

Review Article

Pozzolanic Reaction in Clayey Soils for Stabilization Purposes: A Classical Overview of Sustainable Transport Geotechnics

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Problematic soil stabilization processes involve the application of binders to improve the engineering properties of the soil. This is done to change the undesirable properties of these soils to meet basic design standards. However, very little attention has been given to the reactive phase of soil stabilization. This phase is the most important in every stabilization protocol because it embodies the reactions that lead to the bonding of the dispersed particles of clayey soil. Hence, this reactive phase is reviewed. When clayey soils which make up the greatest fraction of expansive soil come in contact with moisture, they experience volume changes due to adsorbed moisture that forms films of double diffused layer on the particles. When this happens, the clayey particles disperse and float, increasing the pore spaces or voids that exist in the soil mass. Stabilizations of these soils are conducted to close the gaps between the dispersed clayey soil particles. This is achieved by mixing additives that will release calcium, aluminum, silicon, etc., in the presence of adsorbed moisture, and a hydration reaction occurs. This is followed by the displacement reaction based on the metallic order in the electrochemical series. This causes a calcination reaction, a process whereby calcium displaces the hydrogen ions of the dipole adsorbed moisture and displaces the sodium ion responsible for the swelling potential of clayey soils. These whole processes lead to a pozzolanic reaction, which finally forms calcium alumina-silica hydrate. This formation is responsible for soil stabilization.

1. Introduction

The concept of pozzolanization in the fields of geo-environmental engineering, geotechnical, and earth work as a whole is little talked about and little understood by experts and researchers. However, this concept is at the center of soil stabilization for clayey expansive soils and for the whole

family of lateritic soils [1, 2]. The pozzolanic reaction has been expressed and defined in different ways according to different experts. First, pozzolanas are construction materials possessing binding characteristics, which are applied in holding together the particles of a mass being worked on [3, 4]. In this context, pozzolanization is the process of binding particles together to form a workable mass of a

construction material [3]. According to the British Standard International [5] and American Standard for Testing and Materials [6], pozzolanas are materials possessing alumina (Al_2O_3), silica (SiO_2), and ferrite (Fe_2O_3), with the sum total of their composition by weight equal to or greater than 70%. Cement, fly ash, ground granulated blast furnace slag, bitumen, quicklime, hydrated lime, calcite, etc., have been in use as conventional binders having fulfilled the above minimum standard requirements, in various civil engineering and earth works [5, 6]. This is because they possess cementitious properties. Another group of materials which possesses similar properties is ash. Ash has been derived from the direct combustion of biomass or solid waste materials. These materials have been applied to improve the properties of soil in the earth and improve the properties of concrete, asphalt, etc., in other civil engineering areas of responsibility [7–9]. In geoenvironmental earth works, clayey soils have been at the center of all construction activities in the formation of foundations for road pavement, airfield pavement, landfill, backfills, embankments, slope stability problems, etc. [8]. It is of serious concern to understand the behavior of clayey soils as they form the major element of various structures. Worthy of consideration in this work is the behavior of clayey soils when exposed to moisture effects. This is important because clayey soils as they are utilized as construction materials cannot be handled without molding moisture, which triggers the reactions in the clay leading to stabilization [7, 9]. Thus also, it is, after construction, due to the rise and fall of the water table, and foundations made of clayey soil are constantly exposed to moisture, either by runoff, migration through cracks, or capillary action [10]. The most important aspect of this investigation is the role moisture plays in the pozzolanic reaction that occurs in the faces, edges, and planes of clayey soils during soil stabilization procedures [8, 10]. Clayey soils have the capacity to swelling immediately as they come in contact with moisture. During this state of moisture percolation, the clay minerals become charged with the negative ion on the surface and positive ions on the edge [3, 8]. The adsorbed moisture also dissociates to its dipole forming hydrogen (H^+) and hydroxyl (OH^-) ions presented in Figure 1. This process is called hydration of the clayey soil where the soil is impregnated with moisture to its optimum content [3]. Due to the problematic properties of the clayey soil as a result of its erratic behavior, it is technically important that such problematic soils are treated with modifiers or binders that trigger processes that will lead to agglomeration of the particles that must have dispersed when moisture was introduced. Conventionally, cement, which contains primarily calcium oxide (CaO), is used during this stabilization process. In addition, in recent years, due to the carbon footprint of cement, the utilization of environmentally friendly materials like ash has been on the rise. According to previous research results, ash is an amorphous material known for its high composition of aluminosilicates (Al-Si-Fe), which satisfies the design standard conditions [5, 6, 11]. For this reason, they release ionized metals such as Al^{3+} , S^{2+} , and Fe^{3+} , and research has shown that these metallic compounds trigger pozzolanic

