Sulfuric Acid Attack on Ordinary Portland Cement and Geopolymer Material

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The resistance of ordinary Portland cement binder towards acid had been widely discussed by researchers. The deterioration effect of this binder may cost high repair expense and rehabilitation. Geopolymer material is a new binder technology, which has superior durability against acidic attack. The properties of both binder, exposed to acid environment will be discussed in terms of mechanical effect such as compressive strength and weight loss. Electron microscopic (SEM) and energy dispersive X-Ray (EDX) data will be also briefly summarized as well as, the corrosion mechanism of both binder.

Keywords: sulfuric acid attack, geopolymer, portland cement, mechanical properties, SEM-EDX

For the last decade, ordinary Portland cement (OPC) have been widely used as a binder for the construction all over the world. The hydration product and its chemical reaction mechanism are well elucidated by Taylor [1]. As the world was very competitive to the industrial development, there were some problems connected with these activities. One of the problems was the durability of the cementitious material, (OPC) to the chemical attack released or used by industrial environment.

The resistance of the OPC concrete in acidic environment had been studied intensively by a lot of authors during the past fifty years [2-6]. The deteriorating effect of acidic environment on cement-based structural materials has attained more attention and several methods have been tried to be applied on cement composite such as application of polymer concrete [7, 8], incorporating admixture into concretes [9], coated-OPC concrete [10, 11] and modification of concrete through inclusion of natural latex rubber [12]. Resistance of acid attack gained priority aspect in the chemical, petrochemical, cellulose and paper plants and thermal power stations ensuring the durability of technological equipment, building and protective constructions [13]. These aggressive environment required massive durability towards chemical attack.It is known that OPC concrete has not high acid resistance due to the chemical composition and hydration product.

World needs an improvement in the development of the binder technology. In 1940, the alkali activated material was researched by Purdon [14]. According to that research, the author used blast furnace slag activated by sodium hydroxide. After that, researcher from Ukraine, Glukhovsky [15] in his book ' *gruntosilikaty*' came out with the investigation of Roman and Egyption construction and concluded that the structure material composed of aluminosilicate calcium hydrate similar to OPC and crystalline phase of natural rock that retained the structure for a long time is analcite. Thus, according to those researches, *'soil cement'* terminology was acknowledged.
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After that, Davidovits [16] proposed the *'geopolymer'* mechanism. He made several investigations and made huge impact on alkali activated binder history and even claimed pyramids were not been made by natural stone but casted. For the chemical designation, he proposed 'poly-sialate' and 'sialate' for chemical abbreviation of aluminosilicate oxide. Under highly alkaline condition, the reaction mechanism involves the reaction between various alumino-silicate oxides yielding polymeric Si-O-Al-O which he called as sialate monomer. The monomer of sialate which he concluded began the polymer network to form geopolymer. The reaction mechanism and terminology of alkali activated material is fully summarized in [17-19].

Glukhovsky [15] and Davidovits [16] reported that alkali activated material has superior durability towards chemical attack than ordinary Portland cement (OPC). Therefore, this article summarized an overview of OPC and alkali-activated material towards acid attack regarding the following several issues.

Experimental part
Mechanical Effect

As studied by Thockchom et al [20], the alkali activated material under acid attack did not exhibit any noticeable colour change and showed no visible signs of deterioration after 18 weeks exposure in 10% sulfuric acid solution. The specimens remained structurally intact. Allahverdi and Skvara [21] stated that in case of sulfuric acid attack on ordinary Portland, the acid manifest itself by deposition of a white layer of gypsum crystals on the acid-exposed surface of the specimens. Contrarily there is no visual evidence to show the decomposition of gypsum on the surface of alkali activated binder.

Fernando and Said [22] exposed in figure 1 that the results are not only dependent on the type of acid, but also on the type of aggregate. In alkali activated mine waste, the decreased weight is due to the detachment of little particles from the leaching of unreacted particles of sodium and result to an increase in porosity allowing the acid ion

Fig. 1. Visual appearance of the specimens in sulfuric acid solution (a) OPC concrete with granitic aggregates; (b) mine waste paste (c) mine waste with granitic aggregates (d) mine waste with limestone aggregate (e) OPC concrete with limestone aggregate [22]

to enter inside the specimen. For OPC specimens, the acid reacts with calcium hydroxide present at the surface of samples and exposed the aggregate. Visual examination by Jimenez et al [23] showed the alkali activated fly ash (AAFA) appeared to be healthy after 90 days, while the OPC specimens were severely deteriorated after 56 days.

