RESEARCH PAPER

The Resistance of Blast Furnace Slag- and Ferrochrome Slag-Based Geopolymer Concrete Against Acid Attack

Ahmet Özcan[2] · Mehmet Burhan Karakoç[1]

Abstract

In this study, blast furnace slag- (BFS) and Elazığ ferrochrome slag (EFS)-based geopolymer concretes were produced. Samples were immersed in 5% phosphoric acid (H_3PO_4), hydrochloric acid (HCl), hydrofluoric acid (HF) and sulfuric acid (H_2SO_4) solutions for 12 weeks. The compressive strengths, ultrasonic pulse velocities, weight and length changes of the samples were determined in this process. At the same time, visual inspections of the samples were investigated. Scanning electron microscopy (SEM) analysis was performed for the microstructure analysis of the samples removed from the solutions. 5% H_2SO_4 solution had the most negative effect on the samples. As the EFS ratio in the geopolymer concrete mixture increased, the loss rate in the strength of the samples exposed to acid solutions decreased. H_3PO_4 solution caused less weight loss in samples than other acid solutions. It was seen that the samples immersed in H_3PO_4 and HCl solutions shrank and that the samples immersed in HF and H_2SO_4 solutions expanded. Softening, cracking and corruption occurred on the surfaces of the samples exposed to the acid solutions for 12 weeks. With increasing EFS ratio in the mixture, the deterioration of the samples' surfaces exposed to acid solutions decreased. Ettringite formations were seen in the SEM images of geopolymer concretes immersed in 5% H_2SO_4 solution.

1 Introduction

Geopolymer binders are seen as an alternative to Portland cement (PC) because of their resistance to acid and sulfate attacks and their high early strength in addition to being environmentally friendly [1]. Geopolymer is considered to be the third-generation binder after lime and normal PC. The term "geopolymer" is generally used to describe an amorphous aluminosilicate. In addition, geocements, inorganic polymers, alkali-activated binders, alkali-bonded ceramics and hydrocarbons are widely used. Although there are so many terms, all of these terms describe materials synthesized using the same chemistry [2]. The geopolymerization event is a geosynthesis, i.e., it is a reaction that chemically combines minerals that form aluminosilicates [3]. Geopolymerization is an exothermic event; it is assumed that it provides the formation of three-dimensional macromolecular structures by means of oligomers [4]. The main criterion for a geopolymer is that the welding materials are amorphous and have sufficient reactive glass content. Alkali activators such as sodium hydroxide, sodium silicate, potassium hydroxide and potassium silicate are used in the activation of aluminosilicate materials [2]. The iron and chromium oxides in the metal are reduced in the electric arc furnaces using metallurgical coke. At the same time, it is reduced to a part of the silicate. The metal produced in this way is classified as "charge chrome." Charge chrome contains 53% Cr, 7% C and 4–5% Si in the structure [5]. Expanded slag and air-cooled slag are generally used as aggregate in concrete and bitumen applications. It can be used as an additive to cement if it is granulated and turned into a fine powder. Slag can be used as an additional raw material to produce cement clinker [6].

The strength of the PC is good under adverse circumstances. However, it has a weak resistance to acid attack, sulfate attack and high temperatures. Serious damage

✉ Mehmet Burhan Karakoç
   mehmet.karakoc@inonu.edu.tr

   Ahmet Özcan
   ahmet.ozcan1@dpu.edu.tr

1   Department of Civil Engineering, Faculty of Engineering, Inonu University, 44280 Malatya, Turkey

2   Department of Civil Engineering, Kütahya Dumlupınar University, Kütahya, Turkey

occurs to PC exposed to acid attack due to the deterioration of $Ca(OH)_2$ and the degradation of hydrated silicate and aluminum phases. To improve the resistance of normal PC against acid attack, there are many studies conducted by combining different mixtures of fly ash (FA) and silica fume with PC and positive results have been obtained from these studies. It is thought that geopolymer binders may improve the acid resistance of concrete because aluminum silicate is more reliable than hydrated calcium silicate in terms of achieving structural integrity [1].

