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Efflorescence Formation Mechanism and Control for Geopolymer Paste Specimens Made from Natural Pozzolan and Calcium Hydroxide Binders

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Abstract: The use of alkali activated geopolymer binders in the recent years has received much attention because of their outstanding mechanical properties, reduction of CO_2 emissions and low energy for production. While number of researches are being done to develop geopolymer binders, their application is still limited. Efflorescence phenomena is one of the limitations of the extensive use of geopolymers. The efflorescence not only affect the materials aesthetics, but it also affects its mechanical performance. The present study outlines the general features of efflorescence, including its formation mechanism, chemical and mineralogical composition. Natural pozzolan from Songwe – Mbeya, Tanzania, calcium hydroxide, sodium silicate and sodium hydroxide were used as raw materials for geopolymerization process. It has been observed that efflorescence is formed on alkali activated paste specimens which were partially soaked in water. The formation of efflorescence products is formed due to unbalanced concentration of alkaline solution within the specimen. The produced efflorescence powders were tested for chemical and mineralogical compositions. The chemical composition test results indicated the significant percent increase of Na_2O for efflorescence powder. This may be due to migration of Na^+ from the interior of specimen to the surface during efflorescence formation. The efflorescence powder which was tested for mineralogical composition, indicated the present of some amount of calcite, mica, sodium carbonate hydrate and quartz. One of the control process of efflorescence formation on alkali activated geopolymer specimens is by maintaining equilibrium of alkali concentration within the specimens during curing process.

Keywords: Efflorescence, Geopolymer Binder, Sodium Silicate, Alkali Metals, Oxide Compounds, Chemical Composition, Natural Pozzolan, Alkali Activated Materials

1. Introduction

Portland cement is the common material used for mortar and concrete production. Production of Portland cements requires significant amount of energy for drying of materials, calcination process, production of clinkers and grinding to fine powders [10, 14, 20]. The process of producing cement in the factory emits CO_2 to the atmosphere and it is estimated that 1tone of cement produces 550kg of CO_2 to the atmosphere [13, 21]. Furthermore, mortars and concrete made from cement binders are considered to have less mechanical strength and durability resistance in aggressive environments compared to mortars and concrete made from geopolymer binders [1, 2]. Geopolymer binders has emerged as substitute to industrial cement with high potential for manufacturing sustainable concretes and mortars [3]. Geopolymer binders has excellent properties, such as high early strength development, fire resistance, fast hardening and high resistance on aggressive environments [2, 8, 14]. Geopolymer binders are produced by activating materials rich in alumino-silicate by alkali metals which are mainly calcium, sodium and potassium [4, 6, 19, 20]. Regardless of the several advantages of geopolymer binders over industrial cements, the critical challenge is the formation of efflorescence products which generally affects its durability [1, 8, 9, 18]. Efflorescence is the formation of powder deposits on the surface of geopolymer paste, mortar and concrete which is the results of excess alkali metals leaching to the surfaces of specimen which then react with acidic elements or compounds [5, 8, 12].

The efflorescence material has different colors which depend on mineral content which may be white, yellow or brown [9, 10]. The formation mechanism of efflorescence for OPC and geopolymer concrete are different. For OPC concrete, efflorescence involves the reaction of portlandite Ca $(OH)_2$ and carbon dioxide (CO_2) at the surface of the specimens [20, 21]. The efflorescence in Portland cement concrete can be represented chemically as shown in equation 1 [6, 23].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \text{ (evaporates)} \qquad (1)$$

In the case of geopolymer, the formation of efflorescence is due to the open microstructure of materials and it involves the migration of soluble alkalis [5, 10]. The alkalis are dissolved by water and diffuse to the material surface through pores and cracks, and then react with carbonic acid H_2CO_3 to produce efflorescence products [7, 17].

