EVALUATING THE POTENTIAL APPLICATION OF FLY ASH/ BLAST FURNACE SLAG GEOPOLYMER MATERIAL FOR INHIBITING ACID CORROSION, A COMPARATIVE STUDY

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Abstract. The response of hardened paste of a geopolymer cement to acid attack has been investigated and compared to that of ordinary Protland cement. The geopolymer cement was produced by activating a mixture of fly ash and blast furnace slag using a proportioned solution of NaOH and Na_2SiO_3. At relatively lower pH values ($pH \leq 2$), sulfuric acid is less corrosive than nitric acid because of the inhibition caused by gypsum crystals depositing on the acid-exposed surface or inside the corroding layer. The corrosion process very soon becomes diffusion controlled owing to the formation of relatively thick corroded layers. At relatively higher pH values ($pH \geq 3$) and for relatively short exposure time periods ($\leq$ 90 days), mechanism of attack by sulfuric acid approaches that of nitric acid attack. The total rate of deterioration is more effectively controlled by the porosity and the nature of corroding phases than the protective effect of a relatively very thin corroded layer.

Keywords. *Geopolymer cement, Acid resistance, Nitric acid, Sulfuric acid*

1 Introduction

The deteriorating effect of acid media (e.g. acid rains, acid ground-waters, etc) on cement-based construction materials has attained more importance in the recent decades. Hardened paste of Portland cement that is a highly alkaline material with pH above 12.5 is severely attacked by acid media. Authors discussed and reviewed the phenomenon of acid corrosion of hydrated cement-based materials and the literature published during the last two decades thoroughly [1], [2]. At the same time, development of geopolymer cements with improved properties necessitates more detailed investigations.

An interesting property of geopolymer cements is their relatively high resistance to acid media. Blaakmeer [3] investigated the acid resistance of an alkali-activated binder called, Diabind. It is an alkali-activated fly ash/Blast-furnace slag binder developed by the ENCI Central Laboratory (Netherlands BV) to counteract the problem of biogenic sulfuric acid in sewer systems. He submerged a number of concrete specimens made with Diabind, rapid-hardening Portland cement, and low C_3A rapid-hardening Portland cement in a stirred sulfuric acid solution at pH 1 (0.44 N). Expressing the extent of acid attack in terms of millimeters per year, he obtained values of 5.6, 20.7, and 19.1 mm respectively for Diabind, rapid-hardening Portland cement, and low C_3A rapid-hardening Portland cement.

Rostami and Silverstrim [4], [5] developed an alkali-activated material called, Chemically Activated Fly Ash (CAFA), by activating Class F fly ashes. They tested CAFA concrete [4], [5] for durability properties. The resistance of CAFA concrete to chemical attack by acids such as sulfuric, nitric, hydrochloric, and organic acids was claimed to be far better than that of Portland cement concrete [4]. According to Silverstrim *et al* [5], CAFA specimen exposed to 70% nitric acid for 3 months retained its dense microstructure.

Changgao [6] studied the resistance of high performance fly ash/Blast-furnace slag-alkali (FKJ) mortar and concrete to chemical attack and durability in H_2SO_4, HCl, HNO_3, and a number of different aggressive solutions. Mortar specimens of FKJ and ordinary Portland cement (OPC) were immersed into 6 N HCl solution heated up to 90°C. After 2 hours, the strength of FKJ mortar specimens remained the same, i.e. 50.6 MPa, without any decrease whereas Blast-furnace slag cement-mortar specimens with original strength of 30 MPa were so severely corroded and pulverized that the remaining strength was less than 3 MPa. In another attempt, Changgao [6] put FKJ and OPC concrete specimens into H_2SO_4 + HCl + HNO_3 mixed acid solution at pH 2. After 1 year of immersion, the strength of OPC specimens decreased by 43% while the strength of FKJ specimens did not decrease. Changgao concluded that the acid resistance of the FKJ concrete greatly exceeds that of the OPC concrete about 20-30 times.