Sulfuric acid, which is a highly aggressive acid type, reacts with the free lime $(Ca(OH)_2)$ in the concrete and converts it to gypsum $(CaSO_4 \cdot 2H_2O)$. The reaction between these formed gypsum crystals and calcium aluminate produces a more destructive effect. As a result of the reaction between these two products, ettringite $(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$ is formed, which is a less soluble product. Ettringite is a highly expanding compound that causes cracks in concrete because of internal pressure in the concrete [7]. As a result of the interaction of the geopolymer with the acid solution, the exchangeable cations (Na^+, K^+) in the polymer can be replaced with hydronium ions [8].

Ariffin et al. [9] blended ground fuel ash and palm oil fuel ash with alkaline activators and produced geopolymer concrete samples. These samples were immersed in an acid solution for 18 months. Acharya and Patro [10] produced concrete containing 10, 20, 30 and 40% ferrochrome ash and 7% lime replacement of cement. The samples were immersed in 1% H_2SO_4 solution for 28, 91 and 180 days. Nuaklong et al. [11] produced metakaolin-added geopolymer concretes using high-calcium FA. The samples were immersed in 3% sulfuric acid solution for 120 days. Bakharev [8] determined the acid resistance of geopolymer materials produced using alkali-activated FA. The samples were exposed to 5% H_2SO_4 solution for 150 days. Singh and Siddique [12] investigated the use of coal bottom ash as fine aggregate in concrete. The samples were immersed in 3% H_2SO_4 solution after completing their cures for 84 days. Ganesan et al. [13] produced steel fiber-added FA-based geopolymers activated with sodium hydroxide and sodium silicate. Cube samples were exposed to 3% sulfuric acid solution for 180 days. Deb et al. [14] investigated the acid resistance of nanosilica-added FA-based geopolymer mortars. The samples were immersed in 3% H_2SO_4 solution for 90 days after curing. Djobo et al. [15] produced volcanic ash-based geopolymer mortars. The samples were cured at two different temperatures (27 °C and 80 °C). The samples were immersed in 5% H_2SO_4 solution for 180 days after 28 days of curing. Mehta and Siddique [16] produced normal PC-added FA-based geopolymer concretes. These samples were immersed in 2% H_2SO_4 solution for up to 365 days. Sata et al. [17] produced geopolymer mortars using lignite bottom ash and compared the samples with mortars containing PC and PC + FA. Samples were

exposed to 3% H_2SO_4 solution and examined for 120 days. Wei et al. [18] produced vanadium tailing-based geopolymer paste. The samples were immersed in 3% sulfuric acid solution for 28 days. Kwasny et al. [19] produced solid clay-based geopolymer mortar samples with two different compressive strengths (37.5 and 60 MPa). These mortar samples were soaked in three different concentrations (0.10, 0.31 and 0.52 mol/L) sulfuric acid and hydrochloric acid solutions for 8 weeks. When the above studies were examined, it was seen that the most common solution used to determine the acid resistance of concrete was H_2SO_4 solution of different concentrations. In addition, HCl solution was used in some studies. In addition to these solutions, HF and H_3PO_4 solutions were used in this study.

When the literature was examined, it was observed that the studies on the behavior of the Elazığ ferrochrome slag (EFS)-based geopolymer concrete under the acid effect were insufficient. Blast furnace slag (BFS) in different proportions was added to geopolymer concrete mixtures to improve the behavior of EFS under acid action. In addition, there is not enough data about the length change of the samples under acid attack. The effects of four different acid solutions on geopolymer concrete were investigated and their effects were compared with each other.

Current research gives a better idea of the behavior of the two different binder-based geopolymer concretes in the acidic environment. In this study, EFS- and BFS-based geopolymer concretes were produced and these were exposed to concentrations of 5% phosphoric acid (H_3PO_4), hydrochloric acid (HCl), hydrofluoric acid (HF) and sulfuric acid (H_2SO_4) solutions. Compressive strengths, ultrasonic pulse velocities (UPV), weight and length changes of the samples were measured to determine the damage caused by these acids. Five groups of geopolymer concrete mixes were produced using EFS instead of BFS from 0 to 100% with a 25% rate of increase. Results of the samples that were immersed in acid solutions for 12 weeks were examined and compared with the literature.

