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Geopolymer Stabilization as Novel Technique of Reducing Carbon Dioxide Emissions

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Abstract

The paper discusses geopolymerisation which is chemical reaction within an alkaline solution as well as a solid reaction of both aluminium and silicon. It highlights origin of silicates, pozzolanic composite or alumino-silicates that could be melted within alkaline solution that may be utilized as a source of geopolymers creation. Materials that possess plenty aluminium, silicon and others such as metakaolin, microsilica, pozzolanas, ashes, red mud, kaolin clay and slags can be used as raw materials with the activators to create geopolymers. Also geopolymer end product after the exothermic procedure carried out via oligomers, as well as three stages of geopolymerisation which are suspension, when hard or solid alumino-silicates matter and stuff is dissolved because of the occurrence of water together with alkali activator. After jettisoning of a small quantity of water, the reorientation outsets and then the cluster atoms take their position in the structure. In the course of the solidification at 20^0C (twenty Celsius degree) or higher temperature of roughly 1000^0C, the water (H_2O) is almost absolutely jettisoned and the material displays his final look.

Keywords: Kaolin clay; Silicates; Pozzolanic compound; Alumino-silicates.

1. Introduction

Due to the CO_2 (Carbon Dioxide) emissions produced during the manufacturing of chemical soil stabilizers, which contribute to greenhouse gases, other soil stabilizers such as geopolymer are being sought out and recommended [1, 2]. The geopolymer concept was initiated thru Davidovits Joseph in the year 1976 for alkali aluminosilicate binders [3]. The transformation of kaolinite into tridimensional tecto-aluminosilicates used for the polycondensation of organic resins at low temperature is extremely related with the thermosetting technique of these materials.

The outcome of the process is a nano-composite that resembles an artificial rock. Similarly, the geosynthesis occur itself in large quantity in nature. The crust of the globe is composed roughly volume of fifty-five percent (55%) from siloxo-sialates as well as sialates, yet, just merely twelve percent are pure silica (quartz).

The geosynthesis techniques is based on vicissitudes stimulated in crystallography of silica backbone via the aluminium ion which are of 6-fold or 4-fold synchronization and on the chemical vicissitudes formed by the similar aluminium ion [4]. These materials possess chemical composition which are related to zeolites comprising of a polymeric Si–O– Al structure or framework, different properties as well as amorphous formation. Their properties are distinctly depending of: the Al-Si origin, the temperature (T^0C), the activator, the aggregate source and its grading, the mix quantities of every material, the water source, the hardening or curing time, the heat therapy, the dimensions of particles, the calcium concentration, if applied [5-7].

Subject to rate and the ultimate preferred properties, there are a comprehensive range of raw materials that can be used to create geopolymers, such as: metakaolin [8], red mud [9], fly ash [9-11], different wastes [10], etc. During manufacturing, the emission of CO2 and energy consumption is very low comparative with Portland cement, because this innovative binder propose a resilient diminution of the universal warming by freeing just one hundred and sixty nine (169) kg CO2/m3 when ordinary Portland cements release 306 kg CO2/m3 for the same mechanical properties, which signifies a decrease of emission by 45% [10].

Scrutinies and assessments are being performed in synthesizing alternative and eco-friendly soil stabilizers from waste materials, which can allow a decrease in CO2 emissions and, simultaneously decrease cost in earthwork construction [10, 11]. An alternative to stabilizing soil is by introducing geopolymer materials and activators. In line with the foregoing, replacing proportions of the Portland cement in Soil Stabilization with Geopolymer (a product of the alkali activation of aluminosilicate materials present in industrial waste materials) such as furnace slag, slag furnace, granulated blast-furnace slag, fly ash, kaolin clay and red mud with geopolymer activators such as sodium silicates activator, potassium and sodium hydroxide activator, will go a long way in mitigating the harsh effects of increased Portland cement production and costs. There are diverse kinds of geopolymer like ground granulated blast-furnace slag (an industrial waste produced from the cement production), kaolin clay (natural occurring waste), and rice husk fibre an agro waste. Besides, globally ground granulated blast-furnace slag and rice husk fiber produced by cement factories and rice industries have been increasing for the past few years.

