

SULFURIC ACID ATTACK ON HARDENED PASTE OF GEOPOLYMER CEMENTS PART 2. CORROSION MECHANISM AT MILD AND RELATIVELY LOW CONCENTRATIONS

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At mild concentrations of sulfuric acid ($pH \approx 2$), the first step of the total corrosion process, i.e. the ion exchange reaction between the charge compensating cations of the framework (Na^+ and Ca^{2+}) and 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, 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 ($pH \approx 3$) 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.

INTRODUCTION

Cement and concrete products made from ordinary Portland cement and its derivatives are highly vulnerable to acid media. This is because none of their hydration products (calcium silicate hydrates with different C/S ratios) is stable below $pH = 8.8$ [1]. Cement and concrete products can be subjected to attack by various inorganic and organic acids including sulfuric, nitric, hydrochloric, phosphoric, acetic, lactic, and so on. However, sulfuric acid can be considered as the most common cause of deterioration of these products, since attack by which occurs in many various and popular ways. Authors have thoroughly discussed and reviewed the phenomenon of acid corrosion of hydrated cement-based materials and the literature published during the last two decades [2,3]. The importance of the phenomenon necessitates more experimental work and research activities for developing new inorganic binders with considerably improved acid resistance.

In a number of publications [4-8], authors claimed an acid resistance for geopolymer cements far better than that of Portland cement. Experimental results [9,10] showed that nitric acid attack on hardened paste of geopolymer cements consists of a leaching process in

which charge compensating cations of the aluminosilicate framework (sodium and calcium) 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 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 that is relatively hard but brittle. The presence of such a corroded layer, i.e. an acid resistant highly siliceous framework, can effectively inhibit the process of corrosion by acting as a barrier to the transport of acid molecules and/or ions as well as dissolved constituents provided that the shrinkage cracks due to the leaching of soluble constituents are minimized.

The purpose of the present work is to investigate the response of hardened paste of geopolymer cements to sulfuric acid attack. The first part of this article [11] was devoted to the study of the corrosion process of hardened paste of geopolymer cements at relatively high concentrations ($pH \approx 1$) of sulfuric acid. The present article deals with the corrosion mechanism at mild and relatively low concentrations of sulfuric acid ($pH \approx 2$ and 3).

EXPERIMENTAL

The geopolymer cement used in this work was produced according to the work of Škvára and Bohuněk [12]. They reported that alkali activation brought about by the effect of NaOH and Na₂SiO₃ solutions can significantly increase the reactivity of substances with latent hydraulic properties such as fly ash or mixtures of fly ash and blast furnace slag. The materials used for this study and the procedures for specimens preparation and test method were all discussed in part 1 [11].

RESULTS AND DISCUSSION

Visual observations

During the course of corrosion the changes in the appearance of the specimens were visually monitored. The observations are as follows:

pH 2: No change in colour; a slight expansion along with very fine cracks; a relatively hard and difficult to remove corroded layer.

pH 3: No change in colour and appearance; a soft and easily removable surface layer.

Attack at *pH 2*

At *pH 2* the mechanism of attack is different. Investigations by SEM and EDAX (using ZAF correction) on the corroding specimens confirmed the presence of a few gypsum crystals inside the cracks and not inside the corroding matrix. Figure 1 shows a typical 40× magnified SEM image of the corroded layer developed after 60 days of exposure to *pH 2* sulfuric acid. As seen, the corroded layer is extremely cracked, and wider cracks have been filled with gypsum crystals (cracks which are white). A typical 1000× magnified SEM image of the

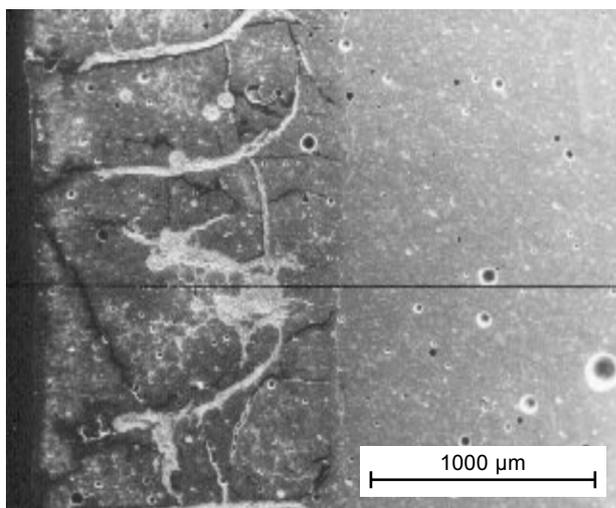


Figure 1. Corroded layer of the paste specimen developed at *pH 2* sulfuric acid after 60 days of exposure.