The main causes of efflorescence are connected to the physio-chemical characteristics of the precursor materials and alkali metal type [5, 17]. In the presence of moisture in geopolymer concrete, alkali cations (Na^+, K^+, Ca^{2+}) moves within the pore network [10, 12, 14]. These alkali cations deposit on the surface when the water evaporates from the concrete. The deposited alkali cations react with carbonic acid (H_2CO_3) formed by CO_2 of the atmosphere and produce powdery carbonate products on the concrete surface, referred to as efflorescence [12, 17]. The chemical equation of efflorescence formation for geopolymer materials is as shown in equations 2 and 3 [15, 19, 22, 23].

$$CO_2 \text{ (g)} + 2OH^- \text{ (aq)} \rightarrow CO_3^{2-} \text{ (aq)} + H_2O \qquad (2)$$

$$Na^+ \text{ (aq)} + CO_3^{2-} \text{ (aq)} + xH_2O \rightarrow Na_2CO_3.xH_2O \qquad (3)$$

The formation of efflorescence in geopolymer is the combination of base and acid elements. The common base elements are Na^+, K^+ and Ca^{2+} [8, 12]. The acidic elements or compounds which reacts with alkali to form efflorescence products are carbonic, sulfuric and chloric [4, 9]. Generally, the efflorescence can occur at the surface of the materials as a result of alkali being carried towards the surface of the material structures through pores and cracks, but also the efflorescence can occur within the pores which has effect in mechanical properties of materials due to increase in pore volume [8, 11, 22].

The efflorescence system can be represented as $wP^{m+}\bullet x(T)^n\bullet yR^{i-}\bullet zH$ similar to ettringite formation in cement paste, mortar and concrete [20], in which "P" stands for base elements (Na^+, K^+, Ca^{2+}) and "R" stands for sulfuric, chloric or carbonic. The substitution elements are represented by "T" which may be base or acid or both.

The curing processes have great influence on the formation of efflorescence products. Usually, common curing process for materials includes ambient temperature, thermal and water curing [4, 8, 16]. The alkaline cation migration process and air dissolving process are caused by the moisture difference between the inner and outer surfaces of the material. Therefore, different curing conditions will provide geopolymer with varying moisture conditions, resulting in different efflorescence rates which affect the integrity of the materials [3, 8, 12].

The small quantity of efflorescence on the surface of the structure has no effect on its durability and strength [11, 14, 18]. However, when a higher quantity of efflorescence is formed, it impairs the appearance and increase the permeability which in turn reduces the durability of concrete [14, 15]. Furthermore, efflorescence may indicate the presence of mold or mildew, both of which pose health risks to home occupants [14].

To control the efflorescence in geopolymer materials, efforts includes the use of admixtures and adjustment of the precursor materials characteristics have been extensively studied [4, 11]. The additional of silica fume, calcium oxide, calcium sulpho-aluminate, kyanite or magnesium oxide compounds are known to limit the shrinkage and improve the volume stability [6, 10, 18]. Particularly, the use of synthetic magnesium oxide in geopolymer formulation is able to form magnesium hydroxide which control the pore size of pastes and increase the compressive strength [16, 17].

Other researchers have already proposed the appropriate methods to reduce the efflorescence in geopolymer concrete. Najafi et al. [5] proposed to include high alumina cement admixtures, which encourage to the extent of crosslinking in the geopolymer binder. This reduces the mobility of alkali in the geopolymer binder system, which helps to minimize the efflorescence in geopolymer [5, 7]. They also have recommended using high-temperature curing method to reduce the efflorescence effects [3, 6]. Researchers have reported that the curing of geopolymer specimens at temperatures of 65°C or higher minimize formation of efflorescence [11, 15, 22]. In the other hand, coating is used to inhibit efflorescence in geopolymer. Xue- sen Lv et al. [15] used polymethyl siloxane (PS) and mica to inhibit efflorescence in geopolymer. Polymethyl siloxane (PS) and mica could reduce the pore size distribution and porosity and are helpful to establish a waterproof structure, leading to water absorption and the alkali leaching rate being significantly suppressed. Chengula 2018 suggested optimum combination of chemical combination of material ingredients to reduce ettringite formation in concrete, the procedure which can also be adopted for geopolymer concrete and mortars [20].

For this study, the formation of efflorescence from alkali activated geopolymer paste specimens made from natural pozzolan - calcium hydroxide mixtures were investigated. The alkali activator solution used for this study was the mixture of sodium silicate and sodium hydroxide. The curing process and precursor materials affect greatly formation of salt of efflorescence to the paste specimens.