reactions [3, 12–14]. When clayey soil particles disperse due to moisture impregnation, the particles form double diffused layers, which keeps them separated to overcome van der Waals intergranular particles. And during organic or inorganic additive stabilization, hydration reaction, calcination, and carbonation reactions occur. A replacement reaction between these processes occurs between hydrogen ions and calcium, aluminum, and silicon ions. Because these other metallic ions are higher in the electrochemical series ($\text{Li}^+ < \text{Na}^+ < \text{H}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+} < \text{Fe}^{2+}$) than hydrogen, they tend to displace it within the adsorbed moisture to form flocs. Furthermore, the sodium ion attached to octahedral and tetrahedral structures of the clay is replaced under the same principle and this removes its swelling components from the clayey soil [3, 8, 14–16]. This whole process is called the pozzolanic reaction. The primary objective of this work is to review the pozzolanic reaction as it affects the stabilization of clayey soils. The emphases or focus are on the utilization of organic- and inorganic-based additives.

2. Review of Literature

2.1. Electrochemical Series and Pozzolanic Reaction in Treated Clayey Soils. The reactive activities in a soil stabilization process and precisely at the phase of pozzolanic reaction where displacement reactions happen depend fundamentally on the arrangement of the metallic oxides in the electrochemical series [3, 17–20]. This is an arrangement of the metal in the order of their oxidation [3, 8, 17]. Table 1 presents this order whereby the displacement of one metal by another is determined by the respective positions in the series. Once the elements released during a soil stabilization procedure are identified, it will be possible to identify the outcome of an additive soil stabilization process [15–18]. As can be seen from the table, the hydrogen ion from the dipolar water molecule of the adsorbed moisture that triggers the hydration reaction is lowest in the series compared to all other metallic elements released during additive soil stabilization. Hence, the replacement of hydrogen ions is very possible within the adsorbed complex or double diffused layer of clay particles.

2.2. Clayey Soils. Clayey soils are characterized by certain dominant minerals in their lattice structure [4, 7, 8]. During a soil stabilization procedure, it is a prerequisite to identify the dominant mineral present in any clayey soil being studied for improvement by applying the X-ray fluorescence method (XRF) [4–7]. Table 2 presents the possible minerals that can be found in any clayey soil. These minerals determine the basic characteristics of the clayey soil. This is due to their tetrahedral or octahedral arrangement [4]. These minerals also determine the interaction between clayey soil and moisture [3]. For instance, the three major minerals of kaolinite, illite, and montmorillonite determine the activity, plasticity, and expansive nature of clayey soil [4, 7, 8]. As soon as these minerals are identified, working of clayey soils to improve their problematic properties would not be any

