Physicochemistry of Pozzolanic Stabilization of a Class A-2-7 Lateritic Soil

Ahmed O. Apampa, Yinusa A. Jimoh

Abstract—The paper examines the mechanism of pozzolan-soil reactions, using a recent study on the chemical stabilization of a Class A-2-7 (3) lateritic soil, with corn cob ash (CCA) as case study. The objectives are to establish a nexus between cation exchange capacity of the soil, the alkaline forming compounds in CCA and percentage CCA addition to soil beyond which no more improvement in strength properties can be achieved; and to propose feasible chemical reactions to explain the chemical stabilization of the lateritic soil with CCA alone. The lateritic soil, as well as CCA of pozzolanic quality Class C were separately analysed for their metallic oxide composition using the X-Ray Fluorescence technique. The cation exchange capacity (CEC) of the soil and the CCA were computed theoretically using the percentage composition of the base cations Ca^{2+}, Mg^{2+} K^+ and Na^{2+} as 1.48 meq/100 g and 61.67 meq/100 g respectively, thus indicating a ratio of 0.024 or 2.4%. This figure, taken as the theoretical amount required to just fill up the exchangeable sites of the clay molecules, compares well with the laboratory observation of 1.5% for the optimum level of CCA addition to lateritic soil. The paper went on to present chemical reaction equations between the alkaline earth metals in the CCA and the silica in the lateritic soil to form silicates, thereby proposing an extension of the theory of mechanism of soil stabilization to cover chemical stabilization with pozzolanic ash only. The paper concluded by recommending further research on the molecular structure of soils stabilized with pozzolanic waste ash alone, with a view to confirming the chemical equations advanced in the study.

Keywords—Cation exchange capacity, corn cob ash, lateritic soil, soil stabilization.

I. INTRODUCTION

LATERITES have been defined as a class of reddish weathered soils rich in iron and aluminium oxides and often containing large amounts of the clay minerals quartz and kaolinite [1]. They occur in abundance in the tropical regions where they are widely used as engineering soils in the structural layers of road pavements as subgrades, sub-base or base courses, depending on the strength parameters, California Bearing Ratio, (CBR) or the Unconfined Compressive Strength, (UCS) and the standard to which the road will be built. For high standard trunk roads, however, the strength requirements often preclude the use of laterite in its natural form as base-course, thereby necessitating the use of either crushed rock or cement stabilized base courses, depending on economic haulage distance considerations. However, increasing worldwide concerns about the energy consumption

and carbon dioxide emissions from non-renewable sources, such as in quarrying and in cement production is generating renewed interest in reducing the volume of quarrying activities and in finding partial or complete substitutes for ordinary Portland cement, in form of pozzolans in the chemical stabilization of soils. In this respect, various pozzolanic materials such as, rice husk ash, locust bean pod ash and CCA have been tried with indications of positive potentials [2]-[4]. While the mechanism of pozzolan stabilizer action in soils is commonly explained in terms of lime, cement lime-pozzolan or cement-pozzolan reactions on the soil [5]-[7], this explanation does not account for the observed increase in UCS and CBR values and noticeable changes in Atterberg limits and compaction characteristics reported in some of the studies [3], [4] when up to 1.5% CCA, with neither lime nor cement, is added to a class A-2-7 lateritic soil. This gap in the explanation of pozzolan-soil stabilization mechanism, if not filled, may not allow for the optimal use of pozzolans as partial replacement for ordinary Portland cement. Based on these observations, this paper presents a reaction mechanism to account for the interactive chemistry between pozzolans and soil clay minerals present in lateritic soils, and offers an explanation for cessation of reaction based on the concept of CEC of the soil.

According to [8], there are two fundamental building blocks for the clay mineral structure. One is the tetrahedral unit in which 4 oxygen atoms (or hydroxyls if needed to balance the structure) having the configuration of a tetrahedron enclose a silicon atom which is equidistant from each of the oxygen atoms. The oxygen atoms at the base of all tetrahedral are in a common plane and each oxygen atom belongs to two tetrahedral. This compound is more conveniently written as $Si_2O_3(OH)_2$. The second building block is an octahedral sheet in which an aluminium, iron or magnesium atom is enclosed by six hydroxyls having the configuration of an octahedron. The octahedral units are combined into sheets which may be considered as a layer of aluminium, iron or magnesium atoms between two layers of densely packed hydroxyls in octahedral coordination, i.e. as $Mg_3(OH)_6$, brucite or $Al_2(OH)_6$, gibbsite.

