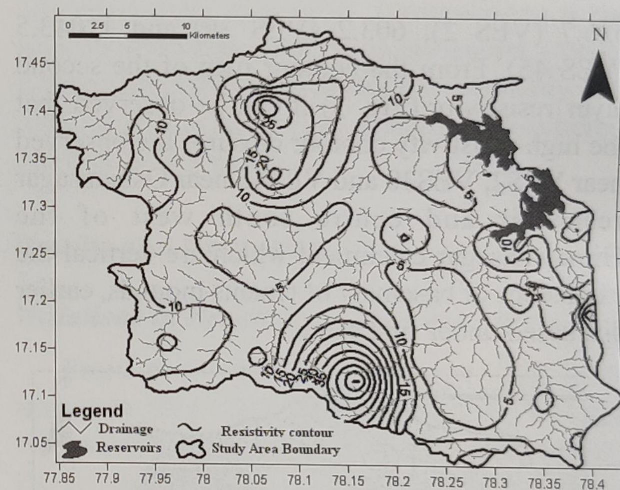

Fig. 7. *Contour map of the Second Layer Thickness*

Variations in the thickness of the Third Layer

From the contour map of third layer thickness it indicates (Fig. 8) that the third layer represents mostly the fractured layer, which may also the main aquifer layer particularly in the case of four layer system where second layer thickness is small. Thickness of this layer varies from a minimum of 0.67 m to maximum of 37.2 m. From the contour map it is also observed that the entire study area is covered with the thickness of below 30 m except near the Himayathsagar reservoir.

Variations in the Depth to basement

From the contour map of depth to electrical

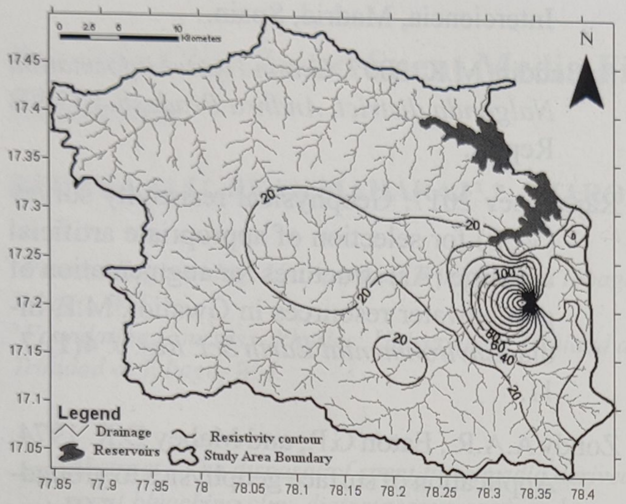

Fig. 8. *Contour map of the Third Layer Thickness*

basement (Fig. 9) it is observed that there is one high thickness contour closure near Himayathsagar reservoir. The maximum depth of 295.30 m is observed at VES53 and the minimum thickness of 2.70 m is observed at VES74. In general depth to electrical basement is more in Himayathsagar catchment where granites are present than Osmansagar catchment where basalts are present. The high weathering and fractured depths in granites may be due to its mineralogical composition predominantly with more feldspar and quartz.

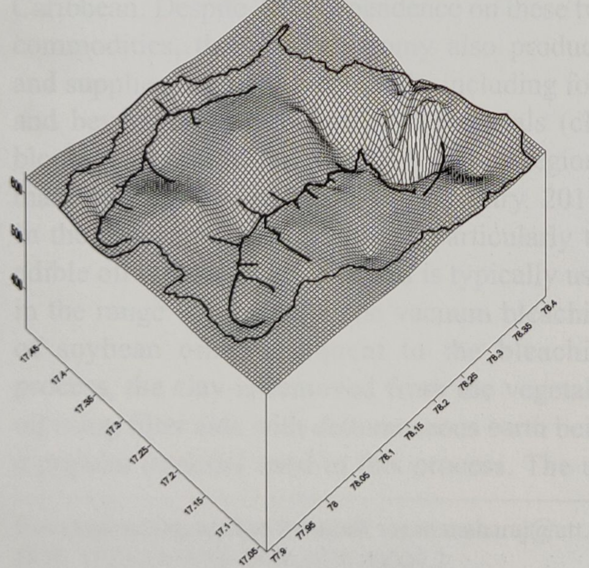

Fig. 10. *3D View of Basement Topography*

Conclusions

From the above result it is observed that the major aquifers are located in the northern half of the basin. More over the entire basin is covered by four principle layers namely soil layer, weathered layer, fractured layer and basement. The major aquifer layers are weathered and fractured layers whose thicknesses are varying from point to point.

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(Received: 14 April 2020, Accepted: 16 September 2020)

Clay Research, Vol. 39, No. 1, pp. 23-30 (2020)

Reusing Clay Based Spent Media Filter to Modify Trinidad Asphaltic Materials

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***Abstract** - The disposal of spent filter media derived from the food processing industry which comprises of spent bleaching clay, diatomaceous earth and an organic (oily component), poses an environmental threat due to the current disposal method being employed. Previous studies conducted in Trinidad and Tobago reusing waste materials similar in nature to the components of spent filter media as an additive for bituminous road paving applications suggest that the waste spent filter media may also improve the mechanical and rheological properties of the modified bituminous binder sand and provide an alternative, environmentally sustainable method for disposal of this waste. The results of this study showed that modifying Trinidad Lake Asphalt (TLA) and Trinidad Petroleum Bitumen (TPB) with spent filter media resulted in changes in the rheological properties of the blends, demonstrated in the deviations in the material's stiffness (G*) and elasticity (δ). The optimum dosages to obtain highest stiffness and elasticity and lowest temperature susceptibility was found for modified TLA and TPB blends containing 1% and 2% spent media filter content respectively.*

***Keywords**:* Complex shear modulus; phase angle; spent media filter; rheology; Trinidad Lake Asphalt, Trinidad Petroleum Bitumen.

Trinidad and Tobago (TT) remains one of the largest producers of oil and gas in the Caribbean. Despite TT's dependence on these two commodities, the local economy also produces and supplies manufactured goods, including food and beverages and construction materials (clay blocks and cement) for both the local and regional markets (Ministry of Trade and Industry, 2018). In the food production industry, particularly the edible oil industry, clay material is typically used in the range 0.3-0.6% for the vacuum bleaching of soybean oil. Subsequent to the bleaching process, the clay is removed from the vegetable oil using filter aids with diatomaceous earth being a popular material used in this process. The use of this process has been stymied due to environmental issues related with the disposal of the spent bleaching clay and diatomaceous earth. Though the organic materials present are biodegradable, indiscriminate dumping of such waste can result in an oil coating of waterways, fuel fires at landfills and encourage unusual microbe growth. Currently, most manufacturing companies utilize landfills for its disposal however, internationally in developed countries, spent clay has been used as an additive to animal feed and in the production of ceramic products such as bricks (Hernandez, *et al.*, 2013).

Unfortunately TT, like most developing countries, lags behind with regards to recycling

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DOI: 10.5958/0974-4509.2020.00004.2

of waste materials (Batayneh, *et al.*, 2008). In recent times, some emphasis have been placed on the development of policies geared towards waste minimization and recycling. One such policy is the National Environment Policy (4) which was introduced in 2006 to advance waste recovery, recycling, reuse or reclamation. The policy also aims to stimulate economic instruments and market incentives concepts centered on the utilization of waste as a source of energy. (Ministry of the Environment and Water Resources, 2011). Trinidad and Tobago is also a signatory to the Basel Convention Regional Centre for Training and Technology Transfer for the Caribbean Region (BCRC-Caribbean) which focuses on the recognition of waste as a resource to mitigate negative environmental impacts, stimulate economic development and to develop innovative employment opportunities and small business entrepreneurs (Basel Convention, 2012).