In an experimental work, Xincheng *et al* [7] studied the resistance of alkali-activated slag concrete to acid solutions. According to their results alkali-activated slag concrete has excellent resistance to thin sulfuric acid attack. After 1 year of immersion in H_2SO_4 at pH 2, strength of alkali-activated slag concrete increased by 66% whereas OPC concrete showed a considerable decrease in strength. The authors claimed that destruction of alkali-activated slag concrete in thin sulfuric acid solution is slight and facial and hence decrease of strength generating from acid attack is lower than the increase of strength resulting from hydration of the binder.

The purpose of this work is to compare the acid resistance of the hardened paste of a geopolymer cement to that of OPC. The geopolymer cement (GC) used in this work was produced according to the work of Škvára and Bohuněk [8]. They reported that alkali activation brought about by the effect of NaOH and Na_2SiO_3 solutions is capable of increasing significantly the reactivity of substances with latent hydraulic properties such as fly ash or mixtures of fly ash and blast furnace slag.

The authors claimed that optimum properties could be achieved with ash-slag mixtures over the composition range of 50-70 wt.% fly ash and 50-30 wt.% slag, activated with alkali activator having a silica modulus ($M_s=SiO_2/Na_2O$) of 0.6, and containing 7 wt.% Na_2O. The geopolymer material and the mechanism of its acid corrosion has been characterized and investigated in previous works [21] - [23].

2 Experimental

2.1 Raw materials

Materials used for this study include: low calcium fly ash and granulated blast furnace slag. These materials were firstly ground in a vibration mill for time periods of 20 and 45 minutes, respectively, to attain higher specific surface areas. The blast furnace slag was ground in the presence of 0.05% (by weight of slag) of a liquid grinding aid (ALSON TEA, Chemotex Company, Czech Rep.). The attained specific surface areas were 650 and 420 m2/kg, respectively, for fly ash and blast furnace slag. Ordinary Portland cement of the type CEM-I 42.5R with a Blain specific surface area of 297 m2/kg was used as reference. The chemical compositions of the materials are shown in table 1.

Table 1. Chemical composition (wt%) of the materials.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	L.O.I
Ash	52.40	26.70	8.60	3.10	1.16	0.87	1.64	0.37	2.08	1.71
Slag	43.25	7.51	0.50	41.47	4.36	0.82	0.63			
OPC	20.66	4.05	2.59	64.03	2.19	2.67	0.97		-	0.50

2.2 Specimens preparation

The ground fly ash and ground granulated blast furnace slag were mixed in equal proportions. The SiO_2/Na_2O ratio (silica modulus, M_s) of the alkali-activator was adjusted to 0.6 by adding enough NaOH to water glass which itself had a modulus of 1.68. The concentration of the alkali-activator was so adjusted that the total Na_2O content of the binder amounted to 7% of the binder weight. Enough water was added to the alkali-activator for preparing a paste with a water/binder ratio of 0.30 that had an acceptable workability. The prepared alkali-activator was then added to the dry mixture, and after mixing for a few minutes, the paste was formed into specimens of 20×20×20 mm in size. The curing procedure used was 24 hrs in moulds at 95% relative humidity at 20°C, then demoulding and heating up to 60°C during 1 hour (20°C/0.5 hr) followed by heating to 80°C during 2 hours (10°C/ hr) in a steam saturated atmosphere. The specimens were then held at the final temperature for an additional 4 hours. After that the specimens were stored dry at 20°C at 40 – 50% relative humidity.

The paste of OPC was prepared simply by adding an amount of water depending on the desired W/C ratio to dry binder, i.e. 0.3. After enough mixing, the paste was formed into specimens of 20×20×20 mm in size. The curing procedure used was 24 hrs in moulds in an atmosphere at 95% relative humidity at 20°C and then demoulding and storing in water at 20°C.

2.3 Test procedure

At the age of 28 days, the exact size of each specimen from the face to be exposed to the acid solution to the opposite one was first measured by a caliper with an accuracy of 0.02 mm. The specimens were then prepared for establishing a unidirectional corrosion process by covering all the faces, except the one to be exposed, with a thin layer of grease. From each of the nitric and sulfuric acids three different solutions at pH values of 1±0.01, 2±0.03, and 3±0.05 were prepared by adding concentrated acid to tap water in six plastic containers. The ratio of solution volume (cm^3) to the total corrosion surface (cm^2) was kept constant at 50 in all the six plastic containers. From each of the cements then, a number of specimens were immersed in each of the six acid solutions with the acid-exposed surfaces facing upward. The pH levels of the solutions were monitored daily with a portable pH-meter of the type WTW pH 597 and concentrated acids were added to maintain the pH values to the stated tolerances. During pH monitoring, an electrical mixer of the type IKA RW16 was used for mixing each of the solutions thoroughly. All the solutions were renewed monthly and the temperature of the solutions was kept constant at 20°C.