The mass production of both ground granulated blast-furnace slag (GGBFS) and rice husk fiber triggers discarding problems and rising in expenses for storage in existing landfills. This in due course poses a menace to the environs if it is not appropriately managed, whereas the usage of geopolymeric materials as soil enhancement is growing daily. Regrettably, few researches have been conducted to discriminate between products that dispense enhanced performance and those that do not [2, 12]. The attribute of soil stabilization prescribes that products can provide soil-precise properties and/or present compatibility with the environs.

In other words, some produces might work well in particular soil categories within a given environment but behave disappointingly when applied to disparate materials in a dissimilar environment [7]. The usage of geopolymer materials as soils stabilizers has been broadly studied and outcomes of such preceding studies specify that geopolymers could be utilized as an operational soil stabilizer. For instances, inorganic types cement [13]: [8], lime [13, 14], fly ash [15], organic polymers [16] and their mixtures [17]. These inorganic stabilizing agents or proxies are mostly utilized in non-ecological soil stabilization, nonetheless they have been found to enhance the engineering properties of soils substantially and significantly, such inorganic materials do deter plant growth as they cannot meet the prerequisites for slope organic stabilization.

It has been itemized that, geopolymers have a low shrinkage capability and exceptional adhesion to aggregates, likewise perform effective soil stabilizers task. As a final point, this paper attempts to appraise or review the impact of the geopolymers on the engineering characteristics of lateritic soil and various geopolymer stabilizer approaches from a chemical point of view.

2. Stabilization Concept

Stabilization technique has been a concern to transportation planners and designers for the past decade as alternatives to cut off or scrap unsuitable materials when encountered on site. An alteration to the physical or engineering properties of a soil mass will require investigation of economic alternatives such as relocation of the site or use of borrowed materials [18, 19]. At present, most of the desirable building sites near urban areas have been used making alternative location not practical. At this time, sites like derelict sanitary landfills (Garbage dumps), swamplands, bays or natural harbor, mashes, hillsides and other bad regions or zones are being utilized for construction deeds, this approach likely to continue as well as accelerate when substitute sites are not accessible or due to environmental issues, inhabitant disapproval and zoning regulation which sternly limit the alternative available [5, 6].

It becomes more indispensible to transform or stabilize the existing soil so as to obtain the essential properties. Economically, feasible solutions may severally task the ingenuity of the geotechnical engineer. The improvement of high strength as well as stiffness in soil is realized by lessening of void space, bonding or affixing particles and aggregates together thru flocculent structures maintenance and swelling dominance [20]. The absorbency is altered via reform of pore size and dispersal, safe or suitable mixing of stabilizers with soil as the greatest significant factor distressing the quality of results [5].

In cases like earthdams, embankments or other fills, where designated materials in appropriate numbers might not be available, selective or choosy utilized the obtainable materials, understanding of both the function of the earth structure as well as the mechanics of the earth mass, could create a pleasing solution via utilization of zoned construction [21, 22]. Besides, tropical (humid) districts lateritic soils fill of about twenty-three percent (23%) land surface, take for highway materials usage could be efficiently seen [12, 17].

3. Geopolymer Stabilization Concept

Geopolymers can be explained as inorganic polymers achieved via chemical reaction. This can also termed as geopolymerisation, within an alkaline solution as well as a solid reach in aluminium plus silicone. There are issues surrounding the alkaline activators utilized in creating geopolymer concrete, because standardized mixture composed of both NaOH and Na_2SO_3 or more chemical in varying quantities are frequently extremely corrosive and hard to maintain. So as to trounce on numerous waste issues from Portland cement that have been used in recent studies in making “friendly” cements by geopolymerisation [23, 24].