2. Materials and Methods

2.1. Materials

The materials used in this study were naturally pozzolan, calcium hydroxide and alkali materials which are sodium silicate solution and sodium hydroxide pellets. Natural pozzolan was obtained from Songwe area in Mbeya region Tanzania, calcium hydroxide and alkali materials were obtained from local suppliers in Mbeya region. The two alkali activators were mixed together at a proportion of 2.5 (Na_2SiO_3):1(NaOH) to make alkali solution for making geopolymer paste. The sodium hydroxide pellets (NaOH) had a purity of 97% with proportions of 77.53% of Na_2O and 22.47% of H_2O by mass. The Sodium silicate (Na_2SiO_3) solution had a purity of 98% with proportions of 34.78% of SiO_2, 16.22% of Na_2O and 49.00% of H_2O by mass.

2.2. Method

2.2.1. Sample Preparation

Locally available natural pozzolan from Songwe area in Mbeya region were collected and grinded to the fineness of 5621 cm^2/gm and calcium hydroxide had a fineness of 7280 cm^2/gm. The grinded natural pozzolan were mixed with calcium hydroxide at the ratio of 75% natural pozzolan and 25% calcium hydroxide. The cubes (50mm x 50mm x 50mm) of paste specimens mixed with alkali solution to binder ratio of 0.52 were casted. Sodium hydroxide solution was prepared from sodium hydroxide pellets at concentration of 8 moles.

2.2.2. Mixing and Curing Process of Geopolymer Paste Specimens

The powdered natural pozzolan and calcium hydroxide were mixed together at a proportion of 75% pozzolan and 25% calcium hydroxide. The mixture was alkali activated with a mixture of sodium hydroxide and sodium silicate to produce geopolymer binder paste. The paste cubes were cured in two different methods: First approach was by covering the paste cubes with wet hessian materials throughout the duration of curing. Second approach was by partially immersing the paste specimens in water in which the specimens were quarterly immersed in water and three quarter of the specimen exposed to the air. Figure 1 represent curing processes adopted for this study.

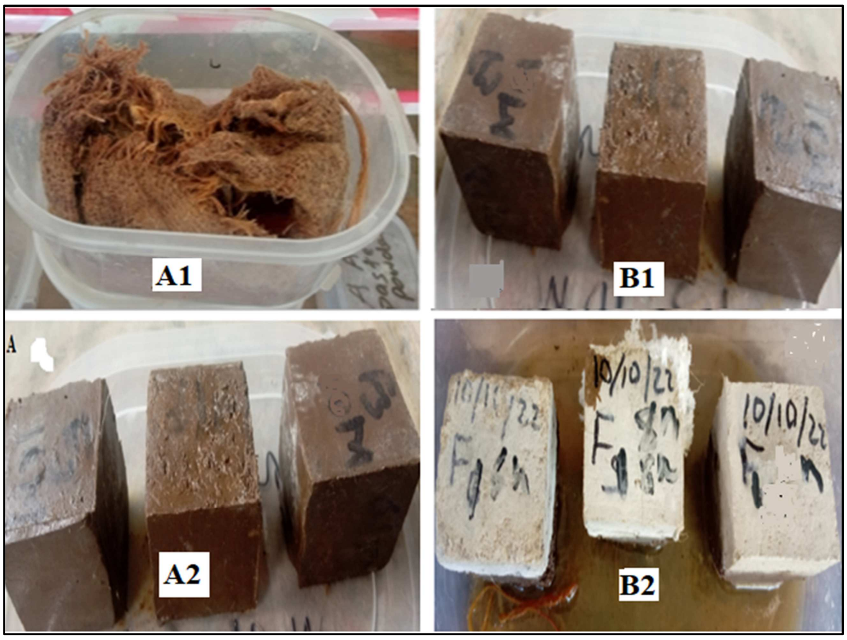

Figure 1. *Photo A1 are specimens wrapped with wet hessian, A2 are 7 days specimens cured under wet hessian, B1 are quarterly immersed specimens in water and B2 are the 7 days half immersed specimens in water.*

In order to understand properties of geopolymer binder and efflorescence formed during curing process, characterization to determine chemical and mineralogical compositions of natural pozzolan, 28 days cured geopolymer paste specimen and efflorescence formed were conducted under laboratory condition. The chemical compositions of the materials were determined by using XRF and mineralogical composition were determined from petrographic scan files using XRD methods. The XRF tests for the materials were carried out at Tanga cement factory and XRD scan files were produced at Tanzania government chemist laboratory Agency in Dar salaam.