During the course of corrosion and at different time intervals, specimens were removed from the acid solutions and after completely removing the corrosion residuals by brushing with a steel-wire brush, the corrosion depths of different binders were determined by accurately measuring the uncorroded parts of the specimens using a caliper and subtracting the values from their accurately measured initial sizes. For each measurement of corrosion depth two specimens were used and the average of the two measurements was reported. The precision and accuracy of the measurements was about 0.02 mm.

3 Results and discussion

3.1 Corrosion mechanism

OPC and its usual derivatives that are highly alkaline with pH values normally above 12.5 [9]-[11] are easily attacked by acid solutions. As the pH of the solution decreases, the equilibrium in the cement matrix is being disturbed and the hydrated cement compounds are essentially altered by hydrolytic decomposition that leads to severe degradation of the technical properties of the material. The final reaction products of acid attack are the corresponding calcium salt of the acid as well as hydro-gels of silicium, aluminum, and ferric oxides [9] - [20].

Mechanism of acid corrosion in hardened paste of geopolymer cements has been thoroughly studied by the authors [21]–[23]. The obtained experimental results reveal that geopolymer cements can be less vulnerable to acid attack compared to Portland cement. The mechanism of attack consists of a leaching process in which sodium and calcium ions are depleted and exchanged by H^+ or H_3O^+ ions from the solution along with an electrophilic attack by acid protons on polymeric Si-O-Al bonds resulting in the ejection of tetrahedral aluminium from the aluminosilicate framework. The framework vacancies are mostly re-occupied by silicon atoms resulting in the formation of an imperfect highly siliceous framework. The ejected aluminium converted to octahedrally coordinated aluminium mostly accumulates in the intraframework space. In the case of nitric acid, the volume contraction of the material during the leaching process results in the formation of shrinkage cracks. These shrinkage cracks can effectively lower the inhibiting effect of the corroded layer by making the transport of ions easier. In the case of sulfuric acid, the exchanged calcium ions diffusing toward the acid solution react with the counter-diffusing sulfate anions resulting in the formation and deposition of gypsum crystals inside the corroding layer. Deposition of gypsum crystals inside corroding matrix provides a protective effect inhibiting the total process of deterioration.

At mild concentrations of sulfuric acid (pH≈2), the first step of the total corrosion process, i.e. the ion exchange reaction, continues until it results in the formation of shrinkage cracks. When shrinkage cracks become wide enough, sulfate anions diffuse into the cracks, and react with the counter-diffusing calcium ions, resulting in the formation and deposition of gypsum crystals. At relatively low concentrations of sulfuric acid (pH≈3) and for limited periods of exposure time (≈90 days), the corrosion mechanism is exactly the same as that of pH 3 nitric acid, i.e. simply leaching of charge compensating cations and ejection of tetrahedral aluminum with no gypsum deposition [21]-[23].

Continued investigations [24], [25] have shown that geopolymer cements with a minimum content of calcium exhibit a significantly higher acid resistance especially against sulfuric acid. The calcium content of geopolymer cements can be presented not only in the form of a cation for balancing the negative charge of Al in 6-fold coordination, but also in the form of CSH. The calcium content in the form of calcium silicate hydrate is a disadvantage for the acid resistance of geopolymer cements. Therefore knowing that the extent of damage is dependent on the amount of CSH one may expect that a decrease in the calcium content of geopolymer cements results in a higher acid resistance by reducing the amount of CSH and producing a more protective corroded layer.