Spent filter media, which is being used for the processing of edible oil, would have mainly an inorganic (bleaching clay and diatomaceous earth) component and an organic, oily component. Previous studies in Trinidad and Tobago have utilized materials of a similar nature to either one of these components as additives in bituminous materials used in road paving, suggesting that there is a promising future for incorporating the waste spent filter media as a modifier to bitumen binder. This approach promotes an environmentally sustainable method for disposing this waste with the added benefit of possibly improving the mechanical and rheological properties of the modified binder (Maharaj, 2009, Maharaj, *et al.*, 2015b).

Reference is made to the study conducted by (Maharaj, 2009) where the potential of exploiting waste cooking oil (WCO) as a performance enhancing additive for road paving applications was investigated through a reuse strategy utilizing Trinidad Lake Asphalt (TLA) and Trinidad Petroleum Bitumen (TPB). The study found that the addition of WCO to the TLA and TPB base binders resulted in changes in stiffness (G^*) and elasticity (δ) in conjunction with the rutting resistance ($G^*/\sin\delta$) and the fatigue cracking resistance ($G^*\sin\delta$), providing evidence to support the reuse of WCO as an asphalt modifier for TLA and TPB. Since the WCO used in this study is likely to be similar in nature (chemical and physical properties) to that of the oily component of the spent media filter, incorporation of thespent media filter into TLA and TPB sample should also acquire favourable results.

In general, bitumen is either derived from natural sources or from the distillation of petroleum at oil refineries. Trinidad Lake Asphalt (TLA) is considered the gold standard for bitumen, and is mined from the world's largest natural lake deposit of bitumen, in La Brea Trinidad (Parliament Republic of Trinidad and Tobago, 2019). TLA possesses unique chemistry, mineralogy and properties that sets it apart from other sources of bitumen (Maharaj, 2009). TLA has been used historically in the road paving industry since the early 19^{th} century locally and late 19^{th} century internationally, giving it a 200-year track record in the industry (Parliament Republic of Trinidad and Tobago, 2019). A key reason for the superior performance attributes of TLA compared to other bituminous materials has been the presence of an inorganic clay material (35.3%) (Widyatmoko, *et al.*, 2008) in the TLA which is not present in TPB and other refinery bitumen. Studies have suggested that the clay component of the TLA influences the colloidal and particle size distribution of the clay/asphalt blends (Smith, *et al.*, 1995), as well as possibly increasing the existence of inter-particle bridging within the asphaltic system, resulting in superior physical and rheological characteristics for TLA and TPB-clay blends (Rios-Donato, *et al.*, 2012). Since the spent filter media that has been used for the processing of edible oil is mainly an inorganic combination of the bleaching clay and diatomaceous earth, it is believed that the addition of this material to TLA and TPB will enhance the rheological and performance properties of the resultant blends as observed by (Smith, *et al.*, 1995).

Literature reviews for previous studies researching the use of spent filter media as a performance enhancer in road paving materials provided limited results. This paper attempts to fill this information gap; the main objective of this study will focus on investigating the influence of the spent filter media on the performance characteristic as measured by changes in rheological properties of TLA and TPB binders and its use as a possible performance enhancer. The study will also evaluate this strategy's potential as an environmentally attractive means of recycling this waste material.

Method and Materials

The TLA and TPB (60/70 penetration) samples were obtained from the Lake Asphalt Company of Trinidad and Tobago and the Petroleum Company of Trinidad and Tobago respectively. Table 1 illustrates the source and specification of the TLA and TPB samples utilized in this study (Mohamed, *et al*., 2017). The spent media filter used in this study was obtained from an established vegetable oil processing plantin located Trinidad.

Table 1. *Source and Specifications of TLA and TPB samples utilized in this study (Maharaj, 2009).*

	TLA	TPB
Packing	Drum	Drum
Penetration at 25°C (ASTM D5)	0-5	60-70
Specific Gravity (ASTM D70)	1.3-1.5 g cm $^{-3}$	1.00-1.06 g cm $^{-3}$
Softening Point (ASTM D36)	89-99° C	225°C
Flash Point (ASTM D92)	255-260°C	49-56°C

Materials and Preparation of Samples

The sample blends were prepared and rheological measurements were obtained based on the process recommended by (Polacco, *et al.*, 2004). Approximately 6g of TLA was measured and transferred into a 50 cm^3 aluminum can. The can was then placed in a thermoelectric heater, Thermo Scientific Precision (Model 6555), where the temperature was elevated to 200°C. A high shear digital mixer, IKA (Model RW20D), was then submerged into the can and set at a speed of 3000rpm. The spent media filter was gradually added, by weight %, to the can whilst the system was maintained at a 200 ± 1 °C temperature. The above procedure was repeated for the TBP sample. Table 2 shows a breakdown of the concentrations of the modified samples analyzed in this study.

At the end of mixing, each blend was stored in a desiccator under static conditions and in an oxygen-free environment. After curing for 24h, the cans were removed from the desiccator, remixed using the high shear mixer, after which the molten mixtures were casted into a ring stamp of dimensions 25 mm in diameter and 1mm in thickness in preparation for rheological testing. Before testing, the samples were cooled at room temperature then stored in a Fisher Isotemp freezer at a temperature of -20 °C.

Sample Characterization

The rheological properties of the asphaltic material were determined using an ATS Rheo Systems Dynamic Shear Rheometer (Viscoanalyzer DSR) (Maharaj, *et al.*, 2015a, Mohamed, *et al.*, 2017). The analyses were performed under the strain-control mode and the applied strain was kept low enough to ensure that it was maintained within the linear viscoelastic range. The maximum temperature for the pavements in actual service ranged from 55 °C to 65 °C. The test geometry used was the plate-plate configuration (diameters 25mm) with a

Table 2. *Concentration of sample blends.*

Mass of sample 6g						
Asphalt blend						
	TLA			TPB		
% Mud required in blends	Actual mass of TLA added (g)	Actual mass of mud added (g)	Actual % mud	Actual mass of TPB added (g)	Actual mass of mud added (g)	Actual % mud
0.00	6.0005	0.0000	0.00	6.0000	0.0000	0.00
1.00	6.0006	0.0602	1.00	6.0088	0.0600	1.00
2.00	6.0018	0.1202	2.00	6.0042	0.1203	2.00
4.00	6.0006	0.2403	4.00	6.0092	0.2404	4.00
6.00	6.0094	0.3602	5.99	6.0098	0.3600	5.99
8.00	6.0013	0.4806	8.01	6.0016	0.4803	8.00
16.00	6.0026	0.9602	16.00	6.0000	0.9608	16.01

1mm gap and the measurements were conducted at 40 °C to 90 °C, at 10 °C intervals, within a 0.1 to 15.91 Hz frequency range. The Dynamic Stress Rheometry testing was software controlled with the lower plate of the machine fixed and the upper plate oscillating backward and forward.

The data obtained at different oscillating shear frequencies and temperatures were stored and the results were analyzed using the Viscoanalyzer software. The values of the rheological parameters associated with the complex shear modulus (G*) and phase angle (δ) were calculated at the different oscillating frequencies and temperatures using the instrument's software.

Results and Discussion

Rheological measurements of the complex shear modulus (G*) and phase angle (δ) of TLA and TPB containing varying amounts of spent media filter were measured. As described by (Mohamed, *et al.*, 2017), the complex shear modulus (G*) is a measure of a materials total resistance to deformation when constantly sheared, while, the phase angle (δ) describes the lag between the applied shear stress and the resulting shear strain. Based on these definitions, a higher G* value would indicate a stiffer material meaning an increase in the likelihood of cracking. Numerically, for phase angle, the higher the value, the more viscous the material would be (δ = 90°, purely viscous verses δ = 0°, purely elastic).