The origins of raw materials are very extensive; any origin of silicates, alumino-silicates and pozzolanic compound that could be liquefied in alkaline solution can be utilized as a source of manufacture of geopolymers.

Geopolymers can be called eco-friendly or green materials, because is a new material with low level emission of CO_2 during producttion compared to manufacturing of the Portland cement and also been used by diverse waste companies [2, 23]. Geopolymers do not require large energy consumption, the ratio of energy utilized is 3/5 for the equivalent quantity of Portland cement.

3.1. Geopolymer Cement

This is studies to be acid resistant, because, dissimilar to the Portland cement, geopolymer cements do not rest on lime, and are not liquefied by acidic solutions. Majority of the studies construed shows that the concentration of

NaOH solution performs the most vital role on the strength of the fly ash created geopolymers [21]. The introduction of calcium oxide plus sodium hydroxide fast-tracks the geopolymerisation in fly ash. But low-calcium.

fly ash is better than high calcium (ASTM group or class C) fly ash for the creation of geopolymers. Since the occurrence of calcium in high amount might affect the polymerization way. The most chosen alkaline solution utilized in geopolymerisation is a blend of sodium hydroxide (NaOH) or potassium hydroxide (KOH) with the sodium silicate or potassium silicate [25].

3.2. Procurement of Geopolymers

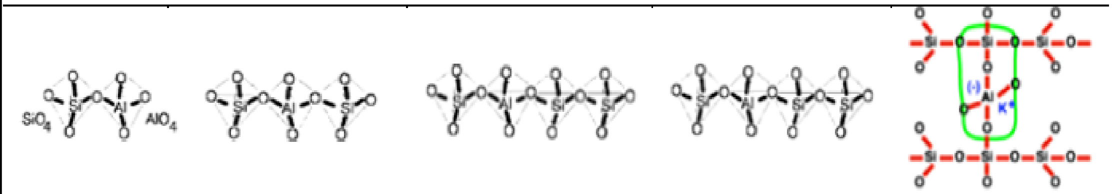
Geopolymers are inorganic or mineral polymeric materials obtained thru mixing of a dry solid (aluminosilicate) with an alkaline solution as well as other components. The main constituent is the origin or source material, which must be rich in silicone (Si) and aluminium (Al). Similarly, they can be natural minerals like clays or kaolinite, etcetera, or slags, red mud, fly ashes, etcetera, identified as "waste" materials. The liquescent is frequently based on sodium hydroxide or sodium silicate, or potassium hydroxide or potassium silicates which are soluble alkali metals [20, 21]. Solidifying time is very short, in first four (4) hours of setting, they obtain seventy percent (70%) of the final compressive strength [17].

The set-up of geopolymers made up of three (3) dimensional silico-aluminate links of sialate which is SiO_4 with AlO_4 tetrahedra, which also share all the oxygen atoms, available as in Figure 1.

3.3. Geopolymerization Reaction

Polymerization reaction is best perceived where there are presence of alkaline medium like sodium hydroxide, or potassium hydroxide, the addition of silicates, ionic composition with good bonding impacts. Also, the reactants in the chain reaction might be accelerated owing to higher molar concentration of alkali ions. Cconversely, the rise in the concentration leads to quick loss in constancy during mixing which is been ascribed as swifter polymer reaction [25, 26].

