

SULFURIC ACID ATTACK ON HARDENED PASTE OF GEOPOLYMER CEMENTS PART 1. MECHANISM OF CORROSION AT RELATIVELY HIGH CONCENTRATIONS

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Mechanism of corrosion of hardened paste of geopolymer cements at relatively high concentrations of sulfuric acid ($pH \approx 1$) consists of two subsequent steps. The first step starts by an ion exchange reaction between the charge compensating cations of the framework, i.e. sodium and calcium, and H^+ or H_3O^+ ions from the solution along with an electrophilic attack by acid protons on polymeric Si–O–Al bonds. The electrophilic attack of acid protons results in the ejection of tetrahedral aluminum from the aluminosilicate framework. In the second step, the exchanged calcium ions diffusing toward the acid solution react with counter-diffusing sulfate anions resulting in the formation and deposition of gypsum crystals inside corroding layer. Deposition of gypsum crystals inside corroding matrix provides a protective effect inhibiting the total process of deterioration.

INTRODUCTION

The deteriorating effect of acid media on cement-based constructions has become a worrying problem all over the world. These media generally occur as solutions in various branches of industry, acid rains and mists, and acid ground-waters. A very popular form of acid attack on concrete that is usually referred to as biogenic sulfuric acid attack also occurs in both industrial and urban sewer systems.

The extent of attack depends not only on the type and concentration of the attacking acid, but also on the properties of the concrete including the type of cement used. Hardened paste of Portland cement that is a highly alkaline material with pH above 12.5 is severely attacked by acid media. The authors thoroughly discussed and reviewed the phenomenon of acid corrosion of hydrated cement-based materials and the literature published during the last two decades [1,2].

The emergence of new cementitious materials, i.e. geopolymer cements or chemically bonded ceramics, during the past decades necessitates detailed experimental work and research activities to investigate their durability in aggressive acid environments. Geopolymer cements that are inorganic or mineral polymers based on alumina and silica can be regarded as amorphous

analogues of natural zeolites resulting from geosynthesis. Based on such a similarity, Joseph Davidovits [3] establishing a new terminology for properly classifying mineral polymers, created and applied the term "geopolymer". The nature and engineering properties of these materials have been discussed in a number of papers [4-14]. Some of the authors [7,8,9,10,12] claimed a comparatively higher acid resistance for geopolymer cements compared to ordinary Portland cement.

Acid corrosion of hardened paste of geopolymer cements in solutions of nitric acid was discussed in previous publications [15,16]. Experimental results showed that mechanism of nitric acid attack on hardened paste of geopolymer cements consists of a leaching process in which sodium and calcium ions, charge compensating cations of the aluminosilicate framework, are depleted and exchanged by H^+ or H_3O^+ ions from the acid solution along with an electrophilic attack by acid protons on polymeric Si–O–Al bonds. The electrophilic attack of acid protons results 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.

The purpose of this work is to investigate the response of hardened paste of geopolymer cements to sulfuric acid attack. Sulfuric acid is a strong mineral acid which is soluble in all proportions of water. Attack by sulfuric acid which occurs in different forms can be considered as the most common cause of acid corrosion of concrete structures. The geopolymer cement used in this work was produced according to the work of Škvára and Bohuněk [11]. They reported that alkali activation brought about by the effect of NaOH and Na₂SiO₃ 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 ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of 0.6, and containing 7 wt.% Na₂O.

EXPERIMENTAL

Materials

Materials used for this study include: fly ash from Chvaletice power plant and granulated blast furnace slag from Vítkovice steel plant (both plants in Czech Republic). 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 Republic). The attained specific surface areas were 650 and 420 m²/kg, respectively, for fly ash and blast furnace slag. Chemical compositions of these materials are listed in table 1. Solutions of sulfuric acid at *pH* values of 1, 2, and 3 were also used.

Specimens Preparation

The ground fly ash and ground granulated blast furnace slag were mixed in equal proportions. The SiO₂/Na₂O 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 Na₂O 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.

Test Procedure

At the age of 28 days, the specimens were immersed in three different solutions of sulfuric acid at *pH* values of 1±0.01, 2±0.03, and 3±0.05. All the solutions were prepared by adding concentrated acid to tap water. 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 at the stated tolerances. During *pH* monitoring, an electrical mixer was used for mixing each of the solutions thoroughly. All solutions were renewed monthly and the temperature of the solutions was kept constantly at 20°C.