Master curves of the TLA and TPB with variations of G* and δ as a function of frequency at a reference temperature of 60 °C were developed and illustrated in Figure 1. The TLA and TPB samples used in this analysis were used in a similar study conducted by (Mohamed, *et al.*, 2017), and produced indistinguishable master curves. Both samples tend to approach a maximum value of G* and a declining δ at higher frequencies when examined at the reference temperature. The maximum value of G* reflects

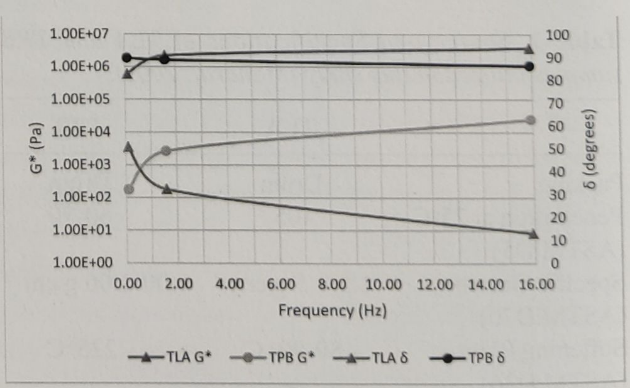

Fig. 1. *The master curves comparing of the complex moduli (G*) and phase angle (δ) of the asphaltic materials TLA and TPB with frequency at temperature 60 °C*

the rigidity of the carbon hydrogen bonds as the asphalts reach their lowest thermodynamic equilibrium volume; the decrease in the value of ä represents the upsurge in the elastic nature of the asphalts at 60 ºC (Mohamed, *et al.*, 2017). When comparing the TLA and TPB materials, the TLA demonstrated higher elasticity and stiffness as measured by lower δ and higher G* compared to the TPB.

Figure 2 captures the trends of deviation of the rheological values of G* and δ for TLA and TPB against temperature at a frequency of 1.59 Hz; the reference of 1.59 Hz was chosen based on its correspondence to vehicular traffic travelling at 80 km/hwith a recommended safety practice of 3 car lengths between each vehicle (Mohamed, *et al.*, 2017). As seen in Figure 2, as the temperature increases, G* decreases, indicating a decline in the material's resistance to deformation, whilst δ increases,signifying a decrease in the material's pliability or ability to store energy. Both the TLA and TPB when exposed to high temperatures tend to lose elasticity with the TPB becoming a viscous liquid at 90 ºC, whereas they both lose stiffness as the temperature was increased. A comparison of the values of the rheological properties of G* and ä for TLA and TPB demonstrates the higher degree of temperature susceptibility of TPB with temperature compared to that of TLA. Overall, the data presented in Figure 1 and Figure 2 shows

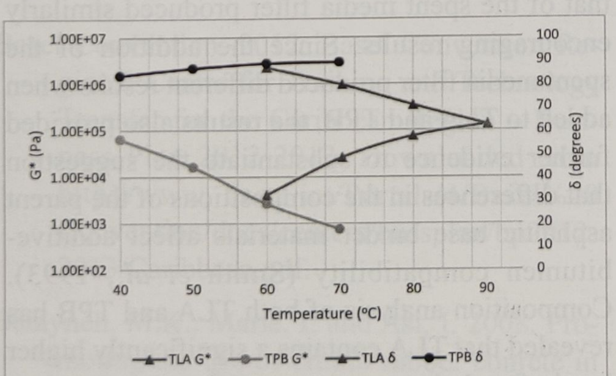

Fig. 2. *The variation of the rheological values of G* and δ with temperature at a loading frequency of 1.59 Hz for the asphaltic materials TLA and TPB*

that the TLA generally has higher G* and lower δ values compared to the TPB, which substantiates the superiority performance properties of TLA as observed in previous studies (Widyatmoko, *et al.*, 2008, Maharaj *et al.*, 2009, Maharaj, *et al.*, 2011, Maharaj *et al.*, 2015a, Maharaj, *et al.*, 2015b, Mohamed, *et al.*, 2017).

The variation of G* due to the addition of the clay based spent media filter to TLA and TPB at varying concentrations and at varied frequencies at 60 ºC are shown in Figure 3. The trends in Figure 3 indicate that TLA blends exhibited a maximum increase in G* at 1% followed by a minimum at 8% at all three measuring frequencies. The TPB blends also seen in Figure 3 had overall lower values of G* compared to TLA and exhibited a minimum G* at 1% and a marginal improvement in stiffness (highest G*) at 2% addition.

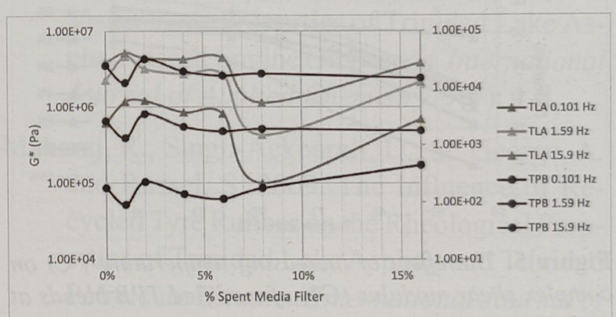

Fig. 3. *The effect of increasing spent media filter content on complex shear modulus (G*) of the modified TLA & TPB blends for different frequencies at 60 ºC*

The effects of increasing temperature on the G* and δ for various spent media filter modified TLA and TPB blends are shown in Figure 4, 5, 6 and 7. Figure 4 illustrated the variation of G* with temperature for the various TLA blends. As described earlier, there was a trend of reduction in G* as temperature increases, however, of greater significance is the observation that the TLA blend containing 1% spent media filter exhibits maximum stiffness over the temperature range showing the least temperature susceptibility. With regards to the variation of G* with temperature for the modified TPB blends and as shown in Figure 5, there were no significant improvements in temperature susceptibilities between the various blends, however, the unmodified as well as the TPB blend containing 2% spent media filter demonstrated marginally lower temperature susceptibility.

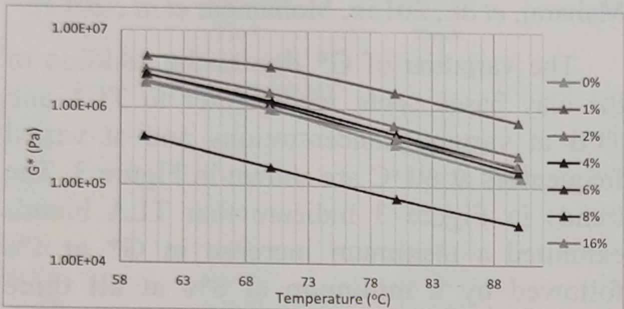

Fig. 4. *The effect of increasing temperature (°C) on complex shear modulus (G*) of modified TLA blends at 1.59 Hz*

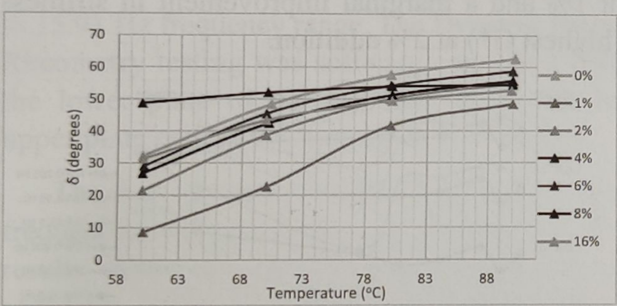

Figure 5. *The effect of increasing temperature (°C) on complex shear modulus (G*) of modified TPB blends at 1.59 Hz*

With regards to the variation of δ with temperature for the various modified TLA blends and as represented in Figure 6, the TLA blend containing 1% spent media filter exhibited the maximum elasticity over the temperature range. To illustrate this point, at 65 °C, the 1% modified blend exhibited more than a 50% reduction in δ (δ decreasing from 48.3 to 22.6) as compared to the pure TLA. As far as the characteristics of the TPB modified blends are concerned, as shown by the trends in Figure 7, the TPB blend containing 2% spent media filter exhibited the maximum elasticity up to about 50 °C, the practical working range for asphalts. Above this

