Microstructural Analysis of Geopolymer and Ordinary Portland Cement Mortar Exposed to Sulfuric Acid

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The vulnerability of ordinary Portland cement (OPC) concrete to acidic attack is a worrying subject regarding the future durability of this binder. On the other side of binder's technology, the new technology of cement called 'geopolymer' had been studied widely in all over the world. Indeed, the major advantage of geopolymer compared to Portland cement is chemical resistance. This paper presents a study about the microstructural properties of geopolymer and OPC mortar. Visual inspection of both mortars had been performed. Stereo microscope device and Secondary Electron Microscope (SEM) were used to investigate the microstructural changes of the specimens. It was found that geopolymer mortars were less susceptible to the attack by sulfuric acid solution than the OPC cement mortars.

Keywords: geopolymer, sulfuric acid attack, microstructural, SEM.

Alkali activated cement was found in late 1940s. But before that, the history of this type of cement had been used from at least the time of Nebuchadnezzar [1]. This novel cement is a mineral polymer which synthesized using geosynthesis technique and is very similar to the analogue of zeolites, which is later described as a 'geopolymer' by Davidovits [2, 3]. Portland cement, which had been used now over the world is such an example for 'great' binder in our history. Unfortunately, in some cases such as the durability of ordinary Portland cement in an extreme environment, the performance of OPC is in doubt. Deterioration of OPC, physically and chemically as a result of acidic attack have been reported by several authors [4-9]. But, on the other side of new cement technology which is geopolymer cement, the result is totally different. Geopolymer possessed superior durability towards acidic attack [10-14]. This research investigated the analysis of microstructural of geopolymer and OPC mortar which have been exposed to sulfuric acid for 120 days. Sulfuric acid attack is the most common acidic corrosion in concrete all over the world and occurs in different forms such as biogenic sulfuric acid corrosion, acidic groundwater and acid rain. Stereo Microscope and Scanning Electron Microscope (SEM) images were investigated and analyzed during this research.

Experimental part

Materials

The fly ash used in this study was obtained from Manjung power station, Lumut, Perak, Malaysia and classified as F Class according to ASTM C 618 [15]. The ordinary Portland cement (OPC) used was of Type I. The chemical composition of both material was described in table 1. The alkaline activator used for geopolymer was sodium silicate (Na_2O = 9.4%, SiO_2 = 30.1% and H_2O = 60.5%) and sodium hydroxide with 97% purity. The test for sulfuric acid resistances of mortars were made by modified test method B in accordance with ASTM C 267 [16]. Ordinary Portland cement (OPC) Type I was used during this experiment. A local river sand was mixed together in this research.

Specimens preparation

As seen in table 2, the ratio of a binder material to river sand was kept 0.36 for both OPC and geopolymer mixing. For OPC, the ratio of binder to water was 2.12. For geopolymer system, sodium hydroxide was dissolved to 12M. The ratio of fly ash to alkaline activator was kept 1.34 and sodium silicate to sodium hydroxide was 2.5.

Table 1
CHEMICAL COMPOSITION OF FLY ASH

Component	SiO_2	Al_2O_3	CaO	Fe_2O_3	P_2O_5	SO_3	K_2O	TiO_2	LOI
Fly ash	26.4	9.25	21.6	30.13	0.67	1.30	2.58	3.07	4.48
OPC Type I	21.5	4.5	62.7	3.1	-	3.5	0.7	0.1	1.3

Table 2
MIX PROPORTIONS OF MORTAR

Type of materials	OPC (g)	Fly Ash (g)	Sodium Silicate (g)	Sodium Hydroxide (g)	Water (g)	Sand (g)	Flow (%)
OPC	100	0	0	0	47	275	110
Geopolymer	0	100	53.5	21.4	0	275	60

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Material	Weight change (%)						
	0 Day	7 Days	14 Days	28 Days	56 Days	84 Days	120 Days
OPC mortar	0.0	-0.22	-1.27	-1.77	-10.88	-14.02	-18.5
Geopolymer mortar	0.0	-0.41	-1.65	-2.28	-3.14	-3.20	-3.66

Table 3
WEIGHT CHANGES OF THE SAMPLES EXPOSED TO 3% SULFURIC ACIDS

Material	Strength Degradation (%)						
	0 days	7 days	14 days	28 days	56 days	84 days	120 days
OPC mortar	0.0	-1.72	-19.17	-25.99	-65	-66.67	-69.26
Geopolymer mortar	0.0	-4.72	-10.40	-16.01	-16.42	-22.11	-24.13

Table 4
STRENGTH DEGRADATION OF BOTH MATERIALS: OPC AND GEOPOLYMER BINDER

The OPC samples were mixed and the flow followed exactly the ASTM C1437 [17]. Both OPC and geopolymer mortars were molded in 50 x 50 x 50 mm cube molds. OPC mortars were demolded after one day and kept in the water until 7 days and immersed in the 3% sulfuric acid for 120 days. Geopolymer mortar were molded and wrapped in plastic sheet and cured in an oven at 70°C for 24 h [18]. The samples were demolded the next day and kept in the plastic for 7 days and being immersed in 3% sulfuric acid for 120 days.