3.2 Corrosion depth

One may think that it is more accurate to use a light microscope or even a scanning electron microscope for measuring the extent of corrosion. It should be noted however that direct measurement of corrosion depths by simply measuring the corroded parts of the specimens is not only inaccurate, but also in most of the cases impossible. The corroded parts of the specimens undergo significant shrinkage or expansion and in most of the cases since the developed corroded layers have no bonding properties, they are partly or almost completely spalled off spontaneously and particularly under drying. In some cases all the corrosion products are well soluble and the corrosion process does not result in the formation of a corroded layer. The corrosion depths therefore should be measured indirectly by measuring the uncorroded parts of the specimens and subtracting the values from their accurately measured initial sizes. Such a procedure makes the use of a light or scanning electron microscope difficult, time consuming, and even costly. Using a caliper especially for the cases with relatively lower pH values and longer exposure times however, one can simply and enough accurately measure the corrosion depth.

It should be considered that the reported values for the corrosion depths represent the thickness of the corroded layers with no or reduced bonding properties which can be simply removed by brushing with a steel-wire brush and not the core-layer or probably very thin partially corroded sub-layers of corrosion zone which are relatively hard and difficult to remove. In the case of GC specimens particularly those corroded at pH 1 and 2 of sulfuric acid, the corroded layers exhibiting some bonding properties were relatively hard and difficult to remove by simply brushing. For the case of OPC specimens corroded at pH 1 and 2 of sulfuric acid also the relatively thin and dense sub-layer of gypsum adjacent to the corrosion zone was hard and difficult to remove. In these cases the corroded layers and the thin gypsum sub-layers were firstly removed with the help of a knife and the specimens were then brushed with a steel-wire brush. The measured values of corrosion depths for each of the tested cements and acid solutions are presented in figures 1 to 6.

3.3 Extent of corrosion at pH 1

Figure 1 represents the measured corrosion depths versus exposure time for the hardened paste specimens of each of the tested cements in pH 1 nitric acid solution. After 90 days of exposure, the OPC specimens were corroded approximately to depths of 8 mm. At the same time approximately 5.8 mm of GC specimens were corroded.

At such a low pH value, all the phases present in each of the tested cements are unstable and dissolution of which occurs incongruently resulting in the formation of residual layers on the acid-exposed surfaces. The rate of corrosion therefore can be greatly influenced by the protective effect of the corroded layers or residuals depositing on the acid-exposed surfaces. The protective effect of a corroded layer depends not only on its density and the presence of shrinkage cracks, but also on its thickness that increases with continued corrosion. Now considering the slope of the curves, i.e. the corrosion rates, it is seen that in all the cases the corrosion rates that are relatively faster at the beginning very soon decrease with time. During the first few days at the beginning of the acid attack, the corrosion process is therefore controlled by diffusion of ions through solution to the surface and/or by the processes taking place at the surface itself. As the corrosion process proceeds, the thickness of the corroded layer and hence its protective effect increases and finally the process becomes entirely diffusion controlled. The effects due to diffusion of ions through solution were reduced by mixing the solutions thoroughly and adding concentrated acid to control the pH value in the range 1±0.01 daily.

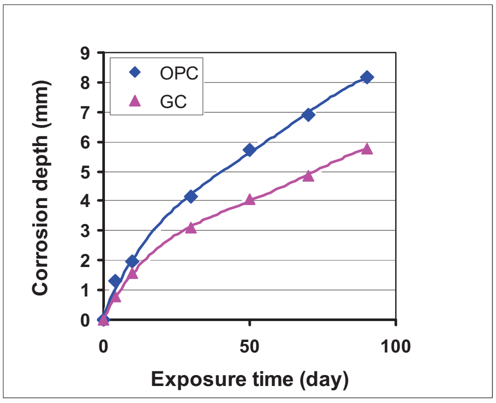

Fig. 1. Extent of corrosion for specimens exposed to pH 1 nitric acid solution.

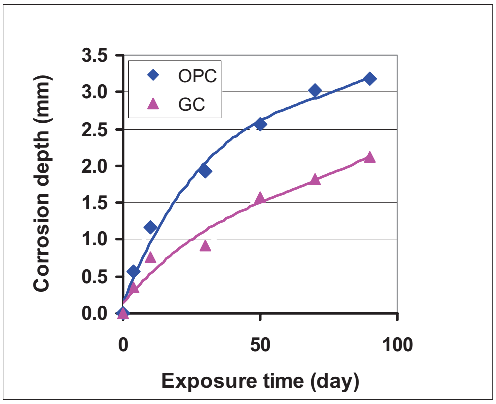

Fig. 2. Extent of corrosion for specimens exposed to pH 1 sulfuric acid solution.