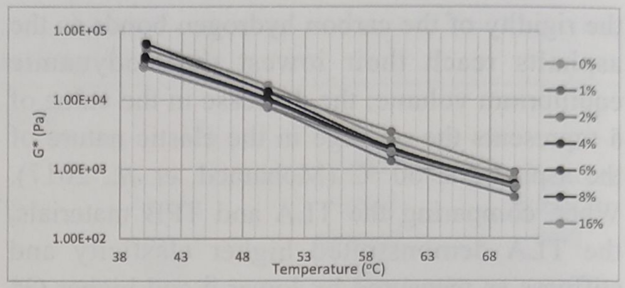

Fig. 6. *The effect of increasing temperature (°C) on phase angle (δ) of modified TLA blends at 1.59 Hz*

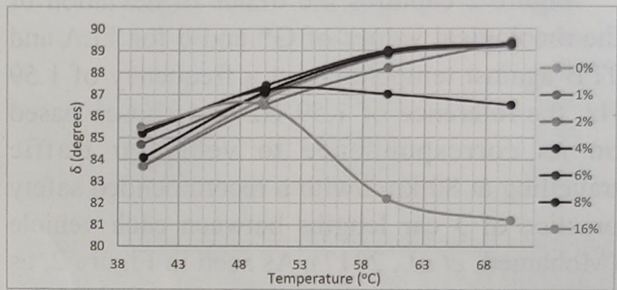

Fig. 7. *The effect of increasing temperature (°C) on phase angle (δ) of modified TPB blends at 1.59 Hz*

temperature, the 8% TPB blend demonstrated improved elasticity.

The results of the study clearly demonstrated that incorporating spent media filter, a waste product of the edible oil industry, into bituminous materials such as TLA and TPB, has the ability to alter the rheological properties of the modified binders. This observation is not surprising as previous studies by (Maharaj, 2009, Maharaj *et al.*, 2015b) using additives similar in nature to that of the spent media filter produced similarly encouraging results. Since the addition of the spent media filter produced different results when added to TLA and TPB, the results also provided further evidence to substantiate the suggestion that differences in the compositions of the parent asphaltic base binder materials affect additive-bitumen compatibility (Smith *et al.*, 1993). Composition analysis of both TLA and TPB has revealed that TLA contains a significantly higher level of asphaltene and organic functional groups content as well as containing 35.3% wt inorganic clay material (Maharaj, 2009, Corbett, 1970). This clay component was not present in TPB. It is believed that the clay affects the rheological behavior of the asphaltic base binder by affecting its particle size distribution, increasing interfacial tension and aggregation within the system (Menon, *et al*., 1988, Schramm, *et al*., 1994).

Conclusions

The modification of the TLA and TPB by the addition of spent filter media resulted in changes in the rheological properties of the blends as demonstrated in the deviations in the material's stiffness (G*) and elasticity (δ). It demonstrated the ability to formulate customized TLA and TPB based asphaltic blends of different rheological properties to suit different applications.In terms of road paving applications, the TLA blend containing 1% spent media filter and the TPB blend containing 2% spent media filter, demonstrated the optimum performance of highest stiffness, elasticity and lowest temperature susceptibility. This study demonstrates that there exists tremendous potential that incorporating the waste spent filter media as a modifier to bitumen binder can provide an environmentally sustainable method for disposing this waste, with the added benefit of possibly improving the mechanical and rheological properties of the modified binder.

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(Received: 06 May 2020, Accepted: 16 September 2020)

Clay Research, Vol. 39, No. 1, pp. 31-43 (2020)

Acid Soils of Manipur of the North-eastern Region of India: Their Mineralogy, Pedology, Taxonomy and Edaphology

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Abstract *– The acid soils of the north-eastern region (NER) of India represent tropical soils of the Indian subcontinent. During the last few decades, ICAR-NBSS&LUP has developed a formidable database on the physical and chemical properties of soils of humid tropical (HT) climate, including some of the states of the NER. However, a detailed mineralogical database for Manipur state is not available. We studied the mineralogy of the soils representing four soil series of Manipur to advance the pedological knowledge on acid soils. The soils belong to Inceptisols and Ultisols that support agricultural land use, forestry, and Jhum cultivation. They have a considerable amount of clay fractions and are rich in organic carbon (OC). Addition of OC and illuviation of clays are the prevailing pedogenic processes in these soils. However, the B horizon is not always the Bt horizon because of the low B/A clay ratio (< 1.2), which is an intriguing issue in pedological parlance. Soils are not kaolinitic; instead, they have dominant kaolin clay mineral (a 0.72 nm mineral interstratified with 1.4 nm mineral), formed from the weathering of hydroxy-interlayered vermiculite (HIV). Hydroxy-interlayering of 2:1 expanding minerals in these acidic soils has caused a decrease in the cation exchange capacity (CEC) of the soils and clays, which often misled the pedologists to designate their mineralogy class as kaolinitic. However, the enhancement of soil and clay CEC after determining the total acidity by using* $BaCl_2$*-TEA, mineralogy class could be fixed as mixed, which is compatible to their present capacity as abetter ecosystem service provider.*

Keywords: Tropical soils, Inceptisols, Ultisols, organic carbon, clay illuviation, weathering, kaolin

The north-eastern region of India with humid tropical (HT) climate has the largest area under acid soils with varying degree of acidity. Manipur has a total geographical area of 22,327 km^2, and nearly 91% of this area is under hilly terrain (Sen *et al.*, 1994). The mean annual temperature is 27.7°C, and mean summer and mean winter temperature differ by more than 12°C and thus, the state has hyperthermic soil temperature regime (Bhattacharyya *et al.*, 1994). The soils of the Manipur are generally derived from sedimentary rocks, and acidic in nature (Nayak *et al.*, 1996). In addition, the soils have low CEC and base saturation (<35 %) (Sen *et al.*, 1994, 1997; Bhattacharyya *et al.*, 1994; Nayak *et al.*, 1996).

The earlier studies stressed on Al toxicity to crops with inductive reasons despite a lack of direct evidence (Sehgal, 1998). Even if the Ultisols and Inceptisols of NER are strongly acidic, these soils have different KCl exchange acidity (< 1 to 6 cmol (p+) kg^{-1}) with low to moderate lime requirement (around < 1 to 12 t ha^{-1}) (Pal *et al.*, 2014). This range of KCl exchange acidity suggests that most of the Al^{+3}

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DOI: 10.5958/0974-4509.2020.00005.4

ions are present as $Al(OH)^{+2}$ ion in the interlayers of 2:1 minerals (vermiculite and smectites) but not in soil solution. This prevents Al toxicity to the plants. This fact is supported by the release of huge amount of Al^{3+}, Fe^{3+} and H^{+} from the 0-30 cm surface soils on extraction with $BaCl_2$-TEA solution (Bhattacharyya *et al.,* 2006). Many soils of NER are low activity clay (LAC) soils because their soil CEC and ECEC of clays are < 16 cmol (p+) kg^{-1} and < 12 cmol (p+) kg^{-1} respectively (Sen *et al.,*1994, 1997; Bhattacharyya *et al.,* 1994; Nayak *et al.,* 1996) and thus, the soil minerals belonged to kaolinitic class (Smith, 1986; Bhattacharyya *et al.,* 2009).

Many of the Ultisols of NER that have Kandic horizon, might have been placed under Oxisols order (Nair and Chamuah, 1988) before the modifications introduced by US Soil Taxonomy (Soil Survey Staff, 1990). However, the clear boundaries between the horizons, the increasing depth distribution of clay particles, and general presence of weatherable minerals do not support the possible presence of an oxic horizon in such Ultisols of tropical India (Bhattacharyya *et al.,* 2000; Chandran *et al.,* 2005). New understanding about the mineralogy, formation, and taxonomy of acid soils of HT climate, in general, and in NER, in particular, has been hitherto achieved by following the genesis and transformation of layer silicates in their silt and clay fractions (Bhattacharyya *et al.,* 1993, 2000; Chandran *et al.,* 2005; Pal *et al.,* 2014). However, acid soils of Manipur still await the critical attention of pedologists and mineralogists in documenting their mineralogy and genesis given the new knowledge developed in other states of the NER (Sen *et al.,*1994; 1997; Bhattacharyya *et al.,* 1994; Nayak *et al.,* 1996; Pal *et al.,* 2014). The present study is an attempt to create a state of the art information on the formation of acid soils of India and tropical soils, which is required to dissolve the long-standing myth about their low fertility and productivity.