2 Experimental Program

2.1 Materials

The EFS was granulated, and then EFS that passed the 45-µm sieve was used in geopolymer concrete mixtures. The specific gravity of EFS was 2.86 g/cm³. The specific surface area and specific gravity of BFS that was supplied in milled form were 3996 cm²/g and 2.86 g/cm³, respectively. SEM images of EFS and BFS are shown in Fig. 1. The chemical composition of EFS and BFS is given in Table 1. Na_2SiO_3 and 10 M NaOH solution were used as the alkaline activator. River aggregate was used as thin and coarse aggregate. The
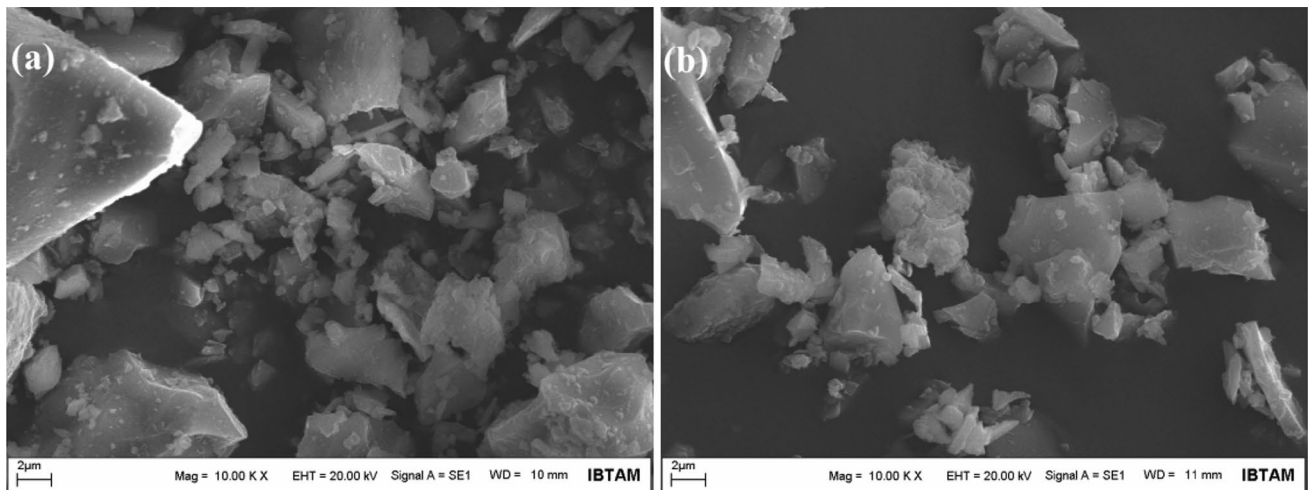
Fig. 1 SEM images: **a** EFS, **b** BFS

Table 1 Oxide composition of EFS and BFS

Component (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Cr_2O_3	SO_3	S^{-2}	Na_2O	K_2O	TiO_2	Mn_2O_3	LOI
EFS	33.80	25.48	0.61	1.10	35.88	2.12	–	–	–	–	–	–	–
BFS	32.47	9.94	1.25	32.45	9.31	–	0.82	0.33	0.31	0.85	1.16	3.51	3.6

Table 2 Properties of alkali activators

Property	Pure sodium hydroxide	Sodium silicate
Molecular formula	NaOH	Na_2SiO_3
Moleculer mass (g/mol)	40.00	122.06
Color	White	White
pH	13–14	–
Relative density (g/cm^3)	2.13	1.38
Na_2O content (%)	–	8.9
SiO_2 content (%)	–	27.5
H_2O content (%)	–	63.6

Table 3 Properties of river aggregate

Property	Aggregate (mm)	
	0–4	4–8
Dry specific gravity (kg/m^3)	2.39	2.60
Saturated dry surface specific gravity (kg/m^3)	2.47	2.63
Visible specific gravity (kg/m^3)	2.55	2.65
Water absorption rate (%)	2.40	1.30

properties of the activators and the river aggregate are given in Tables 2 and 3, respectively.

