

## Mineralogical and sorption characteristics of Aloi Clay as component of engineering structures

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**Abstract:** Clay deposits in Aloi which is part of Mamu Formation in the Northern Anambra Basin have been studied to determine their mineralogical characteristics and sorption capacity for use as component of engineering structures. The deposits vary in colour from dirty white, grayish white to brownish white from the base to the top. Mineralogical analysis shows that the samples consist mainly of Kaolinite and Illite. Non clay minerals; quartz, feldspar and haematite are also detected. The retention of the heavy metals follows the order of  $Zn^{2+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+}$ . The cation exchange capacity of the samples is determined to be between 5.67 and 22.34mEq/100g using the Ag-Tu method. These characteristics, together with relative stability of the dominant clay mineral (kaolinite) suggest that Aloi clay, when used as natural barrier material or component of barrier system can help to successfully remove the toxic materials contained in the leachates.

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**Keywords:** Aloi clay, kaolinite, earth dams, landfills, sorption capacity, XRD Analysis

### Introduction

Clay is essentially made up of alumino-silicates minerals which can either acts as natural barrier material or component of barrier system. In the design of some engineering structures such as earth dams and engineered landfill, one of the key elements is the nature (sorption capacity, mineralogical composition and chemical composition) of the materials to be used as the core in the case of earth dams and liner in the case of landfills. The impermeability of the barrier system is usually the primary concern of the engineers that design these structures but their capacity to remove toxic materials is an added advantage for the barrier system (Sezer *et.al*, 2003)

The cation exchange capacity and sorption behaviour of clay deposits in Nigeria, as an indicator for potential usefulness as a landfill liner and core of earth dams has not really been studied as against much that has been done in other parts of the world. Dubbin and Goh (1995) studied the sorption capacity of Montmorillonite for hydroxyl-Cr polymers and the mode of Cr complexation and indicated the potential role of Montmorillonite in the remediation of contaminated environment. Lagaly (1993) studied the reactions occurring at the surface and at the interlayer sites of bentonites used as adsorbent. Sirinivasan and Fogler, 1986a,b, 1990; Gokturk and Dyer, 1994; Gokturk *et.al.* 1995 have all carried out studies on the cation exchange capacity and sorption behaviour of clay minerals.

Continental clays such as the one encountered in Aloi are fluvial in nature and are widely distributed. This paper therefore, aims to study the mineralogical sorption behaviour of Aloi clay for possible usage as

core of earth dams, liner of landfills or as a component of landfill barrier systems.