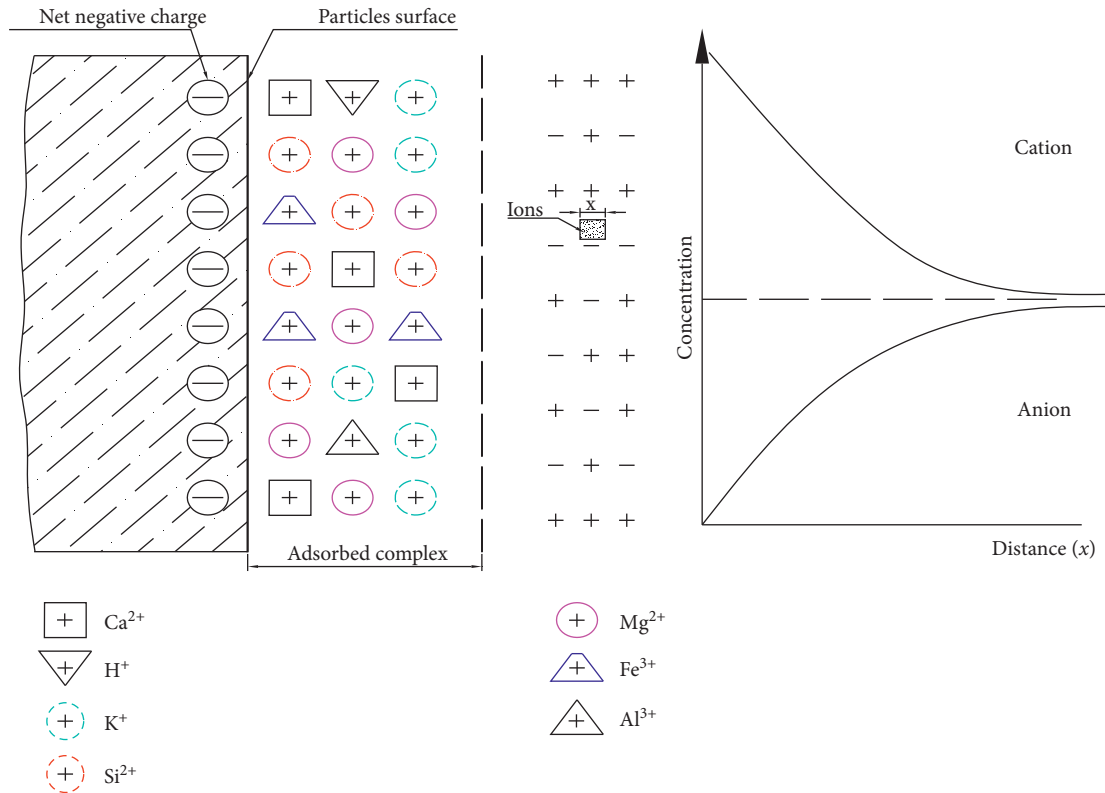


FIGURE 1: Release of ions and cation migration and exchange reaction in the adsorbed complex.

TABLE 1: Electrochemical series in order of ease of oxidation and displacement [3, 8].

Metal	Oxidation reaction		
Lithium	$\text{Li}(s) \rightarrow \text{Li}^+(aq)$	+	e^-
Potassium	$\text{K}(s) \rightarrow \text{K}^+(aq)$	+	e^-
Barium	$\text{Ba}(s) \rightarrow \text{Ba}^{2+}(aq)$	+	$2e^-$
Calcium	$\text{Ca}(s) \rightarrow \text{Ca}^{2+}(aq)$	+	$2e^-$
Sodium	$\text{Na}(s) \rightarrow \text{Na}^+(aq)$	+	e^-
Magnesium	$\text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq)$	+	$2e^-$
Aluminium	$\text{Al}(s) \rightarrow \text{Al}^{3+}(aq)$	+	$3e^-$
Manganese	$\text{Mn}(s) \rightarrow \text{Mn}^{2+}(aq)$	+	$2e^-$
Zinc	$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq)$	+	$2e^-$
Chromium	$\text{Cr}(s) \rightarrow \text{Cr}^{2+}(aq)$	+	$3e^-$
Iron	$\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq)$	+	$2e^-$
Cobalt	$\text{Co}(s) \rightarrow \text{Co}^{2+}(aq)$	+	$2e^-$
Nickel	$\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq)$	+	$2e^-$
Tin	$\text{Sn}(s) \rightarrow \text{Sn}^{2+}(aq)$	+	$2e^-$
Lead	$\text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq)$	+	$2e^-$
Hydrogen	$\text{H}_2(g) \rightarrow 2\text{H}^+(aq)$	+	$2e^-$
Copper	$\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq)$	+	$2e^-$
Silver	$\text{Ag}(s) \rightarrow \text{Ag}^+(aq)$	+	e^-
Mercury	$\text{Hg}(l) \rightarrow \text{Hg}^{2+}(aq)$	+	$2e^-$
Platinum	$\text{Pt}(s) \rightarrow \text{Pt}^{2+}(aq)$	+	$2e^-$
Gold	$\text{Au}(s) \rightarrow \text{Au}^{3+}(aq)$	+	$3e^-$