XRD (Seifert XRD 3000P), EPMA (JEOL Superprobe 733), and SEM (JEOL) were the principal laboratory techniques used to study the corroded specimens. For studies with EPMA and SEM, a number of corroded specimens were cut into halves to expose the total internal surface including the cross section of the corroded layer. The suitable halves were then impregnated with an epoxy resin, polished, and coated with carbon. The electron probe measurements were performed not only on selected points, but also along imaginary lines extending from the corroded sections through corrosion zone and towards the internal unaffected parts of the specimens. This paper deals with corrosion process of hardened paste of geopolymer cements at relatively high concentrations (*pH* ≈ 1) of sulfuric acid. The next part of this paper is devoted to the study of the corrosion mechanism at medium and relatively low concentrations (*pH* ≈ 2 and 3) of sulfuric acid.

Table 1. Chemical composition of Chvaletice fly ash and Vítkovice slag (wt.%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	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	-	-	-

concentration profiles of a typical X-ray line analysis along an imaginary line extending from somewhere in the corroded layer on the left side through corrosion zone and toward the unaffected section on the right side. The total length of line at a magnification of 40 \times is 2.910 mm. As seen in sulfur profile, the sulfur content of the corroded section of the specimen has significantly and sharply increased. Comparing the profiles of sulfur and calcium, it is seen that, in the corroded section, these two profiles exactly coincide with each other, confirming that all the sulfur and calcium in the corroded layer are present in the form of gypsum.

Comparing the profiles of sodium and sulfur, it is seen that, sodium has been leached to a somewhat higher depth than gypsum deposition. The calcium profile also shows depletion in a very thin sub-layer between

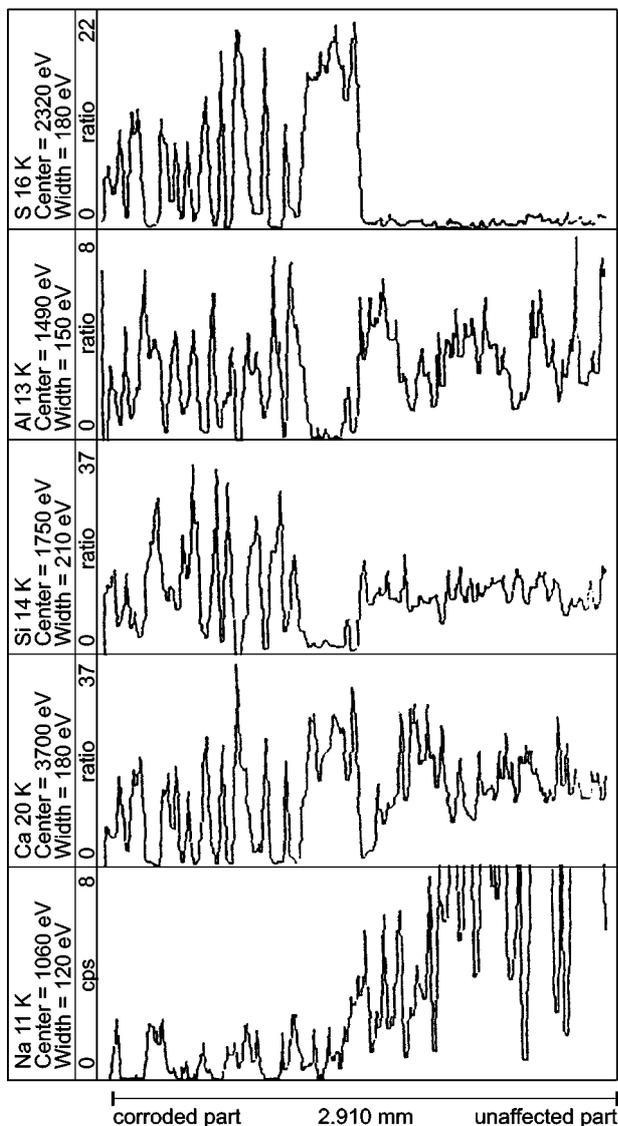


Figure 4. X-ray line analysis (EDS) of the paste specimen after 60 days of exposure to *pH* 1 sulfuric acid (magnification = 40 \times).

the two sections of the specimen. These observations implies that calcium is first depleted by an ion exchange reaction with the H^+ or H_3O^+ ions, and thereafter when diffusing toward the acid solution, by a reaction in which sulfate anion diffusing from the acid solution, results in the deposition of gypsum crystals in the corroding layer.