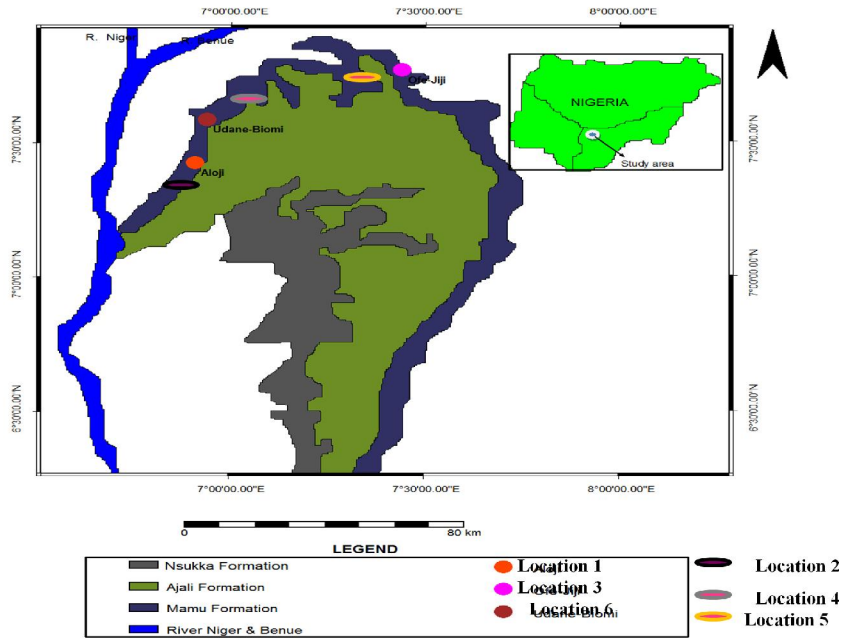
### Geology of the area

Aloi clay is part of Mamu formation in the Northern Anambra basin. Anambra basin is bounded to the north by Bida basin and Northern Nigerian massif, to the east by Benue Trough, to the west by West African massif, and to the south by Niger Delta (Obaje, 2009). The Anambra basin is a Cretaceous basin having almost a roughly triangular shape (Fig.1) with a total sediment thickness of about 9km which covers an area of about 40,000 sq.km. It is characterized by enormous lithologic heterogeneity in both lateral and vertical extensions derived from a range of paleo-environmental settings (Akaegbobi, 2005) According to Obaje (2009) sedimentation in the Anambra Basin commenced with the Campanian-Maastrichtian marine and paralic shales of the Enugu and Nkporo Formations, overlain by the coal measures of the Mamu Formation. The fluvio-deltaic sandstones of the Ajali and Oweli Formations constitute lateral equivalents that lie on the Mamu Formation. The marine shales of the Imo and Nsukka Formations overlie the Ajali. The tidal Nanka Sandstone of Eocene age overlies the Nsukka Formation. Towards the Niger Delta, the Akata Shale and Agbada Formation constitute the Paleogene equivalents of the Anambra Basin (Obaje, 2009).

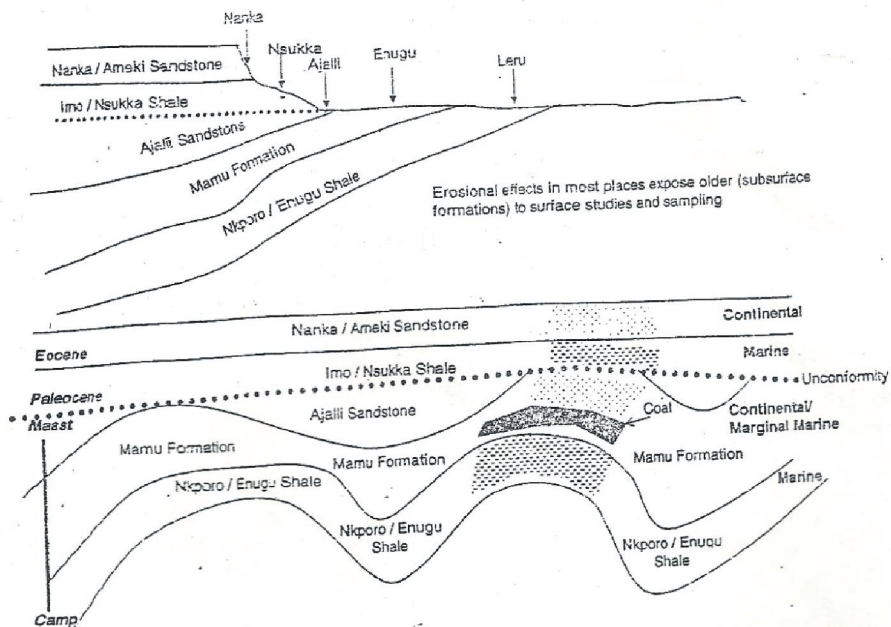
Enugu and the Nkporo shales represent the brackish marsh and fossiliferous pro-delta facies of the Late Campanian-Early Maastrichtian depositional cycle (Reijers and Nwajide, 1998, Obaje, 2009). Deposition of the sediments of the Nkporo/Enugu formations reflect a funnel-shaped shallow marine setting that graded into channeled low-energy

marshes. The overlying Mamu Formation occurs as a narrow strip trending north-south of the Calabar flank, swinging west around the Ankpa Plateau and terminating at Idah near the River Niger (Obaje, 2009). The Ajali Sandstone which overlies the Mamu marks the height of the regression at a time when the coastline was still concave. The converging littoral

drift cells governed the sedimentation and are reflected in the tidal sand waves which are characteristic for the Ajali Sandstone. The Nsukka Formation and the Imo Shale mark the onset of marine transgression in the Anambra Basin during the Paleocene.