3. Results and Discussion

3.1. Efflorescence Formation on Cured Paste Specimens

Efflorescence products were observed from the specimens cured partially immersed under water. From this curing process of geopolymer paste specimens exposed partially to water media and partially dry, that efflorescence products were observed to grow with time. Figure 2 illustrate the development of efflorescence formation from 0 day to over 96 days.

Figure 2. *Photos are specimens quarterly immersed in water at 0 day (C1), 7 days (C2), 14 days (C3), 21 days (C4), 28 days (C5) and over 90 days (C6).*

The efflorescence powder was noticed after seven days of curing (figure 2) and continued to grow with time. This is generally because of unbalanced concentration of alkaline solution within the specimens which makes the alkaline elements to migrate from high concentrations to low concentration through connected pores, fissures and cracks causing chemical reactions with acidic elements within or/and at the surface of the specimens.

The efflorescence formation in geopolymer materials is basically the combination of base and acid. The common bases are sodium (Na), Potassium (K), Calcium (Ca) while the acidic minerals are sulfuric, chloric, and carbonic. Figure 3 illustrate schematic diagram for efflorescence formation process.

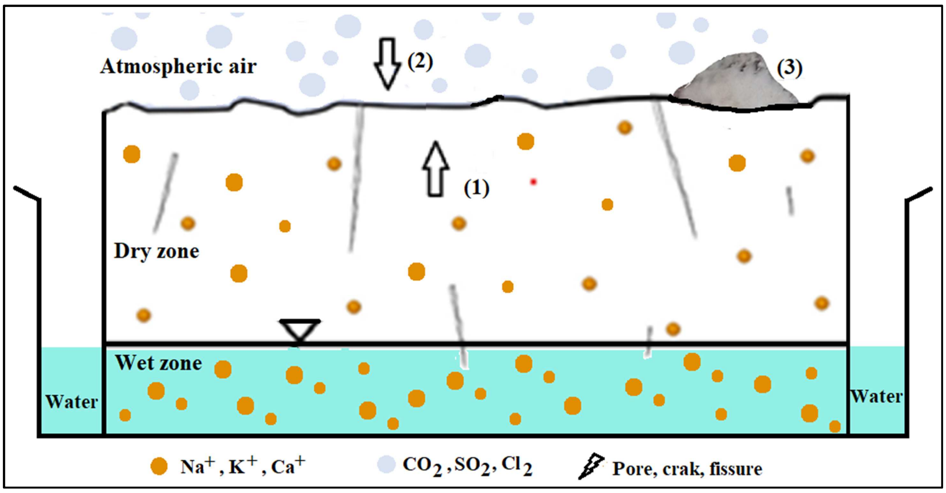

Figure 3. *Schematic diagram for efflorescence formation process [8].*

The efflorescence formation mechanism illustrated in figure 3 involves three process in which process (1) is leaching of alkaline cations from wet zone to dry zone in a bid of balancing concentration of alkali solution, process (2) is moist gases to form acid ions which are carbonic, sulfuric and chloric and stage (3) is a combination of cations and ions at the surface of the specimen to form salt of efflorescence. Under this process the acidic gases can penetrate through the open pores and cracks inside the specimens and the formation of efflorescence can take place inside the specimens. The efflorescence forming at the surface of the specimens at its later stage results into spalling of the surface of geopolymer concrete or mortar which reduces strength of the concrete and mortar. However, when the products of efflorescence forms within the pores and cracks of the specimens internal pressures are developed which may result into disintegration of the specimens.

3.2. Chemical Composition

From the results, the chemical standards for natural pozzolan materials intended for use in concrete were met as per ASTM C618 specifications such that SiO_2 + Al_2O_3+ Fe_2O_3 > 70.0 percent, SO_3 < 4.0 percent and loss on ignition (LOI) < 10 percent as indicated in table 1.