corroded matrix along with such a crack, i.e. filled with gypsum crystals, is shown in figure 2. The horizontal line shown in figure 1 is the line along which X-ray line analysis was conducted. The resulting concentration profiles are shown in figure 3. The total length of line at a magnification of 60× is 1.940 mm. As it is seen, the selected line (figure 1) crosses gypsum crystals only in a small region in the corroded layer and close to the unaffected section. The profiles of sulfur and calcium correspondingly confirm that gypsum is only present in that small region and not anywhere else in the corroded layer.

Neglecting the gypsum deposits inside the cracks, it is seen that, the mechanism of sulfuric acid attack at *pH 2* resembles that of nitric acid attack, discussed in previous papers [15,16]. The important point is the absence of gypsum in the corroded matrix showing that at mild concentrations of sulfuric acid (*pH* ≈ 2) sulfate anions do not diffuse into the corroded matrix. In fact the corrosion process starts first by leaching of soluble constituent elements and ejection of tetrahedral aluminium. The first step 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. Measurements by calliper showed that during the first half of the exposure time there is some shrinkage confirming that leaching process is at work. After an exposure period of 3 months, however, gypsum deposition inside visually observable cracks results in small expansion. It should be considered that deposition of gypsum crystals inside shrinkage cracks provides a protective effect for the unaffected section of the specimen by acting as a barrier to the transport of ions across the corroded layer.

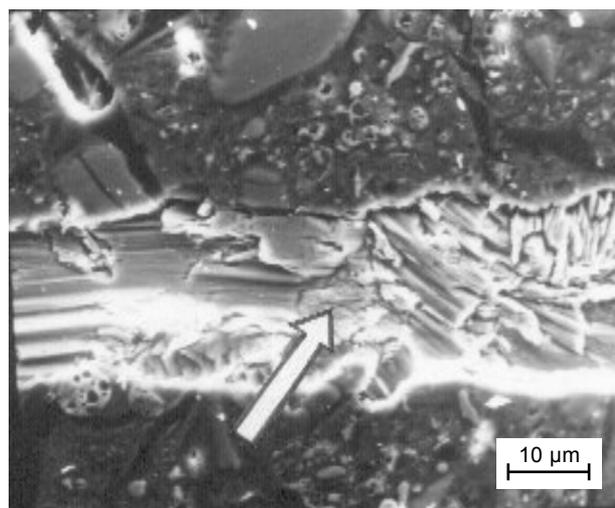


Figure 2. Shrinkage crack, filled with gypsum crystals, developed in corroded layer of a paste specimen after 60 days of exposure to *pH 2* sulfuric acid. EDAX analysis for the point shown by arrow: 58.78 % SO₃, 40.96 % CaO.

Attack at pH 3

Contrary to our expectation for the presence of gypsum, investigations by SEM and EDAX (using ZAF correction) on the corroded specimens showed no gypsum deposition in the corroded layer confirming a corrosion mechanism different than what observed at pH 1 and 2. Figure 4 shows a typical 100× magnified SEM image of a thin corroded layer developed after 60 days of exposure to pH 3 sulfuric acid. The layer consists of a large number of shrinkage micro-cracks, which are not visually observable.