**Fig.1:** Geological Map of Anambra Basin Showing the Study Area (modified from Umeji, 2005)



**Fig.2.** Stratigraphic Succession of the Anambra Basin. (Adapted from Obaje, 2009)

### Materials and methods

Thorough field mapping was carried out at Aloji and its environs in order to establish the local geology of the area. Traversing was along roads cuts and footpaths. Clay exposures were observed and described based on their colours and textures. The representative samples of Aloji clay were obtained from locations where large amount of clay is being mined by local miners for pot making and also from the cut of Itobe-Anyigba road.

All the samples were air-sieved through a 63 $\mu$ m sieve in order to discard the coarser grain fractions (sand and gravel) and silt. After being dried for about 15hours at 100°C, they were stored in the desiccator for future use.

The cation exchange capacity (CEC) of the clay samples were examined by measuring the Ag remaining in the solution Ag-thiourea (Ag-Tu) extracted, this is according to Dohrmann and Elchle, 1995; Sezer *et.al*, 2003. All Ag determinations were done through flame atomic absorption spectrometry (FAAS).

The mineralogical analyses were carried out on oriented and random powder samples by means of X-ray diffraction (XRD) analysis, using an Emparon Powder Diffraction equipped with a Cu – K $\alpha$  radiation source (30Kv, 55mA) inbuilt standards. The diffraction pattern was obtained with the aid of a computer, while the 2 $\theta$ , d-spacing values and peak intensities yielded by the powder patterns were used to identify the minerals at the National Geosciences Research Laboratory (NGRL), Kaduna.

### Results and Discussion

The XRD analyses of the clay samples show that the dominant clay mineral is kaolinite with minor amounts of quartz, illite, feldspar and hematite. Kaolinite alone constitutes between 69.43 to 83.24%, quartz varies from 14.79 to 22.92 and 23.08%, illite ranged from 0.67 to 1.5%, other minerals ranged from 1 to 3.88%. (figure 3-8 and table 1)

Among the clay deposits studied, the clay samples from locations 3 and 4 are the richer in kaolinite compared to those from other locations. The high percentages of kaolinite content in the clay indicate that the investigated deposits can be used as brick clay raw materials. A comparison with the mineral composition of some well known clay deposits indicates that the investigated deposits are similar to Odukpani and Ashenge basin clay deposits with minor variations in the mineral contents.

It is well known that the types and the proportions of individual clay minerals in sediments are linked to the sediment supplying source rocks, weathering conditions on the land and transportation mechanisms (Biscaye, 1965; Liangbiao and Liu, 1999). The results of the field studies, their megascopic features (textures and mode of stratification) and their geologic occurrence in a sedimentary terrain revealed that the clay deposits in the study area originated by sedimentation of weathered silicate materials of detrital origin and later modified by the environment.