problem. Tables 3 and 4 represent the clayey soil classification related to plasticity according to Gopal and Rao [9], V. N. S. Murthy [10], and Das and Sobhan [8]. They in relation to the plasticity evaluation in percentage describe the plastic behavior of soils to enable designers to really understand the extent of plastic failure in clayey soils when exposed to loading. These range from nonplastic, low plastic, medium plastic, and to highly plastic according to Gopal and Roa [9] and V. N. S. Murthy [10] and from nonplastic, slightly plastic, low plastic, medium plastic, highly plastic, and to very highly plastic. These are the severity conditions in terms of the plasticity of the clayey soil. Table 5 shows clayey soils degree of expansion related to swelling potential ($w_s (\%) = 0.00216 * I_p^{2.44}$) according to Seed et al. [21]. The expression shows the direct relationship between swelling potential and plasticity of clayey soils. The swelling potential data further provide guiding standards or information on what to expect during chemical additive soil stabilization. The outcome of pozzolanic reactions, which are preceded by hydration, calcination, and carbonation, is the flocculation of dispersed clayey soil particles so as to form a dense and stabilized structure. This outcome is also monitored with the standard values contained in the tables as discussed above.

TABLE 2: Values of liquid limit, plastic limit, and activity of some clay minerals [8].

Mineral	Liquid limit, w_L (%)	Plastic limit, w_p (%)	Activity, A
Kaolinite	35–100	20–40	0.3–0.5
Illite	60–120	35–60	0.5–1.2
Montmorillonite	100–900	50–100	1.5–7.0
Halloysite 1	50–70	40–60	0.1–0.2
Halloysite 2	40–55	30–45	0.4–0.6
Attapulgite	150–250	100–125	0.4–1.3
Allophane	200–250	120–150	0.4–1.3

TABLE 3: Soil classification related to plasticity index [9, 10].

I_p (%)	0	<7	7–17	>17
Soil description	Nonplastic	Low plastic	Medium plastic	Highly plastic

TABLE 4: Soil classification related to plasticity index [8].

I_p (%)	0	1–5	5–10	10–20	20–40	>40
Soil description	Nonplastic	Slightly plastic	Low plasticity	Medium plasticity	High plasticity	Very high plasticity

2.3. Inorganic Additive-Induced Pozzolanic Reaction. It has been of conventional interest to utilize cement, fly ash, metal slag, quicklime, hydrated lime, and calcite in the stabilization of clayey soils notwithstanding the hazards associated with their use and their greenhouse effect [22–24]. However, the primary focus is to review the benefits of these inorganic chemical compounds to trigger pozzolanic reaction in clayey soil stabilization [3, 4, 7, 8]. Portland cement has been in use for quite some centuries now. The primary components in cement, metal slag, hydrated lime, quicklime, and calcite as presented in Table 6 are the CaO as presented in Figure 2. This is the metallic compound responsible for the calcination reaction when mixed with hydrated clayey soil during a stabilization process. The utilization of these additives releases calcium ion which displaces hydrogen ions in the adsorbed complex as discussed above and reacts with the aluminosilica from soil and hydroxyl ion from the dipole adsorbed moisture to form calcium aluminosilicate hydrate (C-A-S-H) (see Figure 2) in the clayey soil particle double diffused layer forming flocculants. These flocculants settle and strengthening is achieved in the treated soil [9].