Other author [24] studied immersion of alkali activated materials and OPC based binder in acetic acid and sulfuric acid reported that OPC binder has the most significant weight change in both acidic solution; acetic and sulfuric which is 10% and >40% respectively. The OPC samples were completely deteriorated in the first month of the test. In other research [25], which studied the resistance of alkali activated slag (AAS) concrete, showed that the AAS specimens had no change in appearance and had a small increase in mass while OPC, on the contrary, had soft white depositions on the surface, softening of concrete and had the significant increase in the mass of samples. This investigation showed AAS concrete performed better than OPC concrete when exposed to acid solution.

Dan and Janotka [26] which studied the effect of blast-furnace slag portland cement (BFSPC), portland cement (OPC), and sulphoaluminate-belite (SAB) cement in acidic, chloride and sulphate solution concluded that these three types of cement have similarly markedly decreased resistance to acid attack. Several symptoms of acid attack are crumbling of the surface, volume density decrease, and shrinkage of the tested mortars connected with strength loss. Sata et al [27], recently study showed that the geopolymer bottom ash mortars activated with alkaline activator has more stable performance than OPC mortars in 3% sulfuric acid solution with weight loss less than 3.6% compared to OPC which is 95.7% at 120 days.

Davidovits et. al [28], reported weight losses after 28 days. The alkali activated binders remain intact whereas the attack of acid in OPC has destroyed more than 50% (weight loses and volume). Pacheco-Thorgal et al. [29], confirmed the durability of alkali activated material. The authors used mine waste binders activated by alkali and concluded that those binders show good acid resistance than OPC concrete. Gourley and Johnson [30] mentioned that an alkali-activated binders required 1400 immersions cycle to lose the same mass as 80 immersions of cycles in a sulphuric acid solutions. On the other side, some authors [27] studied the lignite bottom ash and concluded that bottom ash mortar showed better performance than OPC mortar which weight loss was less than 3.6% at 120 days. Other researcher [31], mentioned an average mass loss of just 2.6% after being immersed in the sulphuric, hydrochloric and nitric acid during 28 days, whereas OPC concretes possessed twice that value.

Characteristics of the materials

The mineralogical and microstructural characteristics of the materials are explained by SEM and EDX. Jimenez et al [23] in figure 2 showed the microanalysis of alkali activated mortar immersed in hydrochloric acid for 90 days and found that the gel and zeolites were dealuminated according to to the decreasing amount of aluminate in the matrix.

Other researcher [25] concluded from SEM micrographs the deterioration of alkali activated slag binder and OPC binder is due to the chemical and phase composition of the binder; low content of calcium in alkali activated material compared to OPC is the main factor attributed to less vulnerable of acid attack than OPC. While OPC is rich in calcium (Ca) and four major phases of OPC which are alite (Ca_3SiO_5), belite (Ca_2SiO_4), aluminate ($Ca_3Al_2O_6$) and ferrite (Ca_2AlFeO_5) are considerably composed of calcium, [1] which eeact with acetic acid producing a gel-like precipitate, which is calcium acetate is soluble and leaves the OPC paste. Other authors [31], claimed that the exposure of mixtures of activated fly ash and slag with high amount of calcium in sulfuric acid will generate gypsum and EDX confirmed the increased amount of sulfur due to the reaction with sulfuric acid. Sata et al [27], confirmed that low calcium hydration products have more durability towards acid attack according to their study of SEM and EDX on OPC mortar and alkali activated mortar. According to Pavlik [33], elemental analysis of cement phase divided to three phase, which is corroded layer-white part, corroded layer brown zone, and uncorroded cement paste. He later concluded that, cement hydration products were completely decalcified and decomposed in these zones.

While the other researcher [2], explained that acid reacts on the surface of OPC mortar reducing the matrix to a more porous materials and indicated that the deterioration starts at the surface and progress inward. For elemental analysis using EDX, the author highlighted the increases concentration of sulfur content of acid-attacked OPC mortar specimens due to the reaction of sulfuric acid and cement paste with the immersion time. This phenomena is conformed by Chang et. al [34].

Mechanism of Reaction
a. Acid attack on OPC

Hydrochloric, nitric, sulfuric, chloric, chromic acids have seriously damaged the concrete and all the hydration products of cement are decomposed by acid attack. As researched by Zivica and Bajza [35], acid attack on OPC may form several calcium salts that have several solubilities in water.