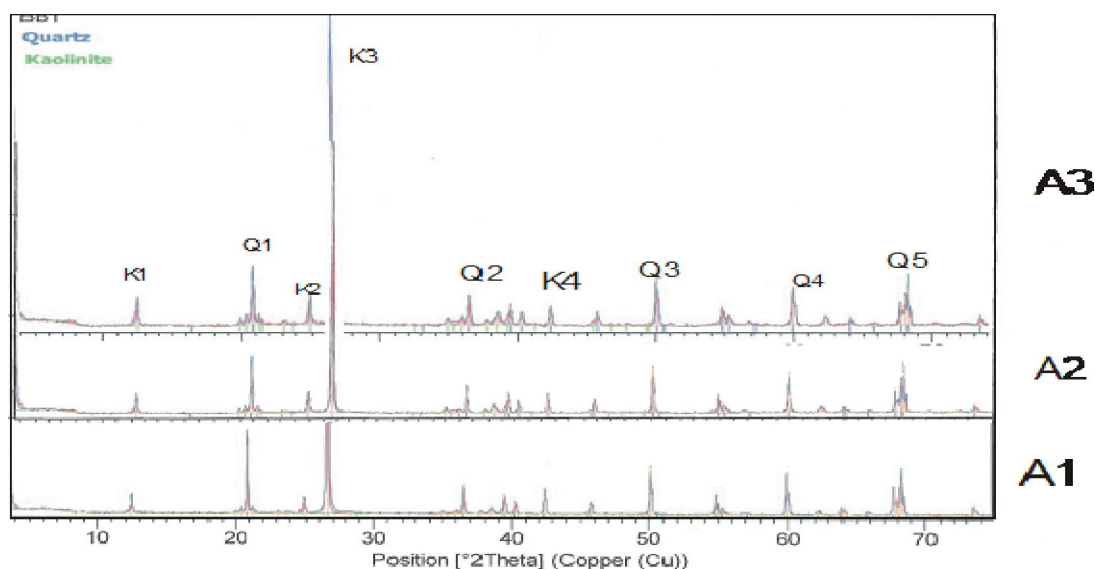


Figure 3. X-ray diffraction pattern of Loc1(A1-Bottom, A2-Midle, A3- Top samples)

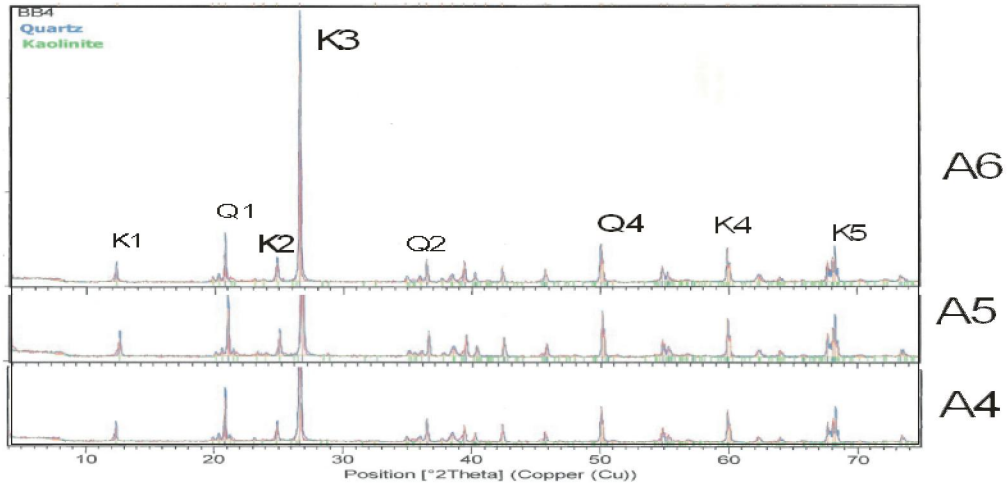


Figure 4. X-ray diffraction of Loc2 (A4-Bottom, A5-Midle, A6-Top samples)

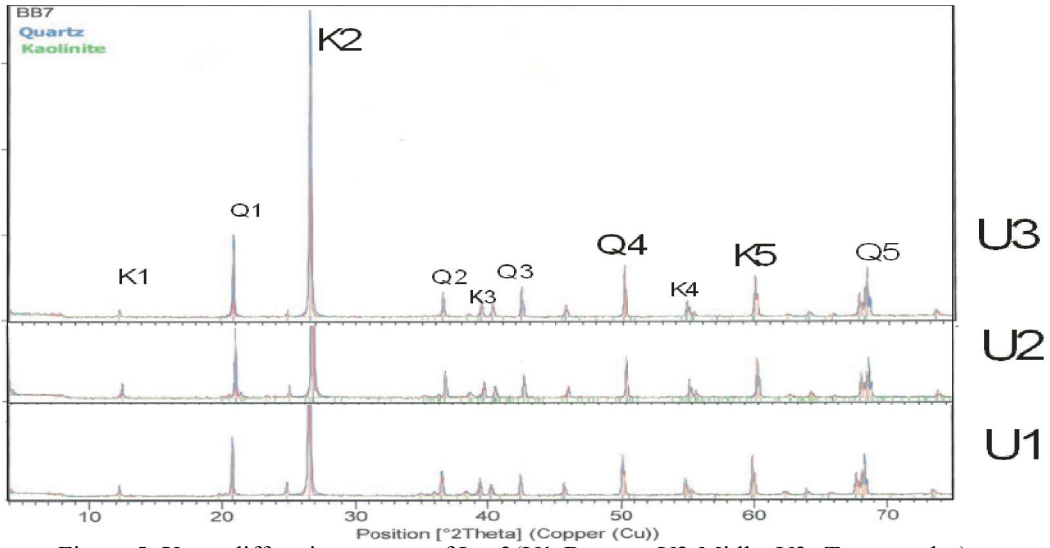


Figure 5. X-ray diffraction pattern of Loc3(U1-Bottom, U2-Midle, U3- Top samples)