2.2 Mixing, Casting and Curing

The maximum aggregate size was chosen as 8 mm. The ratio of grain size of the aggregate was determined as 70% for 0–4 mm and 30% for 4–8 mm. The binder dosage for the geopolymer concrete mixture was selected to be 400 kg/m^3. Five groups of geopolymer concrete mixes were produced using 0, 25, 50, 75 and 100% by weight of BFS instead of EFS. As a result of preliminary experiments, the optimum silica modulus (1.5), the water/binder ratio (0.43), the molarity of NaOH solution (10 M) and the content of sodium oxide (10%) were determined. The mixture amounts of geopolymer concretes are given in Table 4.

The prepared geopolymer concrete mixtures were molded in $50 \times 50 \times 50$ mm^3 and $40 \times 40 \times 160$ mm^3 steel molds. After the geopolymer concrete mixture was placed in the molds, the molds were wrapped with aluminum foil and placed in a drying oven at 80 °C. The samples were stored for 24 h in the drying oven and then removed from the molds and cured in water for 27 days at 23 ± 1 °C.

Measurements to determine acid resistance of geopolymer concretes were made in accordance with the procedure in ASTM C267 [20]. The samples were immersed in 5% H_3PO_4, 5% HCl, 5% HF and 5% H_2SO_4 solutions for 12 weeks. The pH values of H_3PO_4, HCl, HF and H_2SO_4 solutions were 1.91, 0.72, 3.13 and 1.44, respectively. The biweekly change in the pH values of the solutions is shown in Fig. 2. The control

Table 4 Amounts of materials in the mixture (kg/m^3)

Mixture	EFS	BFS	Na$_2$SiO$_3$	10 M NaOH solution	Aggregate (mm)	
					0–4	4–8
E0	–	400	218.18	46.48	1111.07	507.02
E25	100	300	218.18	46.48	1111.07	507.02
E50	200	200	218.18	46.48	1111.07	507.02
E75	300	100	218.18	46.48	1111.07	507.02
E100	400	–	218.18	46.48	1111.07	507.02
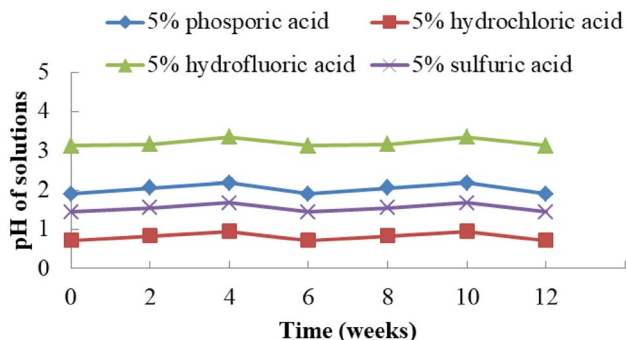
Fig. 2 Change in pH of the solutions depending on the time

sample was cured in water for the same period. The prepared acid solutions were renewed at 4-week intervals. Before starting the measurements, the samples were removed from the solution and the surfaces were cleaned with a soft brush under tap water and weight measurements of samples were made after waiting half an hour in the laboratory. The weight and length changes of samples were determined at 1-, 2-, 4-, 6-, 8-, 10- and 12-week periods; the compressive strengths and UPV measurements of the samples were determined at 4-, 8- and 12-week periods and the visual changes of the samples were examined. The UPV and compressive strength values of geopolymer concrete samples were tested according to ASTM C597 [21] and ASTM C39 [22], respectively. For each group, three specimens were tested and averaged.

Visual observations were made with the naked eye on the geopolymer concrete samples exposed to different solutions. The microstructures of the samples immersed in the solution were analyzed at the end of 12 weeks. Scanning electron microscopy (SEM) was performed to examine the microstructures of the samples. SEM studies were carried out on gold-coated fractured surfaces of geopolymer concrete samples. The SEM analysis was done using a Leo EVO-40.

3 Results and Discussion

3.1 Compressive Strength

The compressive strengths of the samples immersed in acid solutions were measured after 4, 8 and 12 weeks. The compressive strength values of the samples are given in Table 5 and Fig. 3. It was observed that the compressive strength values of the samples exposed to acid solutions decreased. When the effect of acid solutions on the compressive strength of samples was examined, it was seen that the negative effects were in the order $H_2SO_4 > HF > HCl > H_3PO_4$ solutions.