According to the arrangement of these layers and the predominating elements, clay minerals with different compositions are produced broadly into three groups [9]. When silica predominates, and there are two silicon layers to one layer of gibbsite (with some brucite) we have the montmorillonite group, which includes bentonite, widely used as drilling mud in the construction and the oil and gas industries. The second group is known generally as illites. The layers of illite are less marked than for montmorillonite and

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are also more firmly held together, so that they do not break down so readily under remoulding. The third group comprises of china clays and is known as the kaolin group. Kaolinite contains less silica than montmorillonite, having been formed by the weathering of alkaline feldspars, and the silicon and aluminium layers alternate. Kaolinite is the dominant clay mineral in laterite and lateritic soils [10], [11] and its atomic structure is as shown in Fig 1.
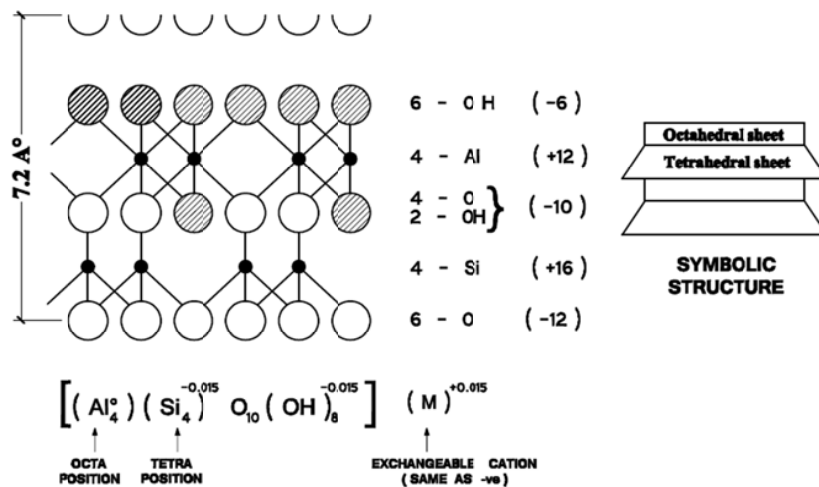

Fig. 1 Atomic Structure of Kaolinite [8]

A key characteristic of clay soils is the negative charge at the particle surface (in form of O^{2-} and OH^-) and the attractions held for available positive ions in its vicinity to bond with it in a cation exchange process. As reported by [12], cation exchange occurs due to the broken bonds around the crystal edges, the substitutions within the lattice and the hydrogen of the exposed surface hydroxyls. The extent to which these conditions exist in a soil is indicative of its CEC, which is otherwise defined as the soil's ability to hold exchangeable positive ions in the external surface of its atomic structure [13]. The negatively charged monovalent ions at the edges of the double layer (octahederal-tetrahedral sheets) attract and adsorb positively charged ions that are held in a weak bond at the surface. These positively charged ions, being in a weak bond are themselves replaceable by other positively charged ions that they may come in contact with, in accordance with the lyotropic series $Na^+ < K^+ < Ca^{2+} < Mg^{2+}$, in which cations on the right tend to replace those on the left. This is the basis for the flocculation reaction in stabilization of soils with lime, cement or cement-lime combinations. Lime or cement being essentially CaO, upon hydration dissolve into Ca^{2+} and OH^-, with the Ca^{2+} migrating to the clay particle surface and bonding with any O^{2-} and OH^- on its surface or displacing any weakly held cation there. The extent to which this reaction can be sustained clearly depends on the amount of negative sites on the clay particle surface i.e. the CEC. It is thought that these flocculation reactions can also be generated by biomass waste ashes alone acting on the soil minerals to the extent of the amount of free lime (CaO) and other reactive alkaline earth metals contained in the ash and CEC of the soil, even without the addition of lime or cement to generate further lime-ash or cement-ash pozzolanic reactions, as is the current practice.