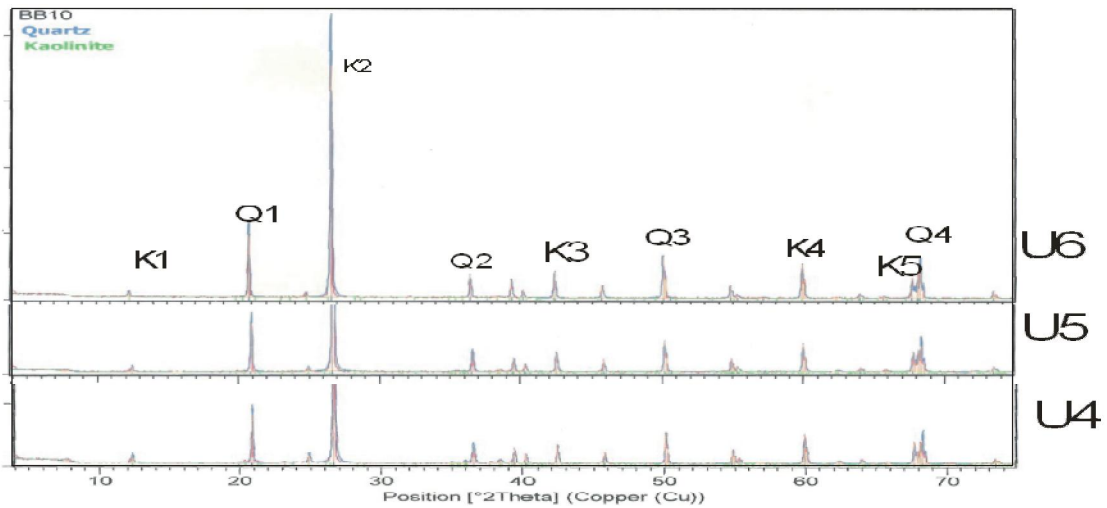


Figure 6. X-ray diffraction of Loc4 (U4-Bottom, U5-Midle, U6-Top samples).

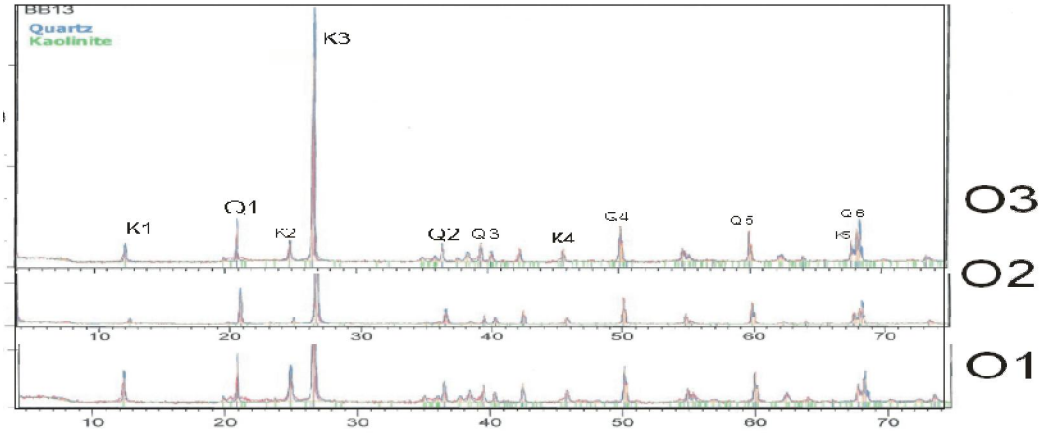


Fig.7. Left: X-ray diffraction pattern of Loc5(O1-Bottom, O2-Midle, O3- Top samples).