The results for alkali activated paste powder contains three major oxides SiO_2 (64.19%), Al_2O_3 (17.71 %) and CaO (18.10%) while that of efflorescence powder contains major oxide of SiO_2 (41.77%), Al_2O_3 (10.29%, CaO (11.85%) and Na_2O (39.09%). The chemical composition of materials is represented in Table 1. From the results, there are different in chemical composition between natural pozzolan and cured paste specimen. Chemical composition difference between the natural pozzolan and cured paste specimen is related to chemical reaction of alkaline solution with natural pozzolan constituents. There is a significant increase of Na_2O for efflorescence powder, this may be due to the migration of Na^+ ions from the interior of materials to the surface to form efflorescence.

Table 1. *Chemical Composition of materials.*

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	TiO_2	LOI	TOTAL
Natural pozzolan	57.42	18.4	8.78	1.01	0.43	0.03	1.64	3.24	0.07	0	8.92	99.94
Calcium hydroxide	7.62	2.16	0.8	79.7	0.6	0.1	0.16	0.4	0.05	0	8.4	99.99
Paste powders	45.74	12.62	4.61	12.90	0.36	0.04	3.43	2.23	0.04	0	18	99.97
Efflorescence powder	31.74	7.67	1.45	8.92	0.57	0.26	26.56	1.70	0.05	0.1	21.78	100.8

For this study, the efflorescence produced comprises of Ca^{2+} and Na^+ as base elements, SiO_2 which is acid and Al_2O_3 which is amphoteric oxide. The results of oxides are different from that of ceramic bricks and masonry mortar determined by another researcher [18]. The efflorescence (from ceramic brick) was characterized by high content of SO_3 (51.2%), alkaline oxides Na_2O (36.7%) and K_2O (12.4%) while that of masonry mortar was presented by a high content of CaO (29.9%) and the negligible quantity of SiO_2 (5.8%) [18]. The reasons for the different efflorescence composition may be due to different precursor materials as they are responsible for efflorescence formation.

The chemical equation of efflorescence produced from geopolymer paste specimens made of mixtures of natural pozzolan, calcium hydroxide, alkaline solution and carbon dioxide of the atmosphere is as indicated by equation 4.

$$Na_2SiO_3.H_2O + Ca(OH)_2 + Al_2O_3SiO_2.H_2O + CO_2 \rightarrow Na_2OAl_2O_3\,2SiO_2.CaCO_3.3H_2O + O_2 \quad (4)$$

Whereby $Na_2SiO_3.H_2O$ is a combination of sodium silicate solution and sodium hydroxide, $Ca(OH)_2$ is a portlandite material, $Al_2O_3SiO_2.H_2O$ is aluminum silicate hydrate from natural pozzolan and CO_2 from the atmosphere. The combination of the elements results into efflorescence sodium alumina silicate carbonate hydrate.

Equation 4 can be represented in general formula as $qNa_2O{\bullet}(nAl_2O_3{\bullet}xSiO_2){\bullet}yCaCO_3{\bullet}zH_2O$, where q, n, x, y and z are integers which may be either 1, 2, 3, 4, etc.

3.3. Mineralogical Composition

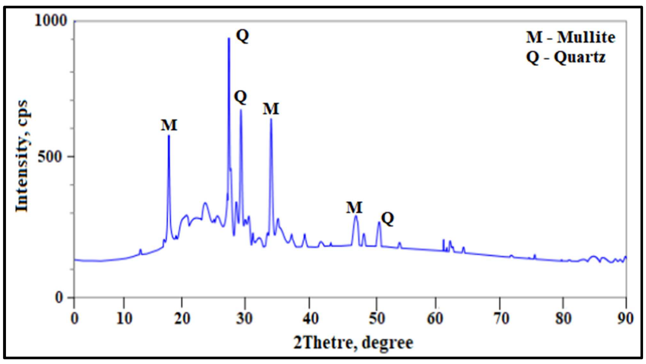

Figure 4. *XRD scan file for natural pozzolan.*

The mineralogical composition of efflorescence products was determined using XRD technique, the test performed at Government Chemist Laboratory Authority in Dar es Salaam, Tanzania. Figure 4 to figure 6 are XRD scan files for natural pozzolan, alkali activated paste specimen and efflorescence powder.