As the EFS ratio in the geopolymer concrete mixtures increased, the loss rate in the compressive strength of geopolymer concrete exposed to acid solutions decreased. When the studies on concrete exposed to acid effects in the literature [1, 7, 23] were examined, it was seen that acids interacted with the calcium components in the concrete and the concrete samples were damaged. In this context, the authors think that BFS, which contains more than 30 times more CaO than EFS, is more affected than EFS by acid solutions.

When the results were examined, there were decreases in the compressive strength of whole samples depending on the waiting period of the samples in acid solutions. While 5% H_3PO_4 solution had the least effect, 5% HCl, 5% HF and 5% H_2SO_4 solutions significantly reduced compressive strengths of the samples. Baradan et al. [23] reported that the attack speed of HCl, HF and H_2SO_4 solutions was fast and that of H_3PO_4 solution was medium. Based on this information, it was thought that 5% H_3PO_4 solution has less effect than other acid solutions.

Bakharev [8] stated that when the compressive strength of geopolymers exposed to 5% H_2SO_4 solution for 150 days was examined, the best resistance was obtained with NaOH-activated geopolymer. Strength losses at the end of 60 days were determined as 89% and 82% for geopolymers activated with NaOH + KOH and Na$_2$SiO$_3$, respectively. Deb et al. [14] reported that strength losses of nanosilica free mortars were in the range of 30–41%, while the strength loss of nanosilica containing 2% was in

Table 5 Compressive strength values of geopolymer concrete samples exposed to acid attack