Results and discussions

Mechanical analysis

Weight change is the most important criteria to investigate the effect of specimens after being exposed to sulfuric acid. Geopolymer samples exhibited very small changes in weight after 120 days of immersion time. Visual inspection of the specimens showed harsh deterioration for OPC samples due to the high amount of calcium (Ca) in these samples. For OPC, white deposition on the surface was detected. After 7 days of immersion, the white deposition progress inward and within 56 days, the OPC samples were severely deteriorated. For geopolymer specimens, there were slightly yellowish lines at the bottom of the samples and will be determined by SEM-EDX.

Table 3 gives the weight loss of both OPC and geopolymer mortars. The most significant changes for OPC mortars detected for 56 days, which had weight loss of 10.88% while for 28 days, it was just 1.77%. For geopolymer mortar, the samples exhibited very small changes in weight in 56 days which is 3.14% from the initial weight. At 120 days, OPC mortar performed very weak resistance in sulfuric acid and had weight loss of 18.5 % compared to geopolymer-based binder which was 3.66%.

Compressive strength

Table 4 shows the gradual degradation of strength for both OPC and geopolymer mortars. OPC mortar possessed severe decrease of strength compared to geopolymer mortar. At 7 days, OPC performed well with 1.72% strength loss whereas geopolymer exhibited 4.72%, slightly higher than OPC. But for 14 days and 28 days, OPC samples started to deteriorate in sulfuric acid solution and degradation of strength were 19.17 and 25.99% respectively.

The most notable decreasing of strength was at 56 days. OPC had about 65% strength reduction and about 16.42% strength decline for geopolymer based system. After 120 days of immersion time the strength loss of OPC mortar was 69.26 % whereas for geopolymer mortar, the strength loss is about 24.13 %. The performance of geopolymer material was good in sulfuric acid attack in strength aspect compared to OPC based binder.

Sulfuric acid attack is the surface phenomenon, that cause much trouble to the ordinary Portland cement (OPC). The durability of OPC and geopolymer in acidic medium is connected to the chemical composition and the hydration products of the samples. But Bakharev [12], proposed that chemistry is not the only factor that affects the properties and morphology is the second most important criterion for the durability performance of the materials. The good performance of geopolymer material, is undoubtedly related to the stability of cross-linked aluminosilicate structure.

Optical Microscopy

Stereo microscope is a device designed for low magnification observation and produce three-dimensional visualization of the sample being examined. Several images were analyzed to compare the mechanism of acidic attack in both binders; OPC and geopolymer. There were no deterioration effect on the surface for both mortars; OPC and geopolymer in figure 1. The specimen structure, and the matrix between aggregate and binder was structurally intact.

As explained by many researchers of OPC scientists, the reaction of OPC with sulfuric acid can be concluded as (eq. 1-3):

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

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

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

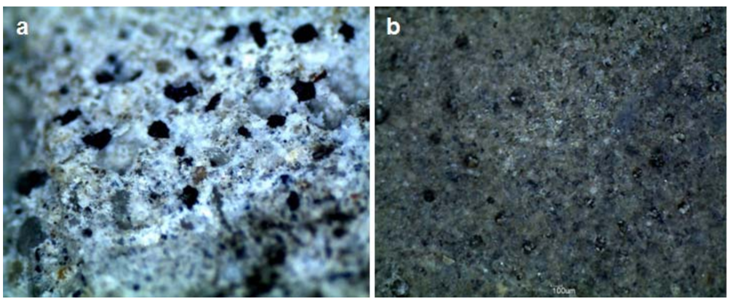

Fig. 1. Stereo microscope images 100X: a - OPC mortar, b - geopolymer mortar before immersed in sulfuric acid