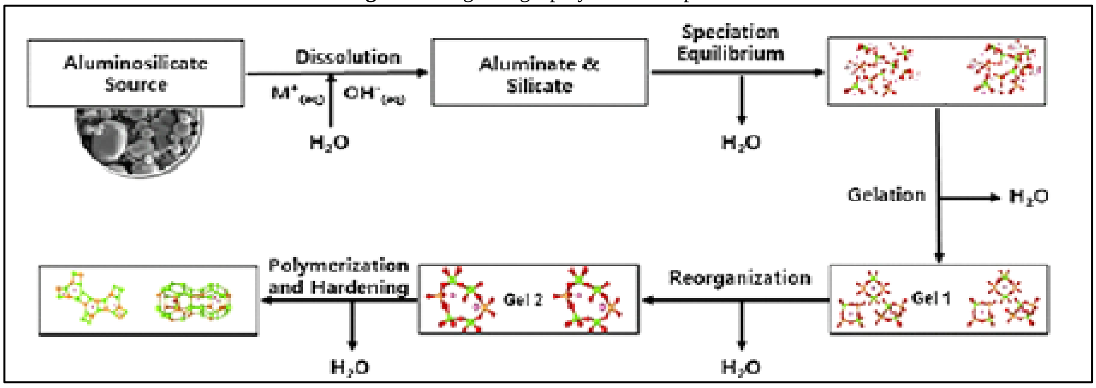
Figure-1. Types of poly (sialates)



Poly(sialate) -Si-O-Al-O-	Poly(sialate-siloxo) -Si-O-Al-O-SI-O-	Poly(sialate-disiloxo) -Si-O-Al-O-Si-O-Si-O-	Poly(sialate-disiloxo) -Si-O-Al-O-Si-O-Si-O-	Sialate link
Si:Al = 1	Si:Al = 2	Si:Al = 3	Si:Al = 3	Si:Al > 3

Source: Upshaw and Cai [5].

Figure-2. Stages of geopolymerisation process



Sources: Ogundiran and Enakerakpo [25].

3.4. Geopolymerization Stages

As a general rule, geopolymerization can be divvied into three stages or junctures, as illustrated in Figure 2. First of them is suspension, when the solid alumino-silicates material is being suspended because of the water as well as alkali activator available. After jettisoning of a little drop of water, the reorientation commences, and then the group atoms take their position in the set-up or the structure. All through the solidification at twenty (20) Celsius degrees or at roughly one thousand degrees Celsius (1000^0C) the water is nearly absolutely jettisoned and the material reveals his final look [27, 28].

3.5. Materials for Geopolymers

Due to the fact that any material rich in aluminium plus silicone as shown in Figure 3, can be utilized as raw materials, there are also other numerous materials that can as well be used to produce geopolymers. For instance kaolinite which was the first material extensively utilized in geopolymer synthesis [29], then after efficaciously uses of this innovative material, the scientists start producing other novel raw materials, like calcinated clays [30]; or industrial waste (for examples slag [27]; ashes [31], waste glass [32], aluminium mine tailings (etcetra), as well as natural silico-aluminates (for instance pure Al_2O_3–$2SiO_2$ powder) [7], zeolites [22, 25], etc.).

3.5.1. Geopolymers Obtained Using Metakaolin

Metakaolin is a pozzolanic material and its usage dates back to year 1962 when it was amalgamated in concrete for Jupia Dam in Brazil. It is produced for use as well as created when china clay which is the mineral kaolinite, heated to between six hundred (600) and eight hundred (800)°C. Likewise, another use of geopolymers was as building artifacts [28], this products consist of fire-resistant chip-board panels, constructed from a wooden core confronted with two coatings and ceramic tiles water-resistant at temperatures below four hundred and fifty (450)°C, without heating. At one hundred and fifty (150)°C kaolinite that is one of the clay components oxidized with caustic soda and its industrialized usage commence in the ceramic company with Olsen in the year 1934 [7]. Metakaolin-based geopolymers can be constructed constantly with a high level of predictableness in hardened physiognomies, as displayed in Figure 3 and 4.