OPC is highly alkaline with pH values normally above 12.5 and easily attacked by acid solutions [36]. When OPC
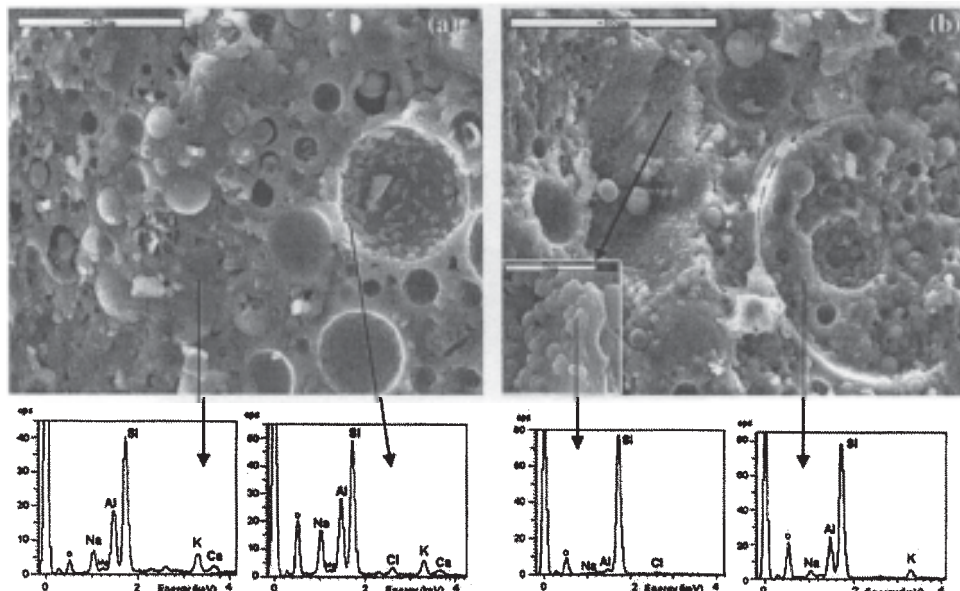
Fig. 2. Micrographs and EDX analysis of alkali activated fly ash (a) not exposed to HCL and (b) immersed in HCL [22]
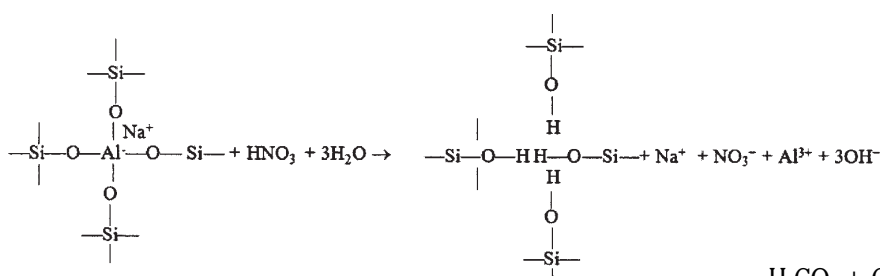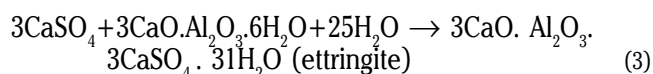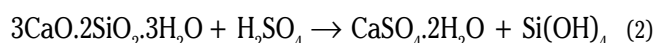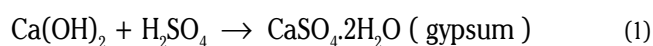

Fig. 3. First step of attacked alkali activated material [39]

is attacked by acid, the pH of the solution decreases, the equilibrium is disturbed and the hydrated OPC compounds are changed due to hydrolytic decomposition. At pH values lower than 12.5 portlandite is the first constituent which starts to dissolve. If pH was lower than stability limits of cement hydration compounds, then the corresponding hydrate loses calcium and decomposes to amorphous hydrogel [36]. The final products of acid attack are the corresponding calcium salt of the acid as well as hydrogels of silicium, aluminium, and ferric oxides [33].

The following reactions occur:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O \text{ (gypsum)} \qquad (1)$$

$$3CaO.2SiO_2.3H_2O + H_2SO_4 \rightarrow CaSO_4.2H_2O + Si(OH)_4 \quad (2)$$

$$3CaSO_4 + 3CaO.Al_2O_3.6H_2O + 25H_2O \rightarrow 3CaO. Al_2O_3. \\ 3CaSO_4 . 31H_2O \text{ (ettringite)} \qquad (3)$$

The chemical reaction involves the formation of gypsum and ettringite (eq. (1-3)) which may contribute to the process of expansive deterioration mechanisms [38]. Attiogbe and Rizkalla [2], showed that formation of calcium sulfate (gypsums) leads to softening (decrease in density) and increase in volume of the concrete resulted from the acidity of sulfuric acid-cement paste which is higher than acid solution. Since the acid attack is a surface phenomenon, the expansion and weight loss of specimens is the major indicator of deterioration of ordinary Portland cement (OPC). As stated earlier, the principle of acidic attack is totally based on alkalinity of cement itself. Acidic-alkaline reaction in the cement network is the main reason of the fundamental of acid attack. Calcium hydroxide $(Ca(OH)_2)$ is the first compound being attacked by acid and this reaction is the main reason for the hydrolytic decomposition in OPC.