Materials and Methods

The state of Manipur of NER lies at a longitude of 92° 58'E to 94° 45' E s and latitude of 23° 50' N to 25° 42'N. The elevation ranges from 790 to 2020 m above the MSL. It has a sub-humid sub-tropical climate with a mean annual rainfall of 1969 mm. Four major soils from Churachandpur, Tamenglong, Senapati, and Ukhrul districts, representing the state were selected for the study (Table 1). Morphological properties were studied as per standard procedure (Soil Survey Division Staff, 1995) and horizon wise samples were collected from the selected profiles. The soil samples were air-dried and analyzed as per standard procedures (Jackson, 1973). The soil texture was determined using the International pipette method (Jackson, 1979). The mineralogy of silt and clay fractions was studied by X-ray examinations of the parallel oriented Ca/K saturated samples with a Philips diffractometer using Ni-filtered Cu-Kα radiation at a scanning speed of $2^{\circ}2\theta$ per minute. Mineral identification was made from the diagnostic peaks of treated samples, and semi-quantitative estimation of the clay minerals was based on the principle outlined by Gjems (1967).

Results

Physical and chemical properties

The soils studied varied widely in their characteristics. The colour ranges from 5YR to 10YR hue with well-developed subangular blocky structure throughout the depth except in surface layers of Yaigangpokp soils (Pedon 4) where the structure is granular (Table 2). The particle size distribution of the soils indicates that these soils contain much less content of sand but have moderate to high amounts silt and clay fractions (Table 2). The clayey nature of the soils suggests that the rate of topsoil formation is much higher than or atleast more than the reported rate of soil loss (Bhattacharyya *et al.,* 2007; Pal *et al.,*2014).

Table 1. *General characteristics of sampling sites*

Site No	Series Name	Location	District	Geology	Elevation (m)	Slope and land use	Classification
1	Kaiphundai	Lat.24°47'18" N and Long. 93°13' 7"E	Tamenglong	Shale	400	Moderately steep slopes and under Jhuming.	Typic Dystrochrepts
2	Suongpeh	Lat.24°18' 44"N and Long 93°47' 16" E	Churachandpur	Weathered shale/ colluviums	800	Moderately steep to steep slopes and under Forests	Typic Hapludults
3	Limakang	Lat. 24°55' N and Long. 93°48' E	Senapati	Shale	1050	Moderately steep hills, rice cultivation in terraces	Umbric Dystrochrepts
4	Yaigangpokp	Lat.24°55' N and Long. 94°10' E	Ukhrul	Shale	1050	Moderately steep hills under Jhum cultivation	Typic Paleudults

This indicates that the formation of clay enriched Inceptisols and Ultisols is caused by clay illuviation (Pal *et al.,* 2014). These soils on the stable landscape have illuviated B horizons but often lack in field identifiable clay skins (Sen *et al.,* 1997). However, the uniform sand and silt distribution in the soil profiles (Table 2), confirms the clay illuviation process with 5-20% clay increase in the B horizons than the overlying A horizons (Table 2). Therefore, the B horizons in Pedons 2 and 4 qualify as the Bt horizons (Pal, 2019). Sen *et al.* (1997) argued that classifying these soils as Dystrochrepts will undermine the major pedogenic processes, and therefore, classified them as Alfisols or Ultisols. The B/A clay ratio in pedons 1 and 3 is 1.16 and 1.15, respectively, falling short of the Bt horizon criteria (≥ 1.2) (Soil Survey Staff, 1999), though the clay illuviation as the major pedogenic process is evident in these soils (Table 2). This is an intriguing situation in pedological parlance, especially when physical, chemical and mineralogical (discussed later) properties of the studied pedons are highly comparable and may have similar edaphological implications.

In situations, where identification of clay skins is difficult, the clay illuviation process can be confirmed by the appearance of pure void argillans in soil thin section study (Pal *et al.,* 1994). The presence of pure void argillans in Ultisols is not a result of current pedogenesis, indicating that clay illuviation in the present acidic chemical environment cannot be operative (Kooistra, 1982; Eswaran and Sys, 1979). Pure void argillans are also observed in yellow paleosols of the Himalayas, which were formed when $CaCO_3$ was leached entirely during the humid to per-humid climatic conditions of the Mid-Miocene geological period (Upreti and Srivastava, 2020). The clay particles disperse under slightly acidic to moderately alkaline pH conditions at a very low electrolyte concentration (Eswaran and Sys, 1979). Therefore, the downward movement of the dispersed clay particles occurs at the initial stage of soil formation when the pH is moderately alkaline (Pal *et al.*, 2014).

Soils are acidic, and the pH varied from 4.0 to 5.4 without much variation with depth (Table 3). The pH is higher in surface soils than the subsurface soils due to replenishment of bases through organic additions. The pH in KCl solution was always less than water pH, and thus the negative ΔpH indicates the occurrence of amorphous sesquioxides with variable charge (Uehara and Gillman, 1980; Bhattacharyya *et al.*, 1994; Chandran *et al.*, 2005). The soils are also not at their point of zero charge and contain a considerable amount of reserve acidity as reported for acid soils of NER (Sen *et al.*, 1997; Nayak *et al.*, 1996). The base saturation is higher in the surface horizons than the subsurface horizons (Table 3). Though acidic, these soils have high exchangeable Ca^{2+} and Mg^{2+} content (Table 3) added through litter-fall (Nayak *et al.*, 1996; Reza *et al.*, 2018).

The OC is high in the surface soils, and it decreased sharply with depth except in the rice-growing soils. In the soils under jhum and forest, the decrease in carbon was conspicuous, but the rice-growing soils have high (≥1%) organic carbon in the subsurface horizons (Table 3). Sahrawat *et al.* (2005) also reported that the rice-growing soils accumulate more amount of OC as compared to other agricultural cropping systems. The soils have CEC much less than 16 cmol (p+) kg^{-1} and base saturation of less than 35%. The ECEC of the soils is also less than 12 cmol

Table 2. *Physical properties of Manipur soils*

Horizon	Depth (cm)	Colour**	Structure*	Particle size distribution (%) Sand	Silt	Clay	Ratio of clay B/A
Kaiphundai series, District : Tamenglong - Typic Dystrochrepts							
A	0-10	10YR3/4	1fsbk	18.5	46.5	35.0	
Bw1	10-28	10YR4/4	1fsbk	17.9	42.1	40.0	
Bw2	28-60	10YR4/6	2fsbk	23.4	36.1	40.5	1.16
Bw3	60-90	7.5YR5/6	m	26.6	34.4	39.0	
Bw4	90-125	7.5YR5/6	m	26.5	45.5	28.0	
Suongpeh series. District : Churachandpur -Typic Hapludults							
A	0-17	10YR5/3	2msbk	17.1	50.7	32.2	
Bt1	17-35	7.5YR5/4	2csbk	12.9	44.6	42.5	
Bt2	35-50	7.5YR5/6	2csbk	12.0	32.2	55.8	1.73
Bt3	50-70	7.5YR5/6	1msbk	19.6	32.8	47.6	
Bt4	70-110	7.5YR5/6	1msbk	16.9	43.4	39.7	
Limakang series, District : Senapati - Umbric Dystrochrepts							
A	0-17	10YR3/2	2csbk	5.1	54.9	40.0	
Bw1	17-34	10YR43	2msbk	7.0	50.5	42.5	
Bw2	34-65	10YR4/4	1msbk	6.1	48.9	45.0	1.15
Bw3	65-95	10YR5/6	1fsbk	9.4	44.5	46.1	
BC	95-125	10YR5/8	m	26.3	45.1	28.6	
Yaigangpokp series District: Ukhrul - Typic Paleudults							
A	0-20	10YR 4/3	1 f gr	10.7	47.8	41.5	
Bt1	20-73	5 YR 4/6	1 f sbk	20.8	23.2	56.0	
Bt2	73 -102	7.5YR 4/4	1 f sbk	9.0	34.5	56.5	
Bt3	102-150	5 YR 5/6	m	6.2	35.3	58.5	1.41

*1= week, 2= moderate, f= fine, m= medium, c= course, gr = granular, m= massive, sbk = sub-angular blocky, abk = angular blocky.