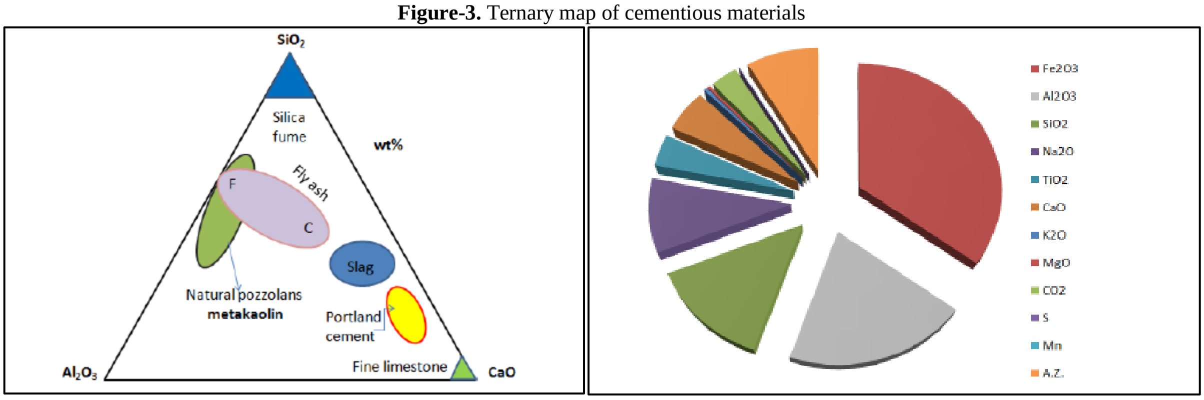
3.5.2. Microsilica (silica fume)

Silicon, ferrosilicon plus other silicon alloys are manufactured via decreasing quartz, with coal and iron or other ores at very extreme temperatures of roughly two hundred degrees Celsius (2000°C) in electric arc furnaces. Some of the silicon gas (or 'fume') is generated in the process, reaches furnace top with other combustion gases, where it becomes rusted or oxidized to silica via the air and then abridges as submicroscopic particles with agglomerated particles ranges between zero point one and zero point five (0.1–0.5 µm) of amorphous silica. This material is frequently known as abridged silica fume (csf) or 'microsilica', and comprises of an ultrafine silica ranges between eighty five to ninety six percent(85–96%), with powder between fifty (50) and hundred (100) times advanced than cement or pfa [27].

3.5.3. Pozzolanas

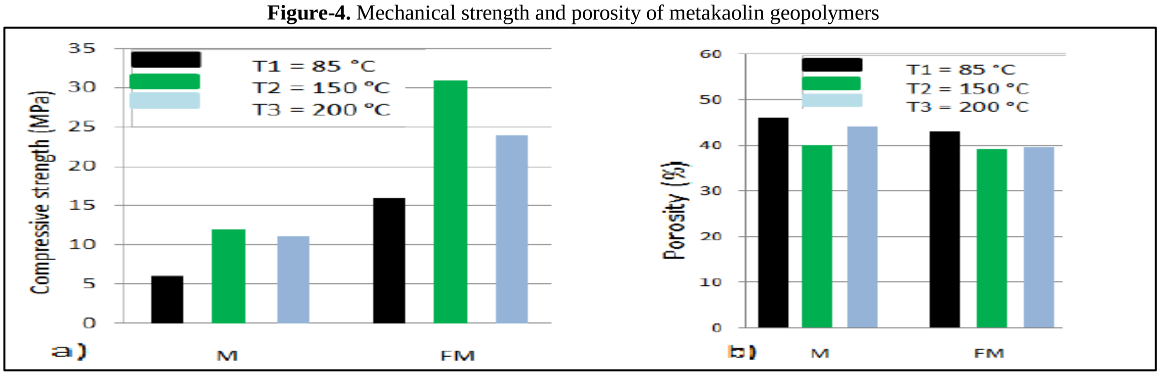
Pozzolanas, or modestly 'pozzolans', might be termed as 'materials which, although not cementitious in themselves, contain components which will merge with lime at ordinary temperatures (T^0C) in the presence of water to create steady insoluble compounds that possess cementing properties'. Synthetic or non-natural pozzolanas comprise of shale that comprising of some brick, pfa, moler (burned diatomaceous earth), burned clay, and rice husk. Whereas, the natural pozzolanas are predominantly volcanic dust as well as ash materials, Appropriate volcanic deposits are also exploited in numerous other places such as the Japan, USA, former USSR, and New Zealand [16].