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \qquad (4)$$
$$CaCO_3 + H_2CO_3 \leftrightarrow Ca(HCO_3)_2 \qquad (5)$$
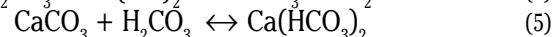
In equation (4), (5), Grube and Rechenberg [37] make a good explanation regarding this issue concluding that the transformation of calcium carbonate into soluble bicarbonate which is depleted by leaching into acidic solution will increase the porosity of OPC. Aggregate like river sand which is inert is resistant to acid, but unfortunately the presence of limestone aggregate will induced the attack. Calcium salt from different type of acidic solution will form in the solution and increase the frequency of acid attack. Finally all of the hydrated product; tobermorite, xonotlite, C_3AH_6, C_4AH_{13}, ettringite, gehlenite hydrate and hydrogarnets will be decomposed and silica, alumina and ferric hydrogels are the final products of this rection mechanism [38].

b. Acid attack on alkali activated cement
The mechanism of alkali activation of alumino silicate material is a complex reaction being studied now progressively by alkali activated material researchers. Publication journal of this new technology of cement states that this alkali activated cement has good durability against chemical attack compared to Portland cement. Bakharev [24] reported that the stability of geopolymer materials in acidic environment is depend on the crystalline phase formation within aluminosilicate network which means more crystalline phase conducted to the higher stability in aggressive environment.

The morphology of the specimen is the second cause of the resistancy of binder to the acidic solution and it was concluded that the median pore size has significant effect on its durability rather than total porosity [24]. Low content of Ca in alkali activated material is the main factor attributed to the superior durability than OPC binder [25]. Mechanism of acid corrosion reaction can be concluded to occur via the figure 3 [39].

Sodium and calcium ions are depleted and exchanged by H^+ and H_3O^+ ions and an electrophilic attack by acidic proton on polymeric Si-O-Al network resulting the ejection of tetrahedral aluminium from the aluminosilicate network. Second step involved re-occupied of silicon atoms resulting in the formation of an imperfect highly siliceous framework. As seen in figure 4, the leached aluminium converted to octahedrally coordinated aluminium mostly accumulates in the intra-framework space [40]. It can be shown that both ordinary Portland cement (OPC) binder
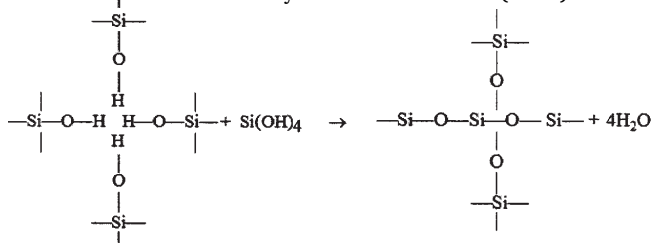

Fig. 4. Second attack of acid on alkali activated material [40]

and alkali activated material binder is vulnerable to acid attack. Those mechanism of attack conformed the reaction in the matrix of OPC and alkali activated material.

Conclusions

Reaction mechanism of acid attack in cement based materials can be concluded at follows:

- for OPC type binder, the attacked calcium hydroxide will make the matrix network inside this binder degraded and followed by the deterioration of mechanical properties of OPC. The other hydration product will decompose, leading to the formation of a gel-like layer consisting of hydrogels of silica, alumina, and ferric oxide;

- sodium and calcium ions are removed from aluminosilicate network, being replaced by H^+ or H_3O^+ ions resulting in the ejection of tetrahedral aluminium. The framework are mostly re-occupied by silicon atoms which lead to the formation of an imperfect highly siliceous framework. The ejected aluminium converted to octahedral coordinated aluminium and assembled mostly in the intra-framework space.

The performance of alkali activated material and OPC binder in terms of degradation of the network binder, visual appearance and mechanical strength as well as of the binder with acid solution totally depend both on the rate of the reaction of hydration product.

From this review, both of ordinary Portland cement and alkali activated material are vulnerable to acid attack. However, alkali activated material has shown higher durability against acid attack compared to OPC.

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