Another important point is that gypsum has not deposited uniformly in the corroded layer. As seen in the profiles of sulfur and calcium, gypsum has deposited in a number of separate thin sub-layers mostly parallel to the acid-exposed surface of the specimen. Now considering the profiles of aluminium and silicon and comparing them to those of sulfur and calcium, it is seen that, the relatively uniform matrix of the specimen has been disintegrated into small parts and layers separated by gypsum sub-layers. This means that in the process of sulfuric acid attack deposition of gypsum crystals inside pores, air voids, and probably shrinkage micro-cracks resulting from the leaching of sodium and calcium tends to cause internal stresses that ultimately lead to expansion and cracking of the corroding layer. Figure 5 shows a 60 \times magnified SEM image of the internal section of a corroded layer developed after 60 days of exposure to *pH* 1 sulfuric acid. The disintegrated corroded matrix along with a large number of expansion cracks filled with gypsum crystals (white in colour) are clearly visible.

It should be considered that gypsum deposition is not extensive enough to cause the spalling of the corroding sections. A 90-day period of acid attack at *pH* 1 results in an expansion of approximately 7%. The corroded layer as mentioned in the visual observations seems as a uniform layer that is very hard and difficult to destroy and remove. The presence of such a corroded layer provides a protective effect that can effectively inhibit the process of acid attack.

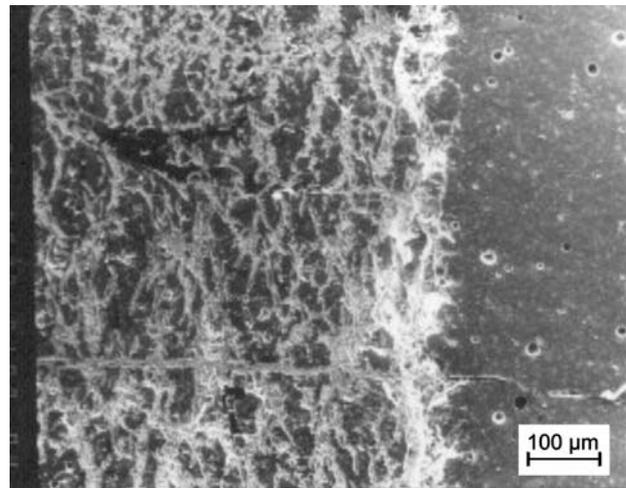


Figure 5. Corroded layer of the paste specimen developed after 60 days of exposure to *pH* 1 sulfuric acid.

CONCLUSION

1. Mechanism of corrosion of hardened paste of geopolymer cements at relatively high concentrations of sulfuric acid (pH 1) consists of two subsequent steps. The first step resembling the mechanism of nitric acid attack, discussed in previous publications [15,16], starts by an ion exchange reaction between the charge compensating cations of the framework, i.e. sodium and calcium, and H^+ or H_3O^+ ions from the solution along with an electrophilic attack by acid protons on polymeric Si–O–Al bonds. The electrophilic attack of acid protons results in the ejection of tetrahedral aluminium from the aluminosilicate framework. In the second step, 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 corroding layer.
2. Deposition of gypsum crystals inside corroding matrix (at pH 1) provides a protective effect inhibiting the total process of deterioration.

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KOROZE ZTUHLÉ PASTY GEOPOLYMERNÍHO CEMENTU KYSELINOU SÍROVOU ČÁST I. KOROZNÍ MECHANISMUS PŘI VYŠŠÍCH KONCENTRACÍCH

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Mechanismus koroze ztuhlé pasty geopolymerního cementu při vyšších koncentracích kyseliny sírové (pH kolem 1) se skládá ze dvou postupných kroků. První krok je zahajován iontovou výměnou mezi strukturními kationty kompenzujícími náboj, tj. sodíkem a vápníkem, a ionty H^+ nebo H_3O^+ z roztoku souběžně s elektrofilním atakem polymerních vazeb Si–O–Al kyselým protonem. Elektrofilní atak kyselými protony způsobuje uvolnění tetraedrálních iontů Al z alumosilikátové mřížky. Ve druhém kroku difundují uvolněné vápenaté ionty do kyselého roztoku a tam reagují se síranovými ionty difundujícími opačným směrem za vzniku krystalů sádrovice v korozní vrstvě. Srážení sádrovcových krystalů v korodující matici brzdí další proces celkového poškození.