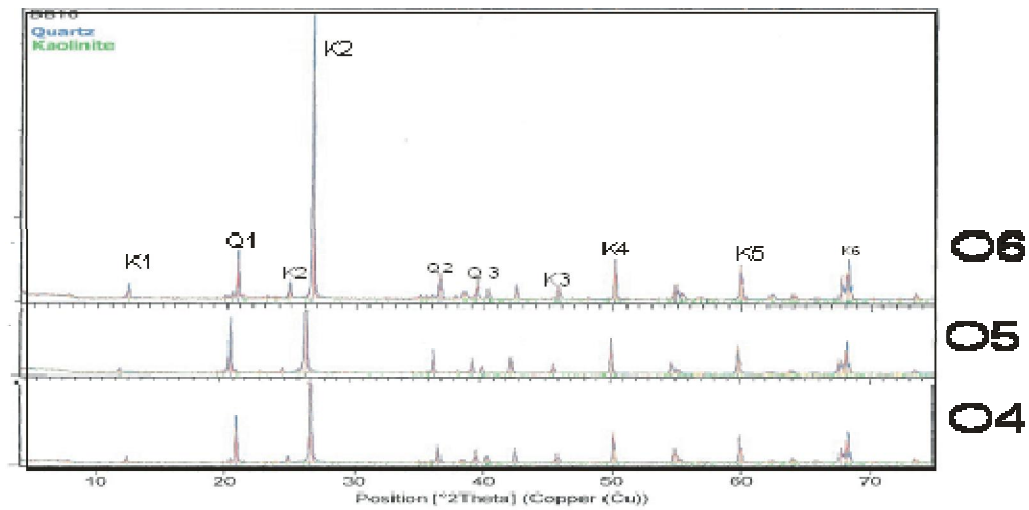


Figure 8. X-ray diffraction of Loc6 (O4-Bottom, O5-Midle, O6-Top samples).

**Table 1. The distribution of clay and non-clay minerals of the clay samples**

	Clay minerals		
	Montmorillonite	kaolinite	Illite
<b>Sample location</b>			
Location 1		*	*
Location 2		*	
Location 3		*	
Location 4		*	
Location 5		*	
Location 6		*	
	Non-clay minerals		
	quartz	Feldspar	haematite
Location 1	*		
Location 2	*		
Location 3	*	*	
Location 4	*		
Location 5	*		*
Location 6	*		*

\* Available

### Cation exchange capacity

Clay generally has the property of fixing reversibly some cations contained in the surrounding solutions. The cation exchange capacity (CEC) corresponds to the number of negative charges likely to fix cations in this manner. The isomorphous substitution of higher valence cation (i.e  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ ) by lower valence cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) is responsible for the net negative charges in clay minerals.

The cation exchange capacity of the clay samples range from 3.78cmol./Kg to 26.34cmol/kg. The type of clay minerals and their relative amount in clay samples, as well as other factors like grain size define the magnitude of cation exchange capacity (CEC). Montmorillonite has a CEC value ranging from 80cmol/kg to 150cmol/kg, Illite has a CEC that ranges from 10cmol/kg to 40cmol/kg while kaolinite has a CEC that ranges from 1cmol/kg to 15cmol/kg. (Grim, 1986). The CEC ranges of value for samples in the study area are therefore typical of soil dominated by Kaolinite and possibly Illite. Perloff and Baron, 1976; Batchelder and Joseph, 1997; Taha and kabir, 2003 reported that clay of low CEC value are typical of soils dominated by kaolinite and Illite which is consistent with the interpretation of the XRD results.

Although, there is no widely acceptable criterion for minimum value, Rowe *et.al.*, 1995; Taha and kabir, 2003 recommended a minimum CEC value of 10meq/100g for materials to be used as landfill liner. The result of the analyses shows that on the basis of CEC, Aloji clay can be used as component of engineering structures like earth dams and landfills.