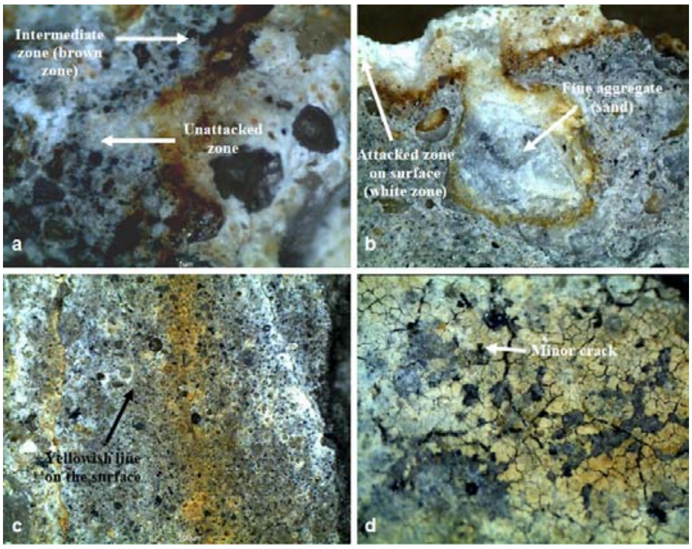

Fig. 2. Stereo microscope images 100X: a and b - OPC mortar, c and d - geopolymer mortar after 120 days of immersion time

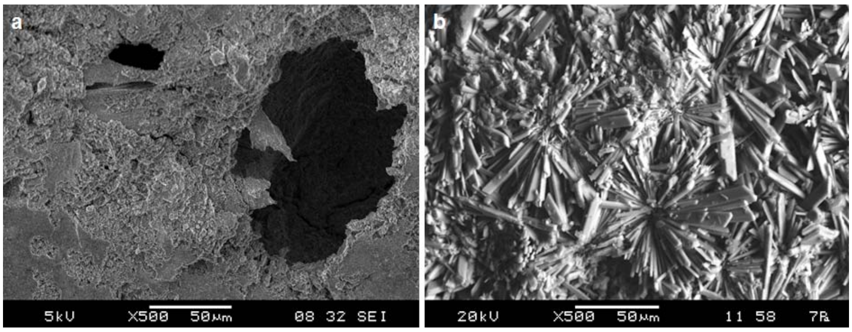

Fig. 3. Representatives SEM pictures of OPC mortar after immersion in 3% sulfuric acid solution for 120 days

The formation of gypsum and ettringite is the main reason of the deterioration of OPC mortar. As we can see in figure 2a, OPC attacked with sulfuric acid resulted in the formation of three layers which are attacked zone (white), unattacked zone and intermediate zone (brown). The attacked zone is soft, porous and has visible cracks. The intermediate zone (brown) according to Pavlik [19], consist of ferric oxide and illustrated that the cement hydration product is completely decomposed in these zones. In figure 2b, as we can see the attacked zone showed severe damage and bounded the aggregate which is the river sand within the matrix of OPC. The deterioration will progress inward from the surface and continuosly damaged the matrix and aggregate. As for geoplymer mortar there were some line produced after 120 days immersed in acid. In figure 2c, the tiny yellowish line had been detected using microscope. The yellowish line at the surface of geopolymer is most probably the result of the reaction of ferum (II) oxide with sulfuric acid and produced ferum (II) sulfate (eq. 4).

$$Fe_2O_3 + 3\,H_2SO_4 \rightarrow Fe_2(SO4)_3 + 3\,H_2O \qquad (4)$$

In figure 2d there were some minor cracks possessed by the attacked mortar on the surface of the specimen. But for geopolymer system, the reaction of sulfuric acid was only on the surface of the mortar and does not progress inward like OPC confirmed by the microscopic images of the samples.

SEM

Ordinary Portland cement (OPC) mortar immersed in 3% sulfuric acid for 120 days had been examined using scanning electron microscopy (SEM). Several pictures were taken. In figure 3a, the cement mortars were severely damaged and the deteriorated surface was clearly visible. The calcium hydration products were vulnerable to acid attack resulting in deterioration of the mortar. Figure 3b revealed possibile presence of elongated crystalline matrix structures of ettringite ($3CaO.Al_2O_3 . 3CaSO_4 . 31H_2O$) due to the reaction in (eq. (1-3)) which may contribute to the process of expansive deterioration mechanisms [6].

In figure 4, the specimens became porous after exposure to the acid solution. As said earlier, the attack of acid on geopolymer were specifically on the surface and never progress inward like OPC. Therefore, there were no signs of severe damages or holes detected in the micrographs photo. But, some fissures and amorphous have been hardly found. The geopolymer mortars showed better performance than OPC mortar concerning the chemical composition of high calcium content (table 1).