The decreasing order in the extent of corrosion of OPC and GC specimens after 90 days of exposure to pH 1 nitric acid can be related to the increasing protective effect of their corroded layers. The corroded layer of OPC specimens consisting mainly of $SiO_2 \cdot H_2O$ gel was highly cracked, porous, and very soft. This corroded layer cannot effectively inhibit the corrosion process. The paste specimens of GC were corroded to a lower extent due to the formation of a relatively more protective corroded layer. The process of acid corrosion of hardened paste of GCs, as discussed previously [22], [23], does not result in complete destruction of the microstructure. The corroded layer is an imperfect highly siliceous framework that is relatively dense and hard providing protecting effect.

The leaching process of soluble constituent elements of the material (i.e. sodium and calcium) however results in the formation of relatively large shrinkage cracks.

The mercury intrusion porosimetry was used to determine the total pore content of the 50-day hardened cement pastes. The total pore contents of the OPC and GC paste specimens were reported as 11.83 and 33.15% respectively. As seen, in contrary to the measured 90-day corrosion depths, the minimum and the maximum values of the total pore contents are those of OPC and GC specimens respectively (table 3). This means that at such a low pH value the pore content of the specimens is not the main governing factor and the protective effect of the corroded layers is more effective.

The corroded layer of OPC was highly cracked with no bonding properties. Such corroded layer can be easily removed by any external mechanical effect, e.g. attrition caused by flow of acid solution, or even spontaneously under continued exposure time. In such a case the corrosion process continues much faster than with intact protective layers. Now assuming that specimens are exposed to strong external mechanical effects such that all the corroded layers including that of GC specimens are continuously removed without any considerable growth, the tested cements are then corroded constantly at the maximum possible rates, i.e. the corresponding initial corrosion rates. Under such conditions therefore the extent of corrosion differs depending on the initial corrosion rates. An inspection of the slopes of the curves at the beginning of the corrosion process reveals that under such conditions OPC specimens exhibit a lower relative acid resistance.

Figure 2 shows the increase in corrosion depth of cement pastes versus exposure time for the case of sulfuric acid attack at pH 1. An exposure period of 3 months results in the corrosion of 3.78 and 2.12 mm OPC and GC specimens respectively. Compared to the results obtained for the case of corrosion at pH 1 nitric acid (figure 1) the tested cements show the same order of relative acid resistances. The 90-day corrosion depths however are considerably reduced. Such considerable reductions in the 90-day corrosion depths are obviously due to the formation and deposition of gypsum crystals inside corroding layers [24].

In the case of OPC, extensive gypsum deposition inside the corroding layer very soon results in the formation of a relatively thick deposit which is very voluminous and soft on the external side and relatively dens and hard in the internal parts. Such a deposit that quickly grows with exposure time can considerably inhibit the total rate of deterioration during the course of corrosion.

In the case of GC specimens, the developing corroded layer is uniform in cross section, relatively dense, very hard and difficult to destroy and remove. GC specimens are therefore corroded more slowly due to the formation of a corroded layer that effectively reduces the rate of transport of ions. Therefore at pH 1 sulfuric acid, the same as what observed in the case of pH 1 nitric acid, the total rate of deterioration and the extent of corrosion after 90 days of exposure are more effectively controlled by the protective effect of the corroded layers than the porosity and the nature of corroding phases.

The effect of other factors such as differences in chemical and mineralogical compositions and the influence of porosity are more announced during the first few days at the beginning of the acid attack or particularly under external mechanical effects where the corroded layers are continuously removed. A careful inspection of the slopes of the curves at the beginning of the corrosion process reveals that under such conditions OPC provides a lower relative acid resistance. However, it should be considered that in the case of sulfuric acid attack and when dissolution of cement paste results in an extensive gypsum deposition, the effect of porosity is more complicated due to a different mechanism of deterioration.