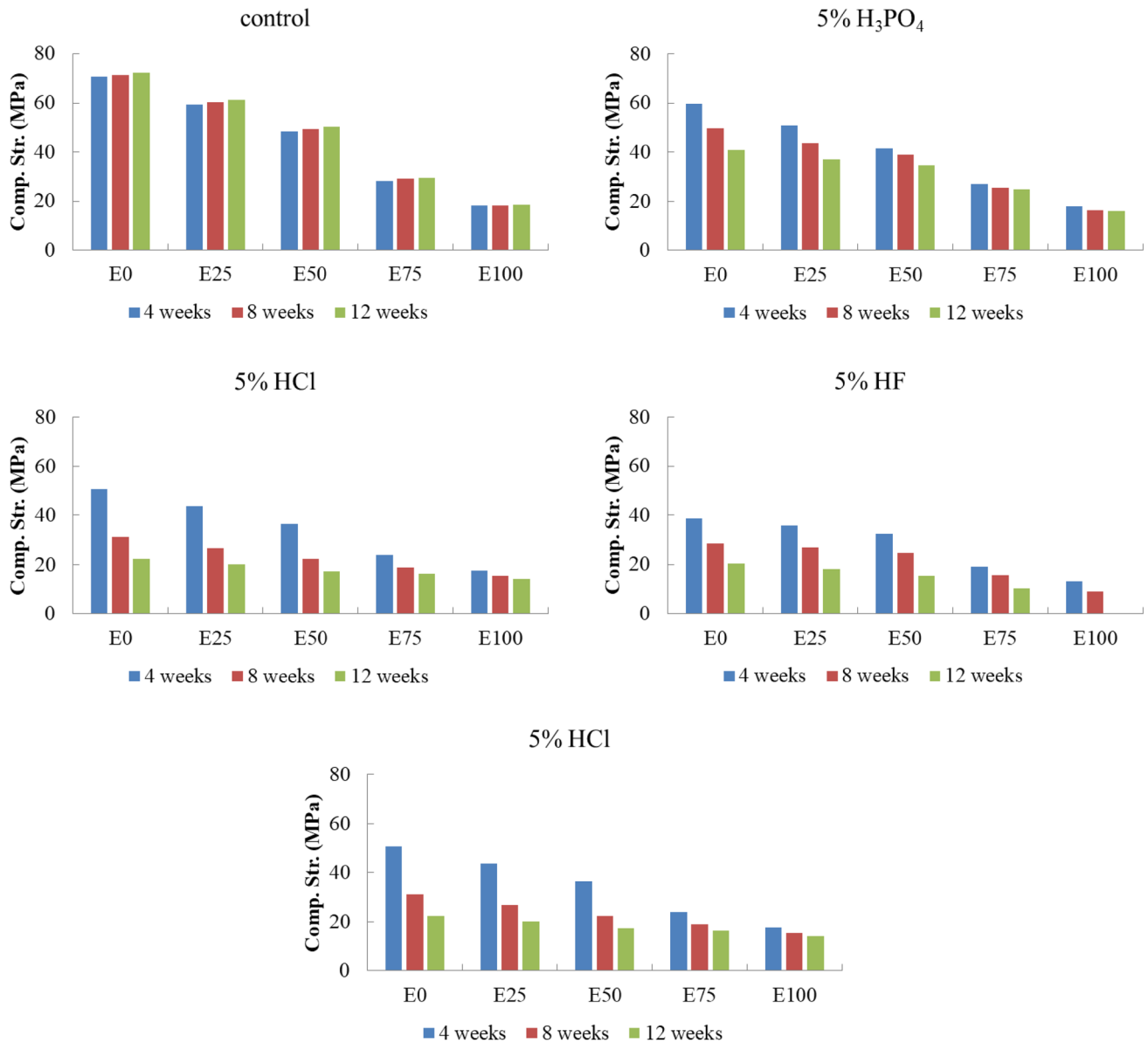| Sample	4 weeks					8 weeks					12 weeks				
	Control	5% H_3PO_4	5% HCl	5% HF	5% H_2SO_4	Control	5% H_3PO_4	5% HCl	5% HF	5% H_2SO_4	Control	5% H_3PO_4	5% HCl	5% HF	5% H_2SO_4
E0															
Comp. strength (MPa)	70.65	59.64	50.47	38.51	42.87	71.23	49.74	31.06	28.45	19.35	72.45	40.91	22.32	20.32	9.89
Reduction %		15.58	28.56	45.49	39.32		30.17	56.39	60.06	72.83		43.53	69.19	71.95	86.35
Standard deviation	0.84	5.23	6.56	4.87	3.75	0.75	3.78	2.86	4.06	3.89	0.95	4.15	2.79	3.56	5.03
E25															
Comp. strength (MPa)	59.48	50.77	43.52	35.77	37.95	60.35	43.54	26.55	26.84	17.27	61.25	36.98	19.91	18.15	8.95
Reduction %		14.64	26.83	39.86	36.20		27.85	56.01	55.53	71.38		39.62	67.49	70.37	85.39
Standard deviation	0.92	4.75	3.56	2.89	3.74	0.82	2.89	3.15	2.25	3.75	0.93	3.77	2.56	1.98	3.75
E50															
Comp. strength (MPa)	48.43	41.59	36.46	32.45	31.24	49.21	39.06	22.23	24.88	14.54	50.17	34.54	17.35	15.23	8.26
Reduction %		14.12	24.72	33.00	35.49		20.63	54.83	49.44	70.45		31.15	65.42	69.64	83.54
Standard deviation	0.76	2.65	3.17	2.85	2.51	0.81	2.55	2.75	2.48	3.56	0.85	1.89	2.06	3.18	2.68
E75															
Comp. strength (MPa)	28.35	26.84	23.74	19.04	18.53	29.17	25.37	18.75	15.54	13.95	29.34	24.64	16.17	10.27	8.11
Reduction %		5.33	16.26	32.84	34.64		13.03	35.72	46.73	52.18		16.02	44.89	65.00	72.36
Standard deviation	0.68	3.23	2.89	3.15	4.13	0.73	2.89	2.95	1.15	1.68	0.89	2.63	1.98	2.32	4.28
E100															
Comp. strength (MPa)	18.14	17.73	17.51	13.25	14.37	18.17	16.38	15.34	9.06	4.07	18.38	15.85	13.96	0	0
Reduction %		2.26	3.47	26.96	20.78		9.85	15.58	50.14	77.60		13.76	24.05	100	100
Standard deviation	0.52	4.32	3.48	3.65	4.12	0.61	2.95	3.18	2.73	1.86	0.76	3.84	3.52	4.03	2.89

Fig. 3 Compressive strength values of the samples in the acid solutions

the range of 9–11%. Djobo et al. [15] reported that the loss percentages of the compressive strength of the geopolymer mortars immersed in 5% H_2SO_4 solution for the samples cured at 27 °C and 80 °C were 24% and 60%, respectively. Acharya and Patro [10] stated that 40% ferrochrome ash and 7% lime substitution samples were better than normal concrete against acid. According to the results of the studies given in the above literature, it was seen that there were decreases in the compressive strength of geopolymers exposed to acid. Likewise, it was observed that there were decreases in the compressive strength of geopolymer concrete samples exposed to acid solutions.