Figure-3. Ternary map of cementious materials



Source: Upshaw and Cai [5], with Typical red mud chemical structure

Figure-4. Mechanical strength and porosity of metakaolin geopolymers



Source: Lahoti, *et al.* [16]

$Si_2O_5,Al_2(OH)_4+NaOH => Na(-Si-O-Al-O)n$ (1)
Kaolinite Hydrosodalite

3.5.4. Geopolymers Obtained Using Ashes

In this state the introduction of ashes inside cements or concretes is a great "green" idea [33]. Besides other benefits are the high mechanical properties, chemical, physical, the positive impact on environment low emission of CO2 and the cost-effective aspect , which plays an important role when this material is being chosen.

For instance fly ashes, they are spherical glassy particles acquired via solidification of coal by-product volatile material. Owing to the fusion-in-suspension these fly ash particles are commonly minute solid spheres as well as hollow ecospheres with some main particles being plerospheres. Fly ash can be divided into two brands based on its origin (source) and composition. Like Class F is a fly ash achieved via burning of bituminous or anthracite coal, which meets chemical composition of SiO2 + Al2O3 + Fe2O3 greater or equal to seventy percent (≥ 70%). Whereas, Class C is typically formed from burning of sub-bituminous or lignite coal and has chemical composition SiO_2 + Al_2O_3 + Fe_2O_3 at greater than or equal to fifty percent (≥ 50%) [34].

3.5.5. Geopolymers Obtained Using Red Mud

There are multiple usages of this extremely alkaline of pH of the order of eleven (1)1 or greater waste produced via aluminium production plants. For one (1) tone of aluminium, two (2) tons of red mud are deposited, nevertheless the recycle rate is slightly and this makes the material become an enormous issue for the environment [33]. For instance, red mud is a mixing of minerals with multifaceted chemical composition, where iron has the greater concentration followed by aluminium, silica, calcium, sodium and low concentration of odd earth chemical elements. Llikewise usually used to produce geopolymer cements with low CO2 emission, low fees and exceptional [15].

3.5.6. Geopolymers Obtained Kaolin Clay

Kaolin, also christened as china clay after the Kao-ling mount in China from which it was extracted for eras. It is soft white clay that is an indispensible ingredient in the production of china as well as porcelain. Also is widely utilized in the production of paint, paper, rubber, and numerous other products [15].

Kaolinite is one of the highly common minerals that is mined, as kaolin, in the United Kingdom,Germany,Malaysia, Vietnam, Brazil, Bulgaria, Bangladesh, France, the Czech Republic, Iran, India, Australia, South Korea, the People's Republic of China, Spain, South Africa, and the United States. Shrouds of kaolinitic saprolite are popular in Western and Northern Europe [35]. Under the electron microscope, is seen to comprise of coarsely hexagonal, platy quartzes ranging in size from about zero point one (0.1) micrometre to ten (10) micrometres or even larger as illustrated in Figure 5 These crystals might take vermicular as well as book-like forms, and sporadically macroscopic shapes resembling millimetre size are located [5, 18].