Investigations done by Israel *et al* [26] showed that the reduced porosity of pore reduced cement compared to OPC (with the same composition) reduces the susceptibility to attack by acids producing soluble calcium salts (e.g. hydrochloric and ethanoic acids) whereas in the case of attack by sulfuric acid both pore reduced cement and OPC paste specimens were damaged to almost the same extent (in some cases even pore reduced cement-paste specimens a little more). The authors concluded that in the case of attack by sulfuric acid, extensive formation and deposition of gypsum in the cement surface regions results in the internal mechanical stresses that ultimately lead to cracking and exposure of fresh surfaces. Many authors [27]-[30] have claimed such a deteriorating mechanism for extensive gypsum deposition. Therefore when dealing with the influence of porosity both the type of acid (producing soluble or insoluble calcium-salt), and the type of cement (intensity of gypsum deposition) must be considered together. Although gypsum deposition can effectively inhibit the total process of deterioration by producing more protective corroded layers (when comparing corrosion of the same material at the same pH value of sulfuric and nitric acids), extensive deposition of which in the corrosion zone or regions close to the corroding surface can accelerate the total rate of deterioration by resulting in expansion and causing disintegrating mechanical stresses (when comparing corrosion of different cementitious materials, e.g. OPC and GC, at the same pH value of sulfuric acid).

3.4 Extent of corrosion at pH 2

At pH 2, the tested cement pastes were corroded to considerably lower extents than at pH 1 confirming that the intensity of the aggression is significantly dependent on the pH value of the acid solution. The results of corrosion depth versus exposure time are presented in figures 3 and 4. After 90 days of exposure to nitric acid solution, GC and OPC paste specimens were corroded to depths of 1.83 and 1.62 mm respectively. The gradual deposition of corrosion products resulted in gradual decrease of corrosion rates. The corrosion depth of GC specimens however is higher than that of OPC specimens. Such a decrease in relative acid resistance of GC specimens compared to those of OPC specimens and compared to what observed at pH 1 can be related to different protective effects of corroded layers developing at pH 2. The corroded layer of GC specimens was the same as what visually observed at pH 1 except shrinkage cracks which were finer. These shrinkage cracks that were extended from the acid-exposed surface to the corrosion zone or regions very close to it provide an easy way for transport of ions across the corroded layer. The protective effect of the relatively hard and dens corroded layer of GC specimens is therefore effectively reduced.

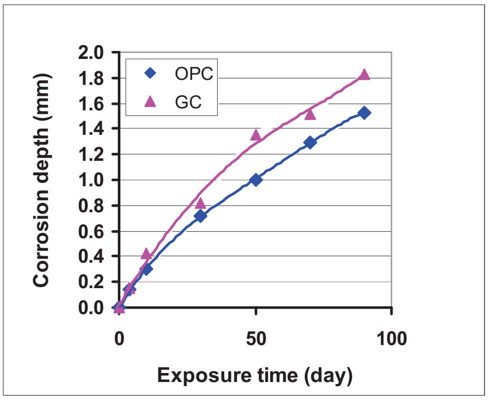

Fig. 3. Extent of corrosion for specimens exposed to pH 2 nitric acid solution.

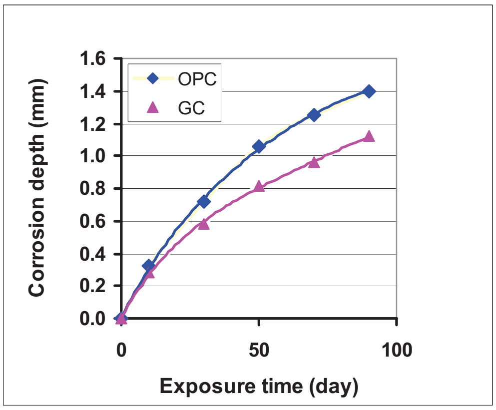

Fig. 4. Extent of corrosion for specimens exposed to pH 2 sulfuric acid solution.