3.2 Ultrasonic Pulse Velocity

UPV measurements of the samples immersed in acid solutions were carried out at periods of 4, 8 and 12 weeks. UPV measurements of the samples are given in Table 6 and Fig. 4. As a result of the chemical reaction of the samples immersed in the HF solution, foaming and so on, formations occurred on the sample surfaces. UPV measurements of these samples could not be performed because of these formations. While evaluating the measurements for the samples, each group was evaluated within themselves.

Table 6 UPV values of geopolymer concrete samples exposed to acid attack

| Sample	4 weeks				8 weeks				12 weeks			
	Control	5% H_3PO_4	5% HCl	5% H_2SO_4	Control	5% H_3PO_4	5% HCl	5% H_2SO_4	Control	5% H_3PO_4	5% HCl	5% H_2SO_4
E0												
UPV (m/s)	4826	4702	4620	4461	4832	4570	4225	3895	4844	4392	3984	3589
Reduction %		2.57	4.27	7.56		5.42	12.56	19.39		9.33	17.75	25.91
Standard deviation	10	18	26	35	27	23	27	25	23	33	15	22
E25												
UPV (m/s)	4741	4623	4502	4408	4751	4529	4223	3824	4762	4388	3929	3036
Reduction %		2.49	5.04	7.02		4.67	11.11	19.51		7.85	17.49	36.25
Standard deviation	12	25	15	26	45	32	38	23	18	17	28	21
E50												
UPV (m/s)	4606	4463	4340	4096	4621	4355	3878	3281	4639	4290	3746	2752
Reduction %		3.10	5.78	11.07		5.76	16.08	29.00		7.52	19.25	40.68
Standard deviation	13	16	42	34	32	22	28	18	17	12	19	24
E75												
UPV (m/s)	4288	4236	4119	3984	4315	4201	3996	3415	4320	4095	3855	3026
Reduction %		1.21	3.94	7.09		2.64	7.39	20.86		5.21	10.76	29.95
Standard deviation	13	35	27	29	29	15	24	31	26	25	16	32
E100												
UPV (m/s)	3921	3871	3845	3465	3924	3708	3582	2421	3950	3644	3316	1629
Reduction %		1.28	1.94	11.63		5.50	8.72	38.30		7.75	16.05	58.76
Standard deviation	26	19	33	21	23	34	18	14	23	13	24	38
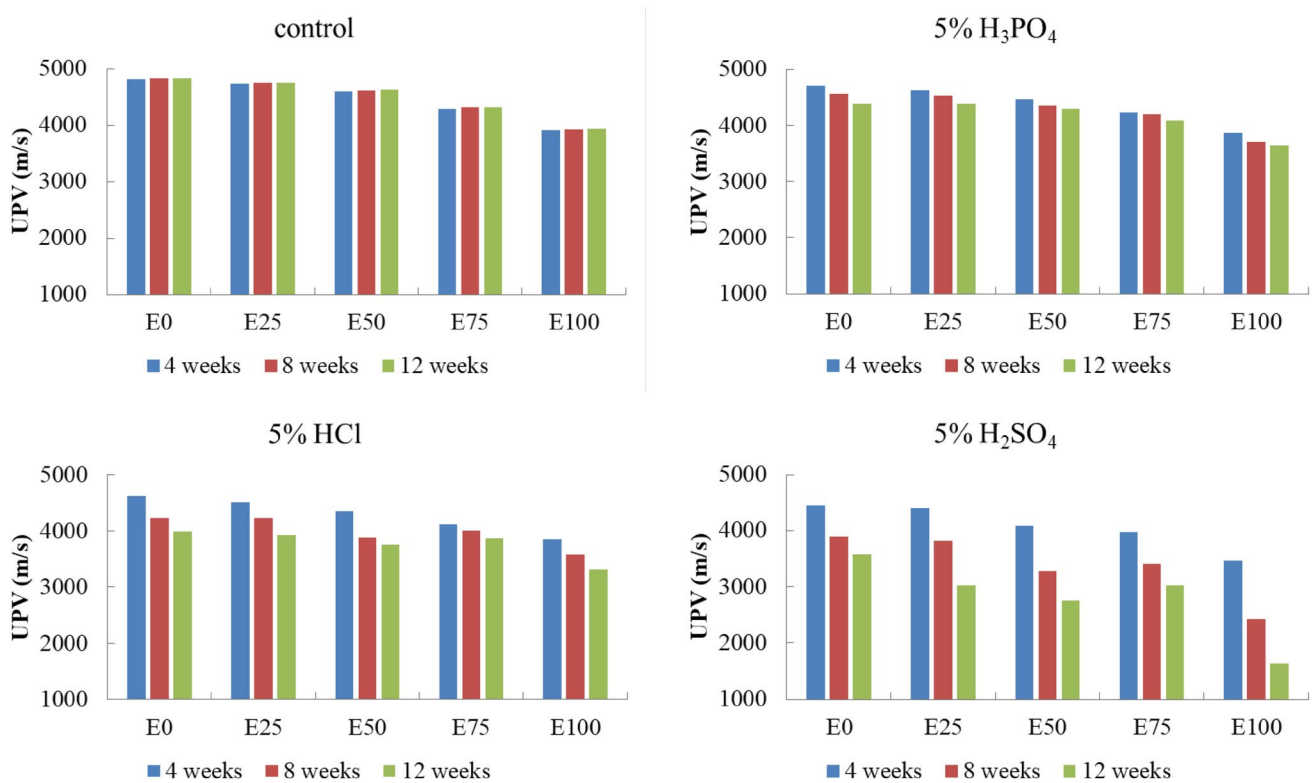
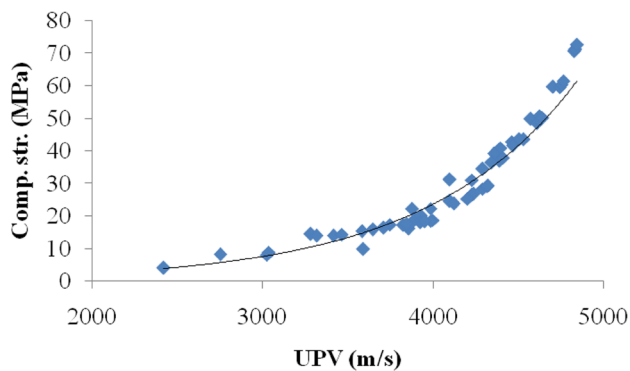**Fig. 4** UPV values of the samples in the acid solutions