II. AIM AND OBJECTIVES

The aim of this paper is to extend the commonly accepted view on the mechanism of soil stabilization [6], [7] to account for the direct pozzolan-soil reactions that have been reported severally, [2]-[4], by presenting the physical chemistry of the interaction between CCA pozzolan and soil clay minerals present in a class A-2-7(3) lateritic soil. The objectives are to:

i. Present the chemical analysis of a sample of a class A-2-7(3) lateritic soil and compute its CEC

ii. Present the chemical analysis of CCA, determine the percentage of alkaline forming compounds contained therein and hence the amount of cations available for exchange.

iii. Compare the computed CEC of the soil with the amount of cations in CCA available for exchange and establish a nexus between this ratio and the optimal CCA content reported for class A-2-7(3) soil.

iv. Determine the possibility of chemical reaction between the oxides of the soil and those of the CCA pozzolan respectively, and present such chemical reaction equations.

III. MATERIALS AND METHODS

A. Source of Lateritic Soil

The studied soil was sampled from a borrow site in the Kobape area of Abeokuta (7.03°N, 3.45°E) and identified as reddish brown silty clayey sand material locally recognized as 'laterite' able to develop CBR values of more than 30% sufficient for application in road works [14]. The chemical composition was analysed in the laboratory of Lafarge-WAPCO using the XRF equipment Thermo Fisher Model ARL 9900.

B. Exchangeable Cations and Base Saturation Values

The basic cations making up CEC of the soil was obtained according to the procedure of soil nutrient chemistry [13], [15], [16], summarized in (1) thus:

$$CEC = \sum[(\%composition\ of\ base\ cation)/(Equivalent\ weight) * 100] \quad (1)$$

C. CCA Artificial Pozzolan

CCA was obtained by controlled incineration at a temperature of about 600 °C, in an electric muffle furnace Model *Carbolite Type Elf 11/148*. The ash residue was passed through the 212 micron sieve and sent to the analytical laboratory of Lafarge-WAPCO for physical and chemical analysis with the XRF equipment.

IV. RESULTS AND DISCUSSION

A. Chemical Analysis of Soil, CCA and Cation Exchange Calculations

The chemical analysis of the soil sample showing the metallic oxide composition is as shown in Table I. From the percentage composition of the base forming cations Ca^{2+} and K^+ shown in Table I, and neglecting the CEC of the potentially acid forming cations Al^{3+} and Fe^{2+} since they are firmly held within the soil structure lattice and therefore not available for exchange [12] CEC was calculated using (1) and presented in Table II.

TABLE I
CHEMICAL ANALYSIS OF SOIL SAMPLE

Compound	% Composition
SiO_2	60.57
Al_2O_3	13.07
Fe_2O_3	19.05
CaO	0.27
MgO	0.00
SO_2	0.00
K_2O	0.05
Na_2O	0.00
Mn_2O_5	0.09
P_2O_5	0.09
TiO_2	1.38
LOI	5.42
Total	99.99

TABLE II
CEC OF SOIL SAMPLE

	Element	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC_{total}
1	Atomic weight (from Periodic Table)	40	24	23	39	
2	Valency	2	2	1	1	
3	Equivalent weight [(1)/(2)]	20	12	23	39	
4	% composition (from Table I)	0.27	0	0	0.05	
5	CEC meq/100gm [(4)/(3)*100]	1.35	0	0	0.13	**1.48**
6	Base Saturation % [(CEC)/(5)]	91.3	0	0	8.7	

The CEC of 1.48 meq/100 g is within the range of 1-3 meq/100 g expected of kaolinite clay and compares well with the theoretical value of 2.2 meq/100 g arrived at by [12] from calculations of the kaolinite microstructure.

The chemical analysis of CCA showing the metallic oxide composition is as presented in Table III, while the analysis of the alkaline forming compounds (CaO, MgO, K_2O and Na_2O) able to produce exchangeable cations is presented in Table IV.