To investigate the relative changes in chemical composition of the corroded layer, a number of X-ray line analyses (energy dispersion measurement, EDS) were conducted by electron probe microanalysis (EPMA). Figure 5 shows the concentration profiles of S, Al, Na, and Ca obtained from such a typical X-ray

line analysis. Each profile shows the relative changes in concentration of a different element along an imaginary line extended from somewhere close to the acid-exposed surface on the left side through corroded layer and corrosion zone towards the unaffected part of the speci-

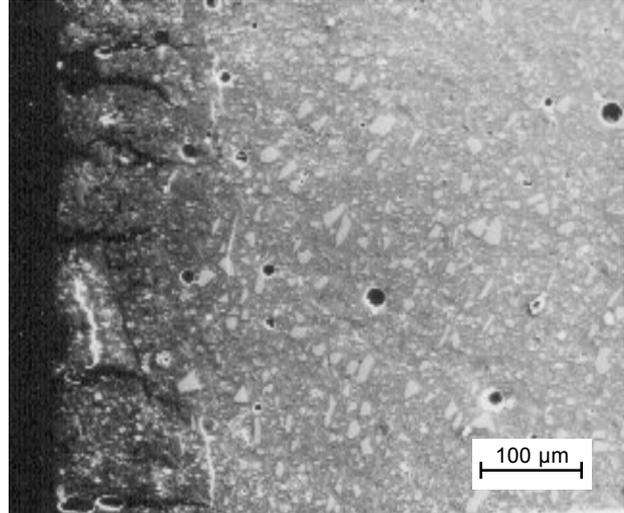


Figure 4. Corroded layer developed at pH 3 sulfuric acid after 60 days of exposure.

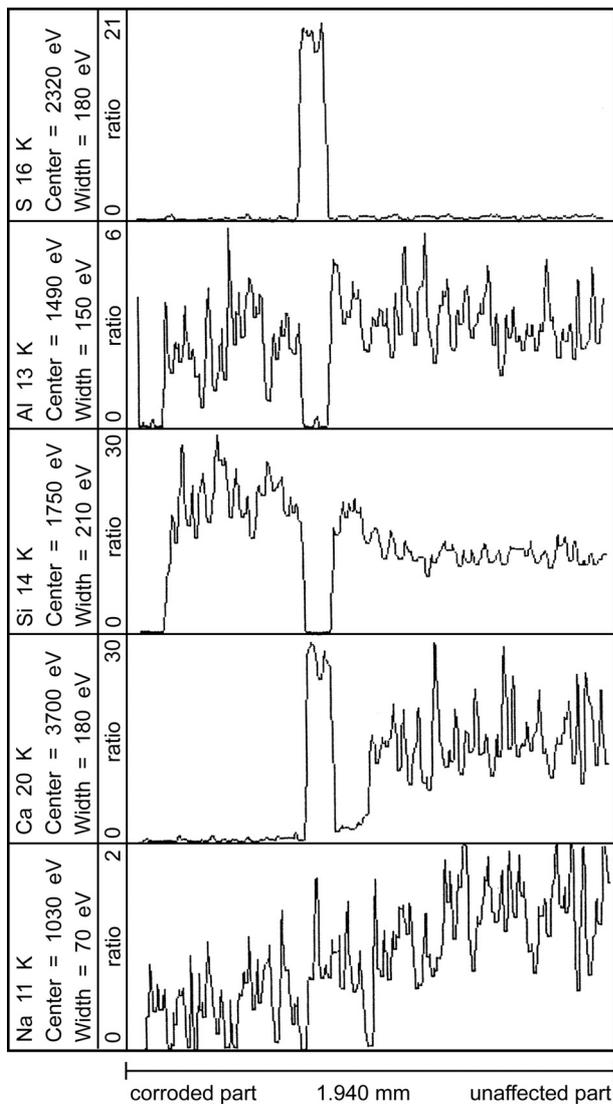


Figure 3. X-ray line analysis (EDS) of the paste specimen after 60 days of exposure to pH 2 sulfuric acid (magnification = 60×).