2.4. Organic Additive-Induced Pozzolanic Reaction. With the advent of the effort to achieve environmentally friendly earth work in geoenvironmental engineering, the application of materials with no carbon footprint, i.e., the utilization of environmentally friendly binding materials has been at the center of civil engineering activities [25–27]. Table 7 presents the chemical oxide composition of the amorphous materials derived from the direct combustion of biomass and some selected solid wastes. It can be observed that the primary oxide composition of these ash materials is alumina-silica-ferrite as presented in Figure 3, which satisfies the basic

requirement for pozzolanas according to design standards [5, 6]. In addition, with a remarkable composition by weight is calcium oxide (CaO). Therefore, during a soil stabilization procedure as discussed earlier, either of these ashes is mixed with hydrated clayey soil which has dipole hydrogen and hydroxyl ions in its adsorbed moisture [3, 4, 8, 9]. Aluminum, silicon, or iron ions from the ionized primary components of the ashes being higher in the electrochemical series have the tendency to displace hydrogen ions in the adsorbed moisture of the dispersed clayey soil to form denser clogs or flocs in a pozzolanic reaction. It is important to note that research results have shown that this pozzolanic process leads to improved clayey soil properties. In addition, contained in the lattice structure of the clayey soil is the sodium ion, which is responsible for the swelling behavior of clays. This element (Na) is also displaced by calcium during the calcination reaction to reduce its volume change influence in clayey soils.

3. Discussion of Results

The entire effort of clayey soil treatment focusing on the improvement of the expansive and plastic properties and other engineering properties of the soil is to achieve the formation of C-A-S-H as presented in Figure 4. This is the component achieved through a pozzolanic reaction responsible for the alteration of the properties of clayey soils [3, 4]. When clayey soils come in contact with moisture, which they do either during the soil stabilization procedures or during the service life of the foundation structures as they are exposed to moisture by runoff, migration through cracks, or pores or suction as the water table rises in a hydraulically bound condition, they experience volume changes. Very highly expansive soils with a swelling potential of 25% and above according to Seed et al. [21] and highly plastic soils

TABLE 5: Clayey soils degree of expansion related to swelling potential (w_s (%) = $0.00216 * I_p^{2.44}$) [21].

Degree of expansion	Very high	High	Medium	Low
Swelling potential, w_s (%)	>25	5–25	1.5–5	0–1.5

TABLE 6: Chemical oxide composition of selected inorganic clayey soil binders [16, 18, 25–27].

Oxides	Chemical composition by weight (%)					
	Cement	Fly ash	Metal slag	Hydrated lime	Quicklime	Calcites
SiO ₂	20.7	55.4	14.23	0.14	1.69	—
Fe ₂ O ₃	4.41	7.84	35.65	0.17	0.384	—
Al ₂ O ₃	11	28.4	5.23	0.11	0.325	—
CaO	57.7	1.59	35.01	74.23	79.7	75
MgO	1.24	2.86	2.95	0.74	2.40	—
Na ₂ O	0.23	0.59	0.31	—	—	—
K ₂ O	2.11	2.09	0.15	—	0.0504	—
SO ₃	1.96	0.09	—	—	0.104	—
CO ₂	—	—	—	—	—	25
CaSO ₄	—	—	—	0.12	—	—
Cl	—	—	—	—	0.0267	—
TiO ₂	—	—	0.62	—	—	—
MnO	—	—	3.60	—	1.12	—
P ₂ O ₅	—	—	1.34	0.08	0.00788	—
LOI	0.65	1.14	0.88	24.35	—	—

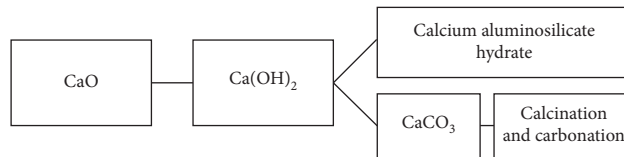


FIGURE 2: Inorganic reaction part of pozzolanic reaction.