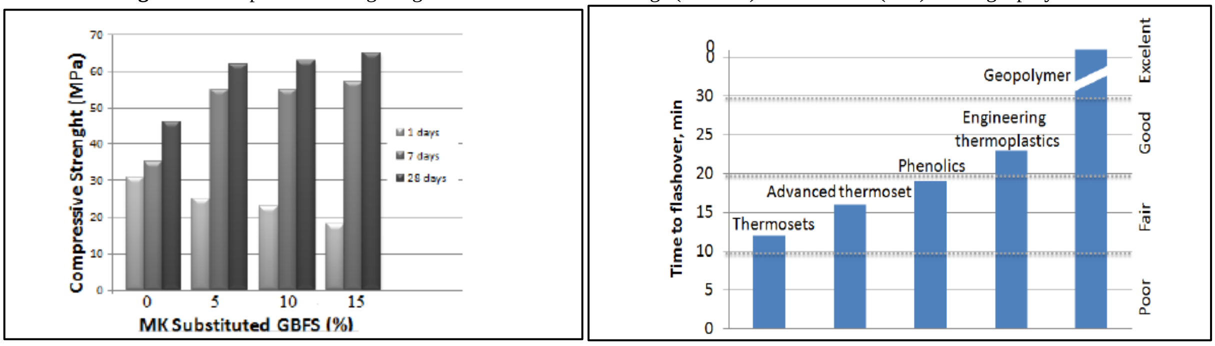
3.5.7. Geopolymers Obtained Using Slags

Ground granulated blast-furnace slag GGBFS or GGBS, are more popularly denoted as slag or slag cement. Slag is a by-product of steel production and predominantly composed of magnesium oxide (MgO), CaO, aluminum oxide (Al_2O_3), and SiO_2. When used as part of a Portland cement concrete, slag oxidizes with both the water (H_2O) latent hydraulic reaction plus the hydrated cement paste which is pozzolanic reaction, resulting in a more enhanced microstructure than that of a plain Portland cement. At initial exposure time, concrete with slag will be analogous to marginally greater diffusion coefficient than in plain Portland cement concrete, but at ages above ninety (90) days, it will possess a lower diffusion constant [36].

The outcome material slag has nebulous structure and chemical structure grasped in calcium aluminates as well as silicates [17]. Similarly, the slags might be utilized in creation of distinctive category of materials [37] and via geopolymerization is used to produce binders [15], mortar [15] and diverse kinds of concretes with good mechanical properties, as demonstrated in Figure 6 [36].

Figure-5. Kaolin clay

Figure-6. Compressive strength figure for several kinds of slags (GGBFS) – metakaolin (MK) based geopolymers



Source: Gao, *et al.* [38] and Time to flashover in minutes for several organic resins equated to geopolymer resin Source:Dungca and Galupino [24].

4. Geopolymer Activators

4.1. Alkaline Activators

Stimulation of the carefully chosen pozzolanic material is the best substantial factor in fabricating a mechanically-sound cementitious material thru the geopolymerization procedure. The activators prompt the precipitation as well as crystallization of the siliceous and aluminous types available in the solution. OH- deeds as a reagent for reactivity, and the metal cation aids in forming a structural component and balance the deleterious framework conceded by the tetrahedral aluminum. The initial mechanism antiphon is compelled by the capability of the alkaline solution to liquefy the pozzolanic material as well as discharge reactive silicon and aluminum into mixture. There are compound activating agents that could be utilized for geopolymerisation (M-alkali ion): M_2SO_4, Alkalis, Strong Salt Acids, and MOH; Weak acid salts, M_2SO_3, M_2CO_3, M_3PO_4, and MF [39].

4.2. Sodium Hydroxide Activator

NaOH named as Sodium Hydroxide is a geopolymer activator frequently utilized as alkaline solution. The sodium cations stimulate improved geopolymerisation, likened with potassium cations, owing to the fact that they can transferred easily via the network or set-up in the gelatin phase being lesser. The strength rate of geopolymers rise with the rising of NaOH concentration. Hitherto, the aged material will be conceded because of excessive OH that transforms morphology in a non-uniform one. These forms of stimulated geopolymers are more constant in sulfates as well as acids environments thru having greater crystallinety.

4.3. Potassium Hydroxide Activator

KOH activator also known as Potassium hydroxide activator enhances the compressive strength of the geopolymers cements as well as their porosity. K^+ will propound a denser final structure equaled with other activators owing to its extreme reactivity with the alumino-silicate material [40].