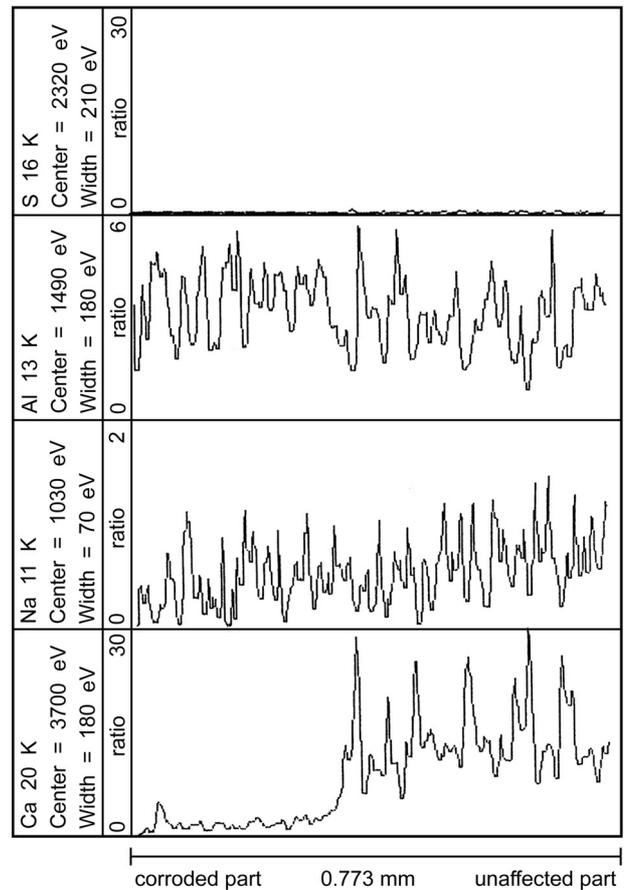


Figure 5. X-ray line analysis (EDS) of the paste specimen after 60 days of exposure to pH 3 sulfuric acid (magnification = 150×).

men on the right side. The total length of line at a magnification of 150 is 0.773 mm. As seen in the sulfur profile, there has been no gypsum deposition in the corroded part of the specimen. Corrosion process resulted in the leaching of calcium and sodium (sodium to a considerably lower extent, but a little bit more dipper than calcium). A small enrichment in the concentration of Al can also be seen. The concentration of Si (the related profile is not presented) has been surely increased due to the leaching of calcium and sodium. All the above-mentioned observations are exactly the same as those obtained and reported [9,10] for the corrosion of hardened paste of geopolymer cements at pH 3 nitric acid. The corrosion mechanism at relatively low concentrations of sulfuric acid with pH values as high as 3 and for limited exposure time periods (≈ 90 days) is therefore exactly the same as that of nitric acid at pH 3 [10]. The important point is the absence of gypsum in the corroded layer showing that at thin concentrations of sulfuric acid ($pH \approx 3$) and for the limited time periods (≈ 90 days), sulfate anions do not diffuse into the corroded part. However, it should be considered that after longer exposure times when shrinkage cracks are formed and enough widened, sulfate anions probably diffuse into the cracks and react with counter-diffusing calcium ions resulting in the formation and deposition of gypsum crystals.

CONCLUSION

1. At mild concentrations of sulfuric acid ($pH \approx 2$), the first step of the total corrosion process, i.e. the ion exchange reaction and the electrophilic attack by acid protons on Si-O-Al bonds, 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.
2. At relatively low concentrations of sulfuric acid ($pH \approx 3$) and for the limited exposure time periods (≈ 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.

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KOROZE ZTUHLÉ PASTY GEOPOLYMERNÍHO CEMENTU KYSELINOU ŠIROVOU ČÁST 2. KOROZNÍ MECHANISMUS PŘI STŘEDNÍCH A RELATIVNĚ NÍZKÝCH KONCENTRACÍCH

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Při nižších koncentracích H_2SO_4 (pH cca 2) dochází v prvé části korozního procesu k iontové výměně 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, kdy elektrofilní atak kyselými protony způsobuje uvolnění tetraedrálních iontů Al z alumosilikátové mřížky. Současně dochází k vytváření smršňovacích trhlinek. V další části korozního procesu difundují siranové aniony do trhlinek a reagují s vápenatými ionty a tam reagují se za vzniku krystalů sádrovce. Při relativně nízkých koncentracích H_2SO_4 (pH cca 3) a při kratších dobách koroze (cca do 90 dnů) je korozní mechanismus analogický jako u koroze HNO_3 při $pH = 3$, tj. koroze probíhá rozpouštěním bez vzniku sádrovcových krystalů.