TABLE 7: Chemical oxide composition of the additive materials [15, 17, 27–30].

Materials	Oxide composition (content by weight, %)												
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	LOI	P ₂ O ₅	SO ₃	ZnO	Free CaO
PBA	60.96	15.49	14.59	0.45	0.89	—	0.81	—	5.8	—	—	—	—
RHA	56.48	22.72	5.56	3.77	4.65	2.76	0.01	3.17	0.88	—	—	—	—
WTA	14.1	2.7	47.0	1.1	0.7	0.01	0.01	0.01	—	0.01	1.2	33.1	—
WPA	28.15	15.77	30.52	1.05	1.94	0.45	0.67	—	17.23	—	0.57	—	—
SBA	57.95	8.23	4.52	3.96	4.47	2.41	—	—	5.0	—	—	—	—

PBA: palm bunch ash; RHA: rice husk ash; WTA: waste tire ash; WPA: waste paper ash; SBA: sugarcane bagasse ash; LOI: loss on ignition.

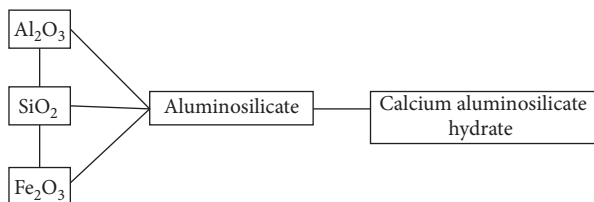


FIGURE 3: Organic reaction part of pozzolanic reaction.

with a consistency index of 17% and above according to Gopal and Rao [9] and V. N. S. Murthy [10] or 20% and above according to Das and Sobhan [8] belong to this group. It can be observed in Figure 4 that CaO, which is a major component of both the organic and inorganic chemical additives, goes through a hydration process as soon as it comes in contact with the adsorbed moisture in a soil stabilization procedure. This results in hydrated calcium oxide

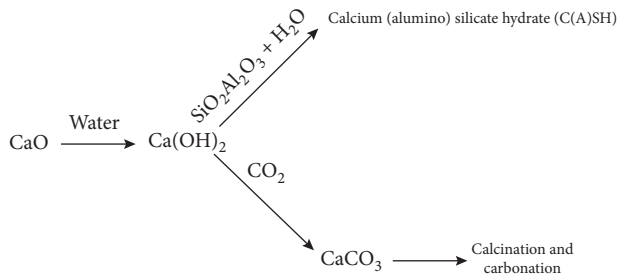


FIGURE 4: Specific reaction paths for hydration, calcination, carbonation, and pozzolanic reactions of soil treatment.

(Ca(OH)₂). This compound undergoes either carbonation to give calcite or pozzolanic reaction in the presence of alumina and silica and further hydration of CaO leading to the formation of the compounds responsible for flocculant formation in clayey soils (C-A-S-H or C-A-H and C-S-H).

4. Conclusions

The improvement of the engineering properties of highly expansive clayey soils through hydration, calcination, and carbonation reactions leading through the pozzolanic reaction which forms flocculants and densified mass of soil has been reviewed. It can be concluded that calcium oxide, alumina, silica, and ferrite are the compounds and elements in aqueous medium (hydrated medium) that trigger a pozzolanic reaction that binds the dispersed particles of clayey soil together by increasing or improving the van der Waal's interparticle forces to form a bonded mass of soil. The release of these pozzolanic components is achieved with either organic or inorganic admixtures. However, to achieve earth work in this era of global warming without any carbon footprint, this review proposes the application of organic additives to achieve pozzolanic reaction and consequently clayey soil stabilization.

Data Availability

The data used to support the findings of this study are presented within this article.

Conflicts of Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this study.

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