### Sorption capacity

The heavy metals present in any soil sample are a reflection of the adsorption capacity of the soil (Chalermyanont *et.al.*, 2009). For all the heavy metals tested, the adsorption capacities of the samples follow the order Location 3> Location 2> Location1> Location 6> Location4> Location 5. As shown in table, the uptake values of the heavy metals present in the samples follow the order Zn> Cu> Pb> Cd> Ni (Table 2 and figure 9). The retention capacities of metals/cations are inversely related to their hydrated diameters (Sanchez *et.al.*). Therefore, Ni having the smallest hydration diameter should be the most retained of the heavy metals encountered. However, in addition to hydration diameter, their retention seems to be affected by other factors such as the presence of Hematite in the matrix (Schwertmann and Taylor, 1995).

**Table 2. Cation exchange capacity and sorption capacity of the samples (CEC)**

Location	(CEC) cmol/kg	Zn (ppm)	Cu (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)
Location 1	22.34	23.5	6.6	1.2	1.0	0.7
Location 2	5.67	21.4	5.3	1.0	1.0	0.6
Location 3	17.36	22.6	6.4	1.5	1.0	0.6
Location 4	13.6	14.23	7.1	1.23	0.8	0.4
Location 5	19.6	17.1	4.7	0.8	0.7	0.3
Location 6	8.91	21.2	7.5	0.9	0.8	0.6

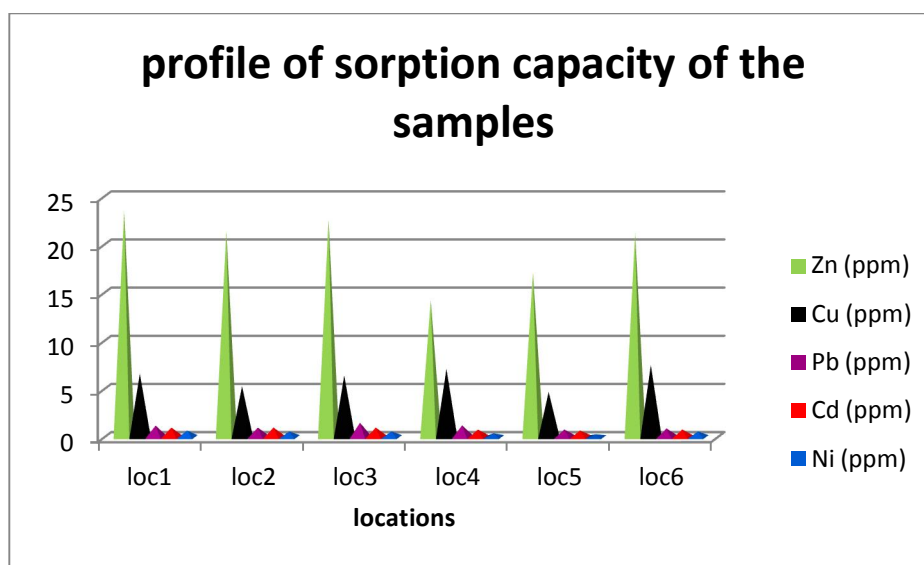


Figure 9. Profile of sorption capacity of the samples



Tijani and Bolaji (2007) posited that the sorption capacity can be considered as one of the most effective properties of fine grained soil for the control of pollutant migration through mineral barrier provided the clay-leachate compatibility problem is not induced. Although, there is a wide range of possible physico-chemical interactions among the contaminants, mineral porous media and pore liquids, the main sorption mechanisms are considered for pollutant migration modeling through containment mineral barriers (Chalermyanont *et.al*, 2009). Based on the result obtained, it will therefore not be out of place that Aloji clay will attenuate the migrating toxic materials if used as landfill liner.

### Conclusion

The cation exchange capacity of Aloji is found to be between 5.67 to 22.34cmol/kg. Its uptake behaviour for metals follows an order of  $Zn^{2+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+}$ . The presence of haematite in its composition enhances the retention of heavy metal ion particularly  $Zn^{2+}$  and  $Cu^{2+}$ . These results show that Aloji clay can be effectively utilized as a component of barrier design in sanitary landfill or as core of earth dams provided the engineering properties are up to the standard. However, despite the suitable chemical, mineralogical, low cost of extraction and supply characteristics of Aloji clay, its low abundance might be a mitigating factor in its usage as component of engineering structures

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