**Munsell colour

Table 3. *Chemical properties of Manipur soils*

Horizon	Depth (cm)	pH		Δ pH (KCl- H_2O)	Org. C. (%)	Exchangeable Bases				Sum of bases	CEC	ECEC	Exchageable acidity 1*N*KCl			BS (%)
		H_2O	KCl			Ca^{2+}	Mg^{2+}	Na^+	K^+	cmol (p+) kg^{-1}			H^+	Al^{3+}	Total	
Kaiphundai Series - District : Tamenglong (Jhum cultivation)- Typic Dystrochrepts																
A	0-10	4.0	3.6	-0.4	1.59	2.5	1.2	0.76	0.20	4.66	9.2	8.16	0.3	3.2	3.5	51
Bw1	10-28	4.0	3.6	-0.4	1.16	1.2	0.52	0.43	0.13	2.28	8.1	7.58	0.2	5.1	5.3	28
Bw2	28-60	4.2	3.8	0.4	0.74	0.7	0.24	0.21	0.09	1.24	7.9	6.04	0.2	4.6	4.8	18
Bw3	60-90	4.2	3.8	-0.4	0.59	0.6	0.17	0.21	0.09	1.06	7.7	5.66	0.1	4.5	4.6	14
Bw4	90-125	4.2	3.9	-0.3	0.30	0.6	0.15	0.18	0.09	1.01	7.8	5.01	0.1	3.9	4.0	13
Suongpeh Series -District : Churachandpur (Forest)- Typic Hapludults																
A	0-17	4.9	3.8	-1.1	2.5	2.06	1.85	0.30	0.46	4.67	14.0	7.17	0.1	2.4	2.5	34
Bt1	17-35	4.9	3.7	-1.2	0.8	0.82	1.44	0.24	0.20	2.70	11.0	7.60	0.4	4.5	4.9	24
Bt2	35-50	4.8	3.8	-1.0	0.4	0.82	1.65	0.22	0.20	2.89	13.0	7.19	0.4	3.9	4.3	22
Bt3	50-70	5.0	3.9	-1.1	0.4	0.93	1.13	0.20	0.20	2.46	11.2	6.86	0.1	4.3	4.4	22
Bt4	70-110	5.0	3.9	-1.1	0.4	1.54	0.82	0.22	0.11	1.29	9.6	4.99	0.1	3.6	3.7	13
Limakang Series - District : Senapati (Rice)- Umbric Dystrochrepts																
A	0-17	5.0	3.9	-1.1	3.9	1.6	0.4	0.26	0.12	2.38	17.3	5.28	0.97	1.93	2.9	14
Bw1	17-34	4.9	3.9	-1.0	3.0	0.8	0.1	0.33	0.11	1.34	15.7	5.34	1.32	2.68	4.0	8
Bw2	34-65	4.8	3.9	-0.9	1.44	0.4	0.3	0.31	0.10	1.11	11.4	5.71	2.10	2.50	4.6	10
Bw3	65-95	4.8	3.9	-0.9	0.92	0.3	0.3	0.29	0.10	0.99	8.7	4.49	1.07	2.43	3.5	11
BC	95-125	4.6	3.8	-0.8	0.56	0.2	0.2	0.27	0.09	0.76	5.8	5.36	1.30	3.30	4.6	13
Yaigangpokp Series- District: Ukhrul (Jhum cultivation)- Typic Paleudults																
A	0-20	5.4	3.8	- 1.6	2.0	1.30	2.00	0.21	0.51	4.02	11.0	11.09	0.27	6.8	7.07	36
Bt1	20-73	5.2	3.7	- 1.5	0.4	0.50	0.90	0.22	0.28	1.90	12.8	10.29	0.69	8.7	8.39	15
Bt2	73 -102	5.1	3.6	- 1.5	0.2	1.20	1.50	0.26	0.14	3.10	14.3	11.37	0.27	8.0	8.27	21
Bt3	102-150	5.3	3.9	- 1.4	0.2	1.50	3.0	0.21	0.13	4.80	13.0	6.87	0.47	1.6	2.07	37

(p+) kg^{-1}. Therefore, the acid soils of Manipur qualify for LAC soils like many acid soils in other states of NER (Nair and Chamuah, 1988; Nayak *et al.*, 1996; Sen *et al.*, 1994, 1997). Despite having much less CEC, the OC content in the first 30 cm of these acid soils show a value >> 1% (1.27% in P1,1.76% in P2, 3.5% in P3 and 1.50% in P4, Table 3), suggesting that OC enhancement may not be a function of the surface area of crystalline clay minerals (Pal, 2019) but to the presence of amorphous ferri-aluminosilicate and allophane content in clay-humus complexes (Datta *et al.*, 2015; Chatterjee *et al.*, 2013). The negative ΔpH of these soils indicate the presence of sesquioxides got trapped in the interlayers of expanding clay minerals (discussed later), and such hydroxy-interlayering might have played a formidable role in OC enrichment in the surface (0-30 cm) of these LAC soils. This contention finds support from an observation on acidic Vertisols of HT climate, which have the dominant amount of the 0.7 nm (kaolin) mineral interstratified with hydroxy-interlayered smectite, (HIS) and shows OC values > 1%, than highly smectitic SAT Vertisols (Pal *et al.*, 2009; Pal, 2019).

Mineralogy of silt fractions

X-ray diffractogram of Ca saturated and glycol solvated silt fractions of all horizon samples are almost similar. The diffractogram of Ca saturated samples showed strong diffractions at 1.4nm, 1.0 nm, 0.72 nm, 0.498 nm, 0.423 nm and 0.312-0.332nm regions (Fig. 1). The 1.4 nm peak remains on glycolation, indicating that 1.4 nm mineral is non-expanding and consisted of

Table 4. *Semi-quantitative estimate of minerals (%) in silt fraction of soils*

Horizon	Depth (cm)	Pedogenic chlorite (PCh)	Vermiculite (HIV)	Mica	Kaolin	Quartz	Feldspar
Kaiphundai Series - Typic Dystrochrepts							
A	0-10	Trace	Trace	19	26	44	8
Bw1	10-28	Trace	Trace	16	36	40	8
Bw2	28-60	Trace	Trace	21	20	54	5.
Bw3	60-90	Trace	Trace	13	28	51	6
Bw4	90-125	Trace	Trace	18	30	42	6
Suongpeh Series - Typic Hapludults							
A	0-17	Trace	Trace	7	11.	77	Trace
Bt1	17-35	Trace	Trace	12	18	60	6
Bt2	35-50	Trace	7	14	22	48	8
Bt3	50-70	Trace	Trace	12	15	60	6
Bt4	70-110	Trace	Trace	12	23	63	6
Limakong Series-Umbric Dystrochrepts							
A	0-17	Trace (2.5)	Trace	19	33	34	12
Bw1	17-34	6	Trace	21	35	30	8
Bw2	34-65	5	Trace	17	20	54	3
Bw3	65-95	5	Trace	15	23	51	7
BC	95-125	6	Trace	20	26	37	11
Yaigangpokp Series - Typic Paleudults							
A	0-20	Trace	Trace	10	22	63	5
Bt1	20-73	Trace	Trace	7	51	37	5
Bt2	73-102	Trace	Trace	10	54	33	Trace
Bt3	102-150	Trace	Trace	8	53	36	Trace

Trace < 5%

vermiculite and chlorite. On K saturation at K 25°C and subsequent heating from 110° to 300°C the intensity of 1.4 nm minerals decreases and reinforces the 1.0 nm peak of mica, indicating the presence of hydroxy-interlayered vermiculite (HIV). Further heating to 550 °C, the 1.4 nm peak shifted towards 1.1-1.2 nm region and finally to 1.1 nm position, indicating the presence of HIV-Chlorite (Ch) mineral and the occasional presence of pedogenic chlorite (PCh). Presence of trace amount of another mixed-layer mineral of 1.0-1.4 (M-HIV) nm was also noticed. The peak at 1.0 nm persisted even after K saturation and heat treatments confirmed the presence of mica. Presence of kaolin being an interstratified mineral of 0.7- HIV combination was evidenced by the presence of a peak at 0.72nm, which disappeared on heating at 550 °C but reinforced the peak intensity of mica. Such changes in 0.72 nm peak suggest this peak is not of pure kaolinite (Pal *et al.*, 1989, Bhattacharyya *et al.*, 1993, 2000; Chandran *et al.*, 2005) (Fig. 1). In addition to these layer silicates, the presence of feldspar and quartz was also detected (Fig. 1). Semi-quantitative estimation of minerals showed the dominance of kaolin mineral followed by mica and 1.4 HIV clay minerals (Table 4).