TABLE III
CHEMICAL ANALYSIS OF CCA

Compound	% Composition	% Alkaline Forming Compounds
SiO_2	64.90	
Al_2O_3	5.80	
Fe_2O_3	2.97	
CaO	3.70	
MgO	2.30	
K_2O	8.39	12.37%
Na_2O	0.48	[CaO+MgO+K_2O+Na_2O]
Mn_2O_3	0.06	
SO_2	1.10	
P_2O_5	2.45	
TiO_2	1.38	
LOI	6.49	
Total	100.02	

TABLE IV
ANALYSIS OF CATIONS AVAILABLE FOR EXCHANGE IN CCA

	Element	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC_{total}
1	Atomic weight (from Periodic Table)	40	24	23	39	
2	Valency	2	2	1	1	
3	Equivalent weight [(1)/(2)]	20	12	23	39	
4	% composition (from Table III)	3.70	2.30	0.48	8.39	
5	CEC meq/100gm [(4)/(3)*100]	18.50	19.17	2.09	21.51	**61.67**
6	Base Saturation % [(CEC)/(5)]	30.0	31.1	3.4	34.9	

It can be seen from Tables II and IV that the CEC for the soil sample is 1.48 meq/100 g and that for the CCA is 61.67 meq/100 g, giving a ratio of 0.024 (i.e. 1.48/61.67) or 2.4%. This is taken to be the theoretical percentage of CCA in the soil-CCA mix, needed to just fill up the exchangeable sites of the soil. Beyond this point, the soil-CCA reaction cannot proceed and further CCA additions may become detrimental to the soil. This probably explains the report from earlier studies [4] indicating improvement in strength parameters of lateritic soil when stabilized with up to 1.5% CCA, but declining thereafter (Figs. 2 and 3) for UCS and CBR.

TABLE V
PHYSICAL CHARACTERISTICS OF CCA SAMPLE

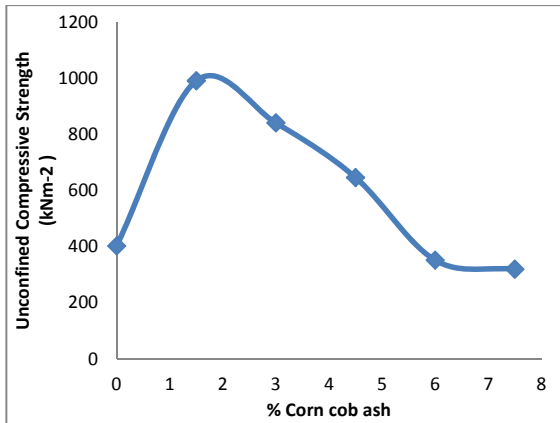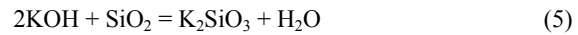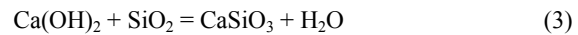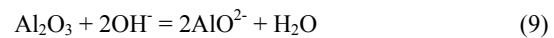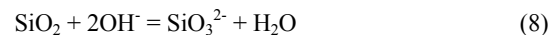| Specific Gravity	Residue on 45 micron sieve	Residue on 90 micron sieve
2.48	32.45	9.62

Fig. 2 UCS vs percentage CCA [4]
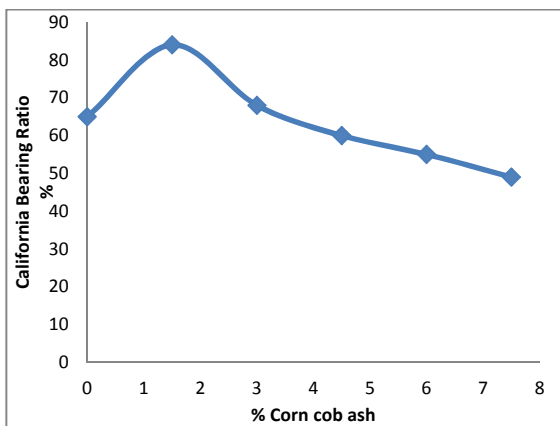
Fig. 3 CBR vs percentage CCA [4]