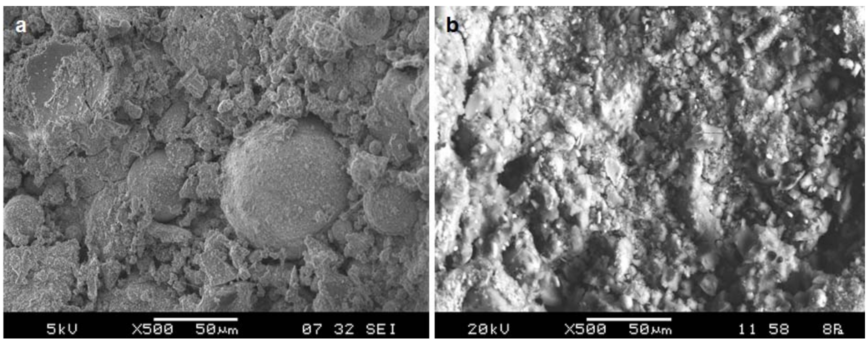

Fig. 4. Representatives SEM pictures of geopolymer mortar after immersion in 3% sulfuric acid solution for 120 days

Conclusions

Both samples, either OPC or geopolymer mortars were vulnerable to acidic attack. The weight changes and strength degradation conform the theory. But, geopolymer mortar exhibited less susceptiblity to acidic attack regarding low percentage of weight changes and strength decline which were 3.66 and 24.13% respectively. OPC mortar showed very weak performance in acidic medium; in both weight changes and strength degradation which were 18.5 and 69.26% respectively.

The stability of both materials; OPC and geopolymer had been detailed in the microstructural images. Exposed surface revealed the corroded section in OPC mortar. Severe deterioration of OPC mortar showed in stereo microscopic and SEM images indicated the vulnerability of OPC mortar in acidic solution due to the high calcium percentage of calcium in OPC. Meanwhile in geopolymer system, the micrographs study conformed the alumino-silicate network in geopolymer was less susceptible in acidic solution medium due to the absence of surface deteriorate symptoms in geopolymer matrix.

References

1.ROY, D.M., Cement and Concrete Research, **29**, 1999, p. 249.
2.DAVIDOVITS, J., Proc. 2nd Intern. Conf. “Geopolymere ’99", St. Quentin, 1999, p. 9-39.
3.MUSTAFA AL BAKRI, A.M., KAMARUDIN, H., NIZAR, I.K., SANDU, A.V., BINHUSSAIN, M., ZARINA, Y., RAFIZA, A.R., Rev. Chim. (Bucharest), **64**, 4, 2013, p. 382.
4.RAJU, P.S.N., Dayaratnam, P., Building and Environment, **19**, 2, 1984, p. 75.
5.ATTIOGBE, E.K., RIZKALLA, S.H., ACI Materials Journal, Technical Paper, Nov-Dec 1988.
6.ZIVICA, V., BAJZA, A., Construction and Building Materials, **15**, 2001, p. 331.
7.ZIVICA V., BAJZA A., Construction and Building Materials, **16**, 2002, p. 215.
8.PURI, A., VOICU, G., BADANOIU, A., Rev Chim (Bucharest), **61**, no. 8, 2010, p. 740
9.GEORGESCU, M., SACA, N., MINCU, G., Rev Chim (Bucharest), **59**, no. 8, 2008, p. 842
10.DAVIDOVITS, J., COMRIE, D.C., LUCKEY, G., PATERSON, J.H., RITCEY, D.J., ACI Concrete International, **12**, 1990, p. 30.
11.FERNANDEZ-JIMENEZ, A., GARCIA LODEIRO, I., PALOMO A., J. Material Science, **42**, 2007, p. 3055.
12.BAKHAREV, T., Cement and Concrete Research, 35, 2005, p. 658.
13.BAKHAREV, T., SANJAYAN, J.G., CHENG, Y.-B., Cement and Concrete Research, **33**, 2003, p. 1607.
14.SATA, V., SATHONSAOWAPHAK, A., CHINDAPRASIRT, P., Cement & Concrete Composites, **34**, 2012, p. 700.
15.*** ASTM C 618. Standard specification for coal fly ash and raw or calcined natural pozzolan for use mineral admixture in portland cement concrete, 2003.
16. *** ASTM C 267. Standard testmethods for chemical resistance of mortars, grouts, and monolithic surfacings and polymer concretes, 2003.
17. *** ASTM C 1437. Standard specification for flow of hydraulic cement mortar, 2003.
18.MOHD MUSTAFA ALBAKRI, A.M., KAMARUDIN, H., BINHUSSAIN, M., KHAIRUL NIZAR, I., RAFIZA, A.R., ZARINA, Y., Advanced Materials Research, **328-330**, 2011, p. 1475.
19.PAVLIK, V., Cement and Concrete Research, **24**, 1994, p. 1495

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