Now excluding the protective effect of corroded layers and assuming that specimens are exposed to strong external mechanical effects such that all the corroded layers are continuously removed without any considerable growth, the tested cements are then corroded constantly at the maximum possible rates, i.e. the corresponding initial corrosion rates. A careful inspection of the slopes of the curves at the beginning of the corrosion process reveals that under such conditions GC specimens exhibit a lower relative acid resistance.

At pH 2 sulfuric acid, the tested cements were corroded to considerably lower extents than those measured at pH 1. The results of corrosion depth versus exposure time are presented in figure 4. After 90 days of exposure, OPC and GC specimens were corroded to depths of 1.40 and 1.00 mm respectively.

Comparing the results to those obtained at pH 2 of nitric acid, it is seen that pH 2 of sulfuric acid is a little less corrosive than pH 2 of nitric acid. This is obviously due to the inhibiting effect produced by gypsum crystals depositing inside corroded layers. The deposition of gypsum crystals results in the formation of relatively more protective layers and thus the tested cements which started corroding more quickly at the beginning of the exposure time were corroding at considerably lower rates at the end of exposure time.

The decreasing order in the extent of corrosion at the end of exposure time is the same as what observed at pH 1 sulfuric acid. GC specimens with a relatively lower acid resistance at pH 2 nitric acid, figure 3, show a lower 90-day corrosion depth. At pH 2 nitric acid, the relative acid resistance of GC specimens is considerably reduced due to the presence of shrinkage cracks. At pH 2 sulfuric acid however, these cracks when formed and enough widened are filled with gypsum crystals [31]. The formation and deposition of gypsum crystals inside shrinkage cracks significantly increases the protective effect of the corroded layer by acting as a barrier to the transport of ions.

3.5 Extent of corrosion at pH 3

When the pH of nitric acid solution was increased to 3, the cement pastes were corroded to quite lower extents. Figure 5 shows the increase in corrosion depth of cement pastes versus time during the last month of exposure. During the first and the second months of exposure, the corrosion depths were so small and close to each other that it was difficult to measure them surely with enough accuracy. Attempts made for measuring corrosion depths during the first and the second months of exposure however confirmed that the specimens of OPC started corroding not just from the beginning of the exposure time as what observed at pH 1 and 2, but lately after a few weeks. Such a delay in the start of corrosion can be related to the alkalinity or neutralizing character of the OPC cement paste.

When cement paste specimens are exposed to limited volume of acid, diffusion of portlandite and free-alkalis through pore solution and from regions close to the acid-exposed surfaces into the solution can neutralize the acid content of the solution before any dissolution of cement paste occurs. At relatively higher pH values, e.g. 3, the acid content of the solution is comparatively very less (based on a logarithmic relationship). During the first few weeks of exposure therefore, the very less acid content of the solution or part of which close to the acid-exposed surface of the specimens can be easily neutralized. Continued exposure at relatively high ratio of the solution volume (cm^3) to the total corrosion surface (cm^2), i.e. 50, along with daily addition of concentrated acid and thoroughly mixing however result in the start of paste dissolution on the acid-exposed surfaces after a few weeks.

The neutralizing character of the tested cements is more announced not only at relatively higher pH values and at the beginning of the exposure time, but also for the cements with a relatively higher alkalinity. Simple measurements were carried out by adding 1 gr of finely ground powder (with particle size less than 100 μm) of hardened pastes of OPC and GC cements to 100 ml of tap water at a pH of 7.46 and measuring the increase in pH value after shaking for a few seconds. The obtained results, table 2, reveal that both OPC and GC pastes are more or less alkaline. The alkalinity of OPC paste with a pH value 11.88 however is higher than that of GC paste with a pH value of 10.36. In addition as previously mentioned, the reported values for the corrosion depths represent the thickness of the corroded layers with no or reduced bonding properties which can be removed by brushing with a steel-wire brush and not the thickness of the total affected layer. This is especially more important at relatively higher pH values and for relatively short periods of exposure time in which the total affected layer is relatively very thin and the completely corroded layer with no or considerably reduced bonding properties is only a small part of which. At lower pH values (pH$\approx$1) however, the corrosion process quickly proceeds and the total affected layer is very close to the completely corroded layer with no bonding properties.

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The accuracy of the measurements therefore reduces at relatively higher pH values.