4.4. Sodium Silicates Activator

Na_2SO_3 which is also termed Sodium silicates are unique single utilized activator for geopolymers being typically react with NaOH to attain enough activation capability. It is used frequently because of its ever-increasing strength as well as alkalinity properties. The commonly utilized geopolymerisation activator is a combination or mishmash between Na_2SO_3 and KOH with diverse value ratio [41].

5. The Influence of Processing Parameters

Owing to the fact that, the ultimate properties of the geopolymer material are decidedly depending of the handling parameters, the impact of diverse processing factors was scrutinized by several scientists such as AASHTO [34]; Lahoti, *et al.* [35]; Cho, *et al.* [36]; [37]; Catauro, *et al.* [12] and Onutai, *et al.* [21]. Their studies it influences of four (4) of the major factors: curing temperature (T^0C) and molar ratios of H_2O/Na_2O, SiO_2/Al_2O_3, and Na_2O/SiO_2. They construe that, by increasing all of these most important factors, the mean value of compressive strength declines. Correspondingly, they observed that, the curing temperature (T^0C) have no substantial impact on this properties on short time basis. After transient of a limit value of SiO_2/ Al_2O_3 at two point nine percent (2.9 %) and Na_2O/SiO_2 at zero point two percent (0.2 %) molar ratio, the set-up will be saturated with Na+ ions and the configuration of oligomers is vetoed [42].

The molar ratio of H_2O/ Na_2O displays the highest negative (-ve) impact by preclusion from alumino silicate dissolving and via high porosity initiated by water extraction, portraying excessive decrees of properties between concentration of thirteen point seventy-five percent (13.75%) and twenty-one point seventy-five percent (21.75 %) [43].

6. Geopolymers Treatment

Thanks to this low-temperature alteration from kaolinite into hydrosodalite, ever since 1979 by Davidovits. This mineral displayed great interest for creation of: thermal insulation [5, 7]; fire resistant materials [44]; low-tech building materials [2]; foundry industry [45]; decorative stone artifacts [19, 21]; thermal shock refractories [2]; biotechnologies (medicinal applications) [46]; infrastructures repair and strengthening composites [47]; low energy ceramic tiles [48]; aircraft interior and automobile composites; [45] refractory items [27]; cements and concretes [2] and radioactive and toxic waste containment [45].

Subject to the Si/Al ratio and structural chemical set-up, geopolymers utilized for low CO2 cements, concretes, radioactive as well as toxic or noxious waste encapsulation are hence with Si/Al ratio 2:1 and 3D set-up, for bricks (clay or cement based) and ceramics are hence with Si/Al ratio 1:1 and 3D set-up, for fire resistant and heat resistant fiber amalgams (are hence with Si/Al ratio 3:1 and a 2D set-up, for sealants utilized in industry vary between 200^oC and 600^oC are hence with Si/Al ratio 2:1 and 2D set-up, for fire protection, fiber glass composites, while foundry equipment's, heat resisters amalgams are in the range of 200^oC - 1000^oC, whereas the tooling for aeronautics titanium proc. deeds are thus with Si/Al ratio 1:1 and 2D set-up [2, 23].

7. Conclusion

New stabilization technique such as geopolymer stabilization can reduce CO_2 (Carbon Dioxide) emissions produced during the manufacturing of chemical soil stabilizers, which contribute to greenhouse gases. These materials have chemical composition analogous to zeolites, likewise comprising of a polymeric Si–O– Al framework with dissimilar properties as well as amorphous set-up. Their properties are extremely depending on: the Al-Si origin, the activator, the aggregate source or origin and its grading, the water source, the mix amounts of every material, the hardening/ or curing time, the temperature (T^0C), the wideness of particles, the calcium concentration, as well as the heat therapy. Likewise serves as ecofriendly or waste reduction method especially some wastes material such as ashes, red mud, kaolin clay and slags, that are rich in alumino-silicates or silicates, and pozzolanic compound that might be liquefied in alkaline solution with the activators to create geopolymers.

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