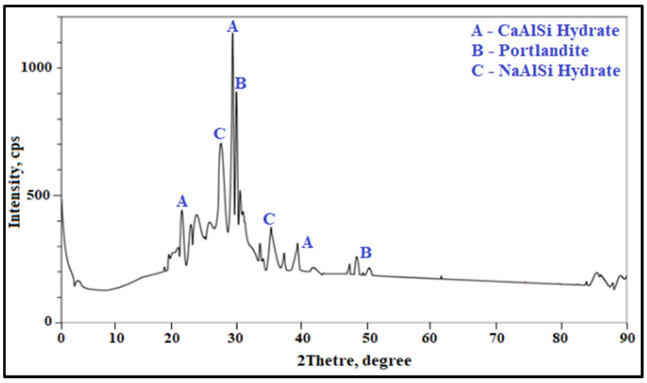

Figure 5. *XRD scan file for alkali activated pozzolan calcium hydroxide paste.*

According to X-ray phase analysis (Figure. 4), crystalline phase for natural pozzolan is represented mainly by Mullite and quartz. Mullite is in the form of aluminum silicate ($3Al_2O_3{\cdot}2SiO_2$) while quartz consists primarily of silica, or silicon dioxide (SiO_2).

For alkali activated paste specimens (figure 5), the main phase is calcium alumina silicate hydrate (Ca-Al-Si-H). Another phase present are portlandite $Ca(OH)_2$ and sodium alumina silicate hydrate (Na-Al-Si-H). The small quantity of alkaline mineral phase is because the geopolymer products formed are in connected chain which acts as amorphous phase when detected by XRD technique [23].

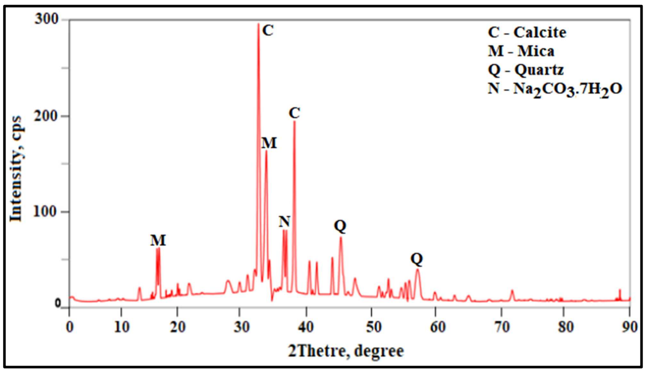

Figure. 6. *XRD scan file for efflorescence powder.*

The XRD patterns of products of efflorescence powder (figure 6) is mainly consists of calcite, mica, quartz and sodium carbonate hydrate ($Na_2CO_3.7H_2O$).

4. Conclusion and Recommendation

The understanding of the formation of efflorescence products in geopolymer is still a knowledge gap and is distinct from that which occurs in PC based materials.

The curing conditions contribute in the formation of efflorescence in geopolymer. For the specimens cured with partially dipped in water, the formation of efflorescence occurred within 7 days and grows with time. This is mainly due to unbalanced concentration of alkaline solution within and at the surface of materials due to leaching of alkaline cations (Na^+) to the surface through pores. The efflorescence formation in geopolymer materials is basically the combination of base and acid. The common bases are sodium (Na), Potassium (K), Calcium (Ca) while the acidic minerals are sulfuric, chloric, and carbonic.

The chemical composition of efflorescence powder indicated the presence of Ca^{2+} and Na^+ as base elements, SiO_2 which is acid and Al_2O_3 which is amphoteric oxide. In mineralogical study, the efflorescence products are composed mainly of calcite, mica, quartz and sodium carbonate hydrate.

Since alkaline cations leaching is the first process related to efflorescence formation, it is recommended to design the materials parameters to minimize the free alkaline cations which will control the efflorescence formation. Also, the curing condition should be considered as it affects the efflorescence formation.

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