B. Reaction Mechanism

It is seen from Tables I and III that while both soil and ash have high percentages of SiO_2, CCA has significant amounts of the alkali earth metals (CaO and MgO) and the alkali K_2O. Furthermore, it is seen from Table V that the SiO_2 in ash is finer (more than 65% passing the 45 micron sieve) and therefore capable of being reactive [17]. On the basis of these, it is posited that, while lime stabilization of clays relies on the ability of Ca^{2+} to exchange the cations of the soil, CCA stabilization relies on the totality of Ca^{2+}, K^+ and Mg^{2+} in the ash (in form of CaO, K_2O and MgO) to combine with the hydroxyls (OH) or replace any weakly bonded mineral adsorbed in the clay structure in a flocculation reaction, according to the lytropic series $Na^+ < K^+ < Ca^{2+} < Mg^{2+}$. The cations on the right tend to replace those on the left, and the monovalent cations being generally replaceable by multivalent cations. The flocculation reaction is facilitated by the high pH environment now provided by the presence of K_2O, Na_2O; and alkaline earth metals CaO and MgO totalling 12.37% present in the ash. The latter reaction promotes the dissolution of the clayey particles and facilitates the cation exchange process between them and the negatively charged hydroxyls at the clay particle surface. The reactions are represented for the alkali earth metals (CaO and MgO), and the alkali, K_2O thus:

$$CaO + H_2O = Ca(OH)_2 \qquad (2)$$

$$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O \qquad (3)$$

$$2K + 2H_2O = 2KOH + H_2 \qquad (4)$$

$$2KOH + SiO_2 = K_2SiO_3 + H_2O \qquad (5)$$

$$MgO + H_2O = Mg(OH)_2 \qquad (6)$$

$$8MgO + 8SiO_2 + 16H_2O = M_8Si_8O_{20}(OH)_8 \cdot 12H_2O. \qquad (7)$$

Equations (6) and (7) are as advanced by [18]. Furthermore, [17] presented hydration reactions for SiO_2, Al_2O_3 and Fe_2O_3 present in fly ash as:

$$SiO_2 + 2OH^- = SiO_3^{2-} + H_2O \qquad (8)$$

$$Al_2O_3 + 2OH^- = 2AlO^{2-} + H_2O \qquad (9)$$

$$Fe_2O_3 + 3H_2O = 2Fe^{3+} + 6OH^- \qquad (10)$$

While the reactions and reaction products of (2)-(5) are fairly standard and easily explained in terms of the hydration of calcium oxide and potassium oxide into calcium hydroxide and potassium hydroxide respectively, whose hydroxides go on to form stable bonds with the clay particle – calcium silicate and potassium silicate respectively; those of (6) and (7) suggesting the reaction of magnesium oxide with silica to form magnesium silicate hydrates are not known to take place at room temperature [18], though [19] reported the formation of magnesium silicate hydrates ($MgO.mSiO_2.nH_2O$) from the combination of magnesium oxide (MgO) and micro silica (SiO_2) in the presence of moisture at room temperature. A further point noted by [17], is that while silica and aluminium oxide consume hydroxides, the earth alkalis (CaO and MgO) and iron oxide produce them. This scenario forms the basis for the interactive chemistry between the pozzolans and the minerals of the clay structure.

The significance of the foregoing is the emphasis of the role of compounds other than silica and the sesquioxides in the assessment of the pozzolanic quality of an ash, contrary to the ASTM C 618 procedure of focussing on minimum percentage of the sum of SiO_2, Fe_2O_3 and Al_2O_3 alone. The action of these other compounds is probably responsible for the observed improvement in soil strength upon the addition of CCA alone to the soil. Furthermore, observed influence of pozzolanic ash alone on a soil's geotechnical properties is explainable from consideration of the soil's CEC and the amount of alkaline forming compounds in the pozzolanic ash. This phenomenon is being reported so that it will be necessary to examine the structure of the CCA stabilized soil with XRD techniques to ascertain the actual nature and structure of the compounds formed in soil-pozzolan reactions at different blend ratios; and to explore additional parameters for pozzolanic identification in qualitative terms.

V.Conclusion and Recommendation

The physical chemistry principles can be used to explain the mechanism of soil stabilization with an artificial pozzolan – CCA. The ability of the calcium, magnesium and potassium oxides in the ash in hydrated forms and with the hydroxyls of the clay platelets, to combine with silica to form silicate compounds form the major basis of the principles.

Further research is needed to examine the compound composition and molecular structure of the CCA stabilized soil to confirm the chemical equations advanced in this study to explain the improved strength parameters observed when pozzolans alone are added to soils. Efforts to explain the physical chemistry of the blended cement-CCA-lateritic soil should also be pursued.

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