Mineralogy of clay fraction

The minerals present in the clay fraction of the soils are almost similar to those of the silt consisting of HIV (1.4 nm), mica (1.0 nm) and kaolin (0.72 nm) minerals. (Fig. 2). Kaolin is the dominant clay mineral followed by mica and HIV (Table 5). Presence of M-HIV with occasional occurrence of HIV-Ch and PCh was also identified but could not be quantified. Presence of small to very small amounts of quartz and feldspar was also detected.

Discussion

The acid soils of Manipur are similar to those of other states of NER in terms of their physical and chemical properties (Bhattacharyya *et al.*, 1994, 2000, 2004; Nayak *et al.*, 1996; Sen *et al.*, 1994, 1997). The Bt horizons in soils and the higher rate of soil formation (Pal *et al.*, 2014) than the reported soil loss due to water erosion (ICAR-NAAS, 2010) indicate that these are

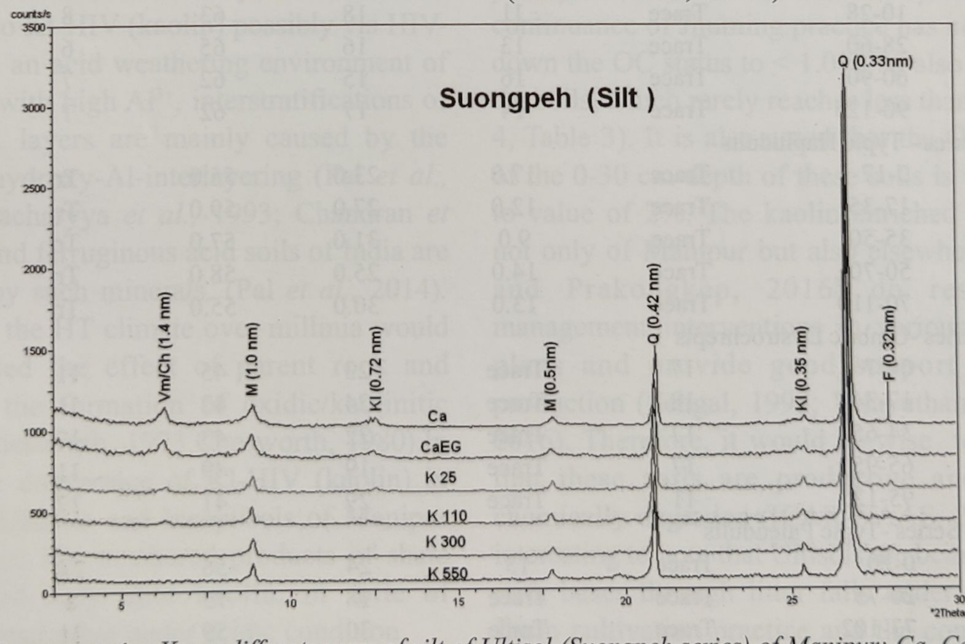

Fig. 1. *Representative X-ray diffractogram of silt of Ultisol (Suongpeh series) of Manipur: Ca, Ca-saturated; Ca-EG, calcium saturated and ethylene-glycol-solvated; K25, K110, K300, K550, K saturated and heated to 25°, 110°, 300°, 550°C, respectively; Vm-vermiculite, Ch-chlorite, M-mica, Kl-kaolin, Q-quartz, F-feldspars.*

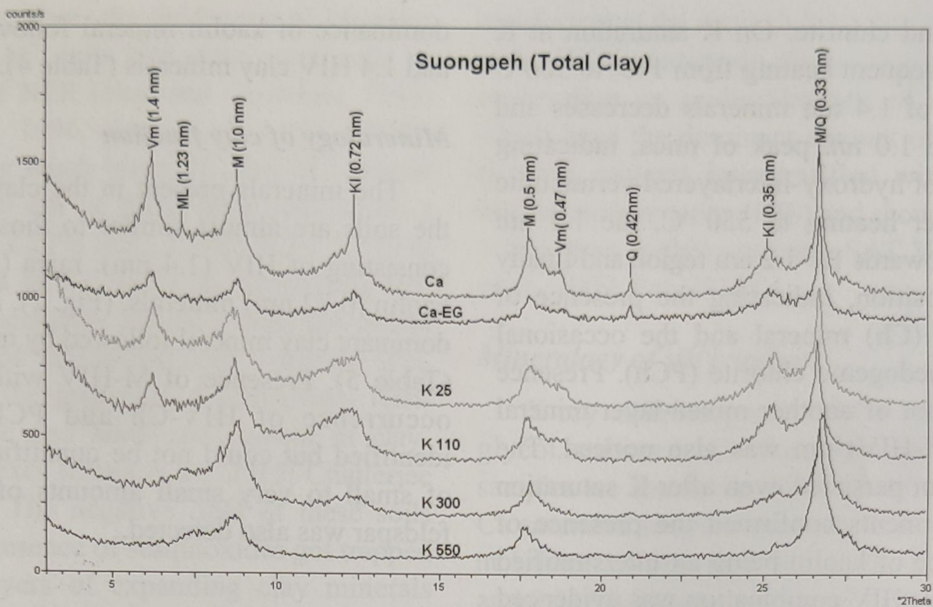

Fig. 2. *Representative X-ray diffractogram of total clay of Ultisol (Suongpeh series) of Manipur: Ca, Ca-saturated; CaEG, calcium saturated and ethylene-glycol-solvated; K25, K110, K300, K550, K saturated and heated to 25°, 110°, 300°, 550 °C, respectively; Vm-vermiculite, ML-mixed layer, M-mica, KI-kaolin, Q-quartz.*

Table 5. *Semi-quantitative estimate of minerals (%) in clay fractions*

Horizon	Depth (cm)	Pedogenic chlorite (PCh)	Vermiculite (HIV)	Mica	Kaolin	Quartz	Feldspar
Kaiphundai Series -Typic Dystrochrepts							
A	0-10	Trace*	13	16	66	6	Trace
Bw1	10-28	Trace	11	18	63	8	Trace
Bw2	28-60	Trace	13	16	65	6	Trace
Bw3	60-90	Trace	16	15	62	7	Trace
Bw4	90-125	Trace	14	17	62	7	Trace
Suongpeh Series - Typic Hapludults							
A	0-17	Trace	17.0	23.0	55.0	Tr	Trace
Bt1	17-35	Trace	12.0	27.0	59.0	Tr	Trace
Bt2	35-50	Trace	9.0	31.0	57.0	Tr	Trace
Bt3	50-70	Trace	14.0	25.0	58.0	Tr	Trace
Bt4	70-110	Trace	13.0	30.0	55.0	Tr	Trace
Limakong Series -Umbric Dystrochrepts							
A	0-17	17	Trace	23	45	11	Trace
Bw1	17-34	18	Trace	24	42	11	6
Bw2	34-65	17	Trace	22	43	12	6
Bw3	65-95	17	Trace	19	49	11	Trace
Bw4	95-125	11	Trace	29	41	17	Trace
Yaigangpokp Series -Typic Paleudults							
A	0-20	Trace	13	24	56	7.0	Trace
Bt1	20-73	Trace	Trace	18	75	8	Trace
Bt2	73-102	Trace	Trace	30	59	11	Trace
Bt3	102-150	Trace	Trace	29	60	11	Trace