Since the tested cements are corroded at comparatively much slower rates, a limited exposure time period of 90 days can result in development of very thin corroded layers with relatively much lower protective effects compared to those observed at pH 1 and 2. On the other hand, the order of increasing acid resistance is the same as the order of decreasing pore content, table 3, revealing that at pH 3 and for the limited exposure time period of three months the effect of porosity and/or the nature of the corroding phases are/is more effective than the protective effect of the corroded layers.

In the case of sulfuric acid, the intensity of attack significantly decreases when pH increases to 3. This is something clear since based on the logarithmic relationship between pH and H^+ ion concentration, a pH 3 solution contains comparatively much lower amount of acid than a pH 2 solution. Figure 6 shows the increase in the corrosion depth of cement pastes versus time during the last month of exposure.

Table 2. Total pore content and relative alkalinity.

	Total pore content (%)	Relative alkalinity (pH)
OPC	11.83	11.88
GC	33.15	10.36

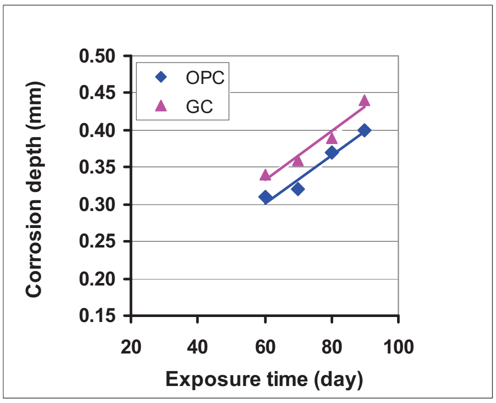

Fig. 5. Extent of corrosion for specimens exposed to pH 3 nitric acid solution.

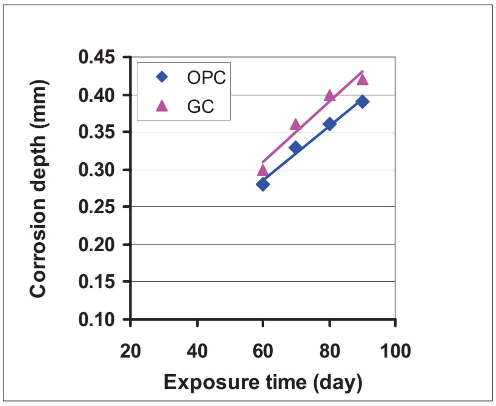

Fig. 6. Extent of corrosion for specimens exposed to pH 3 sulfuric acid solution.

In thin sulfuric acid solutions with pH values as high as 3 and for the limited exposure time period of 90 days, the tested cements are corroded by exactly the same mechanism as what observed at pH 3 nitric acid [31]. Here also a comparison of the results presented in figure 6 to those obtained at pH 3 nitric acid (figure 5) shows that the increasing order in relative acid resistances is the same and the 90-day corrosion depths of the same specimens are very close. However, it should be noted that longer exposure times (more than 90 days) gradually increases the pore contents of the corroding layers. When the pore contents of the corroding layers are enough increased and shrinkage cracks are formed, diffusion of sulfate anions can result in the formation and deposition of gypsum crystals inside the corroding layers (the same as what observed for corrosion of GC specimens at pH 2 of sulfuric acid). For each of the tested cements the total rate of deterioration is then more or less effectively reduced depending on the protective effect provided by gypsum deposition and this may gradually result in a different increasing order in relative acid resistances.

4 Conclusion

1. Ordinary Portland cement and geopolymer cement studied are both vulnerable to acid attack. Their relative acid resistances however differ at different pH values.
2. The extent of the corrosion is significantly dependent on the pH value of the acid solution.
3. At relatively lower pH values (pH≤2), sulfuric acid is less corrosive than nitric acid because of the inhibition caused by gypsum crystals depositing on the acid-exposed surface or inside the corroding layer. The corrosion process very soon becomes diffusion controlled owing to the formation of relatively thick corroded layers.
4. At relatively higher pH values (pH≥3) and for relatively short exposure time periods (≤ 90 days), the total rate of deterioration is more effectively controlled by the porosity and the nature of corroding phases than the protective effect of a relatively very thin corroded layer.

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