Trace < 5%

matured soils. These soils are designated as kaolinitic LAC soils due to their clay CEC and ECEC values, which are less than 16 and 12 cmol (p+) kg^{-1}, respectively (Smith, 1986; Bhattacharyya *et al.,* 2009). However, their kaolinitic mineralogy class needs a revision due to the presence of kaolin mineral in the silt and clay fractions of soils (Figs. 1 and 2). This contention is supported by 3 to5 times increase in total acidity in Suongpeh soils (Table 3) when determined by $BaCl_2$-TEA as compared to that done by using 1N KCl (Nayak *et al.,* 1996; Sen *et al.,* 1997). This suggests that the acid weathering conditions of humid tropics cause hydroxy-interlayering in vermiculite of these acid soils. A mixed mineralogy class instead of conventional kaolinitic needs to be followed due to the presence of M-HIV, HIV, HIV-Ch, mica, and feldspars (Chandran *et al.,* 2004, 2005; Pal *et al.,* 2014).

The occurrence of mica (biotite), HIV, M-HIV, K-HIV and HIV-Ch in both the silt and clay fractions indicates the transformation of micas into M-V and then to M-HIV. Vermiculites adsorbed the Al^{3+} in its interlayer to form HIV and further to Kl-HIV (kaolin) possibly via HIV-Ch stage. In an acid weathering environment of HT climate with high Al^{3+}, interstratifications of 2:1 and 1:1 layers are mainly caused by the process of hydroxy-Al-interlayering (Pal *et al.,* 1989; Bhattacharyya *et al.,* 1993; Chandran *et al.,* 2005), and ferruginous acid soils of India are dominated by such minerals. (Pal *et al.,* 2014). In Manipur, the HT climate over millinia would have nullified the effect of parent rock and resulted in the formation of oxidic/kaolinitic minerals (Chesworth, 1973,Chesworth, 1980).In contrast, the dominance of Kl-HIV (kaolin) in the clay of Ultisols and Inceptisols of Manipur suggested that the weathered products of shale have reached only upto kaolin, in spite of prolonged weathering under acidic condition.

The persistence of the Ultisols and Inceptisols developed on shale in Manipur cannot be explained by the Chesworth's hypothesis of soil formation in humid tropics because the stability of weatherable minerals like feldspars over time was not considered in his model, which otherwise establishes the validity of Jenny's state factor equation (Jenny, 1941) in the formation of HT soils (Pal, 2019). Thus, the formation and persistence of Ultisols and Inceptisols in Manipur for thousands and thousands of years indicate a distinctive example that in an open system such as soil, the existence of a steady-state appears to be more meaningful concept (Smeck *et al.,* 1983; Bhattacharyya *et al.,* 1999; Chandran *et al.,* 2005; Pal, 2017). In view of the contemporary pedogenesis of Ultisols, that does not include desilication under acidic soil environment, its transformation to Oxisols with time is difficult to reconcile as envisaged by Smeck *et al.* (1983) and Lin (2011).

The acid soils of Manipur, especially the Ultisols, enriched with clay and OC have more base saturation in the surface horizon and are fairly rich in exchangeable Ca^{2+} and Mg^{2+} content. These soils efficiently support enterprises like paddy cultivation and forestry. Even the continuance of Jhuming practice has not brought down the OC status to < 1.0%, so also the pH of the soils, which rarely reaches less than 5 (Pedon 4, Table 3). It is also noted that the OC content of the 0-30 cm depth of these soils is very close to value of 2%. The kaolin enriched acid soils not only of Manipur but also elsewhere (Gilkes and Prakongkep, 2016) do respond to management interventions in various land use plans and provide good support for crop production (Sehgal, 1998; Velayutham and Pal, 2016). Therefore, it would be wise to consider that these soils are productive and are not chemically degraded (ICAR-NAAS, 2010). It is interesting to note that Ultisols are being enriched with bases through litter falls under forest and Jhum cultivation practice and the contemporary pedogenetic processes would not allow Ultisols to phase towards Oxisols. Can it then be envisaged that with time these Ultisols under natural vegetation and forest would gain bases > 35% and undergo a reconstruction phase towards Alfisols, which could be a better ecosystem service provider than Ultisols?

Conclusions

Physical, chemical and mineralogical properties observed in the present study on acid soils of Manipur of NER led us to conclude that they are matured soils as evidenced by the presence of the Bt horizon, which was formed in the initial stage soil formation. The clay illuviation in the acidic soil environment is not a current pedogenic process. These soils were formed due to the higher rate of soil formation than the arbitrary value hitherto assigned for soil loss by water erosion. In view of their enrichment of OC, higher base saturation in the surface horizons and successful land use plans like forestry, rice cultivation and even Jhum practice, it would be imprudent to designate such acid soils as chemically degraded soils. These soils support efficient food production system as they are endowed with considerable amount of weatherable minerals and kaolin clay mineral, which has much better capacity to enhance the status of OC in soils than other crystalline clay minerals. With kaolin clay mineral further phasing of Ultisols towards the so called less productive soils (Oxisols) seems improbable. The unique knowledge developed by studying the Manipur soils would further help in fine tuning the existing knowledge base at ICAR-NBSS & LUP on tropical soils to remove long standing myth about poor fertility and productivity of Indian and tropical soils.

Acknowledgements

The thoughts presented in this manuscript have evolved over a period of years in discussion among the authors and several distinguished senior colleagues of the ICAR-NBSS&LUP, whose excellent research contributions on acid soils of the country helped the authors with this manuscript. Special mention is due to Drs. D.K. Pal,T. Bhattacharyya and D.C. Nayak, former Principal Scientists of the ICAR-NBSS&LUP.

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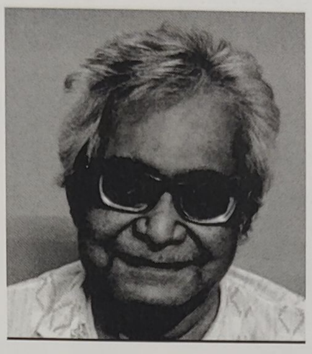
(Received: 27 May 2020, Accepted: 16 June 2020)

OBITUARY

Dr. Sadhan Chandra Ray



Dr. Sadhan Chandra Ray, 78, retired Associated Professor of Bidhan Chandra Krishi Viswavidyalaya, passed away on Monday, May 18, 2020 in Kolkata. He was born on 06 March 1942. He lost his father in childhood and brought up by his mother, who taught in a school. He joined the State College of Agriculture, West Bengal for undergraduate and completed his graduation and obtained doctoral degree from Kalyani University. For his doctoral work he worked on phosphate fixation in different types of clay minerals under renowned Professor Suresh Chandra Das. Dr. Ray was a brilliant teacher and ace motivator. His interest spanned over physical chemistry, clay mineralogy and organic chemistry, especially in organic synthesis. His students adore him for his warmth towards them, unique style of delivery of lessons, and perhaps because of personality marked with tall stature and graceful high power glass. He is survived by his wife, and a large number of admiring students and collegues.

ACKNOWLEDGEMENT

Editorial Board gratefully acknowledge the help received from the following scientists for reviewing the manuscripts:

1. Dr. D.K. Pal, Nagpur, India
2. Dr. Shashi Prakash Dwivedi, Dehradoon, India
3. Dr. Neeraj Patanjali, New Delhi.
4. Dr. Raj Mukhopadhyay, Karnal, Haryana
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Vol. 39 **June 2020** **No. 1**

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