Fig. 5 Relationship between compressive strength and UPV

3.3 Relationship Between Compressive Strength and UPV

The relationship between compressive strengths and UPV of the samples is shown in Fig. 5. Tharmaratnam et al. [24], Demirboğa et al. [25] and Omer et al. [26] used the following Eq. (1) to determine the relationship between compressive strength and UPV. In this equation f_c is the compressive strength, a and b are constants and V is the UPV value:

$$f_c = ae^{bV}. \tag{1}$$

When the results were examined, it was observed that the exponential relationship between the UPV values and the compressive strengths was consistent. The correlation coefficient of geopolymer concretes exposed to different environments was 0.95:

$$f_c = 0.2579e^{0.0011V}. \tag{2}$$

3.4 Weight Change

The weight changes of the samples immersed in the acid solution for 12 weeks were examined. The weight of all geopolymer concrete samples exposed to acid solutions decreased. The least weight loss was seen in the samples immersed in H_3PO_4 solution, while the weight losses of the samples immersed in HF, HCl and H_2SO_4 solutions were close to each other, as seen in Fig. 6. When the weight changes of the samples in 5% H_3PO_4 solution were examined, the weight losses were between 4.42 and 6.66% after 12 weeks. These values were between 10.33 and 12.94% for the samples in 5% HCl solution, between 8.01 and 14.28% for the samples in 5% HF solution and between 6.90 and 16.13% for the samples in 5% H_2SO_4 solution. The weight loss of geopolymer concretes in HCl and HF solutions were 2–2.5 times the weight loss of the samples in H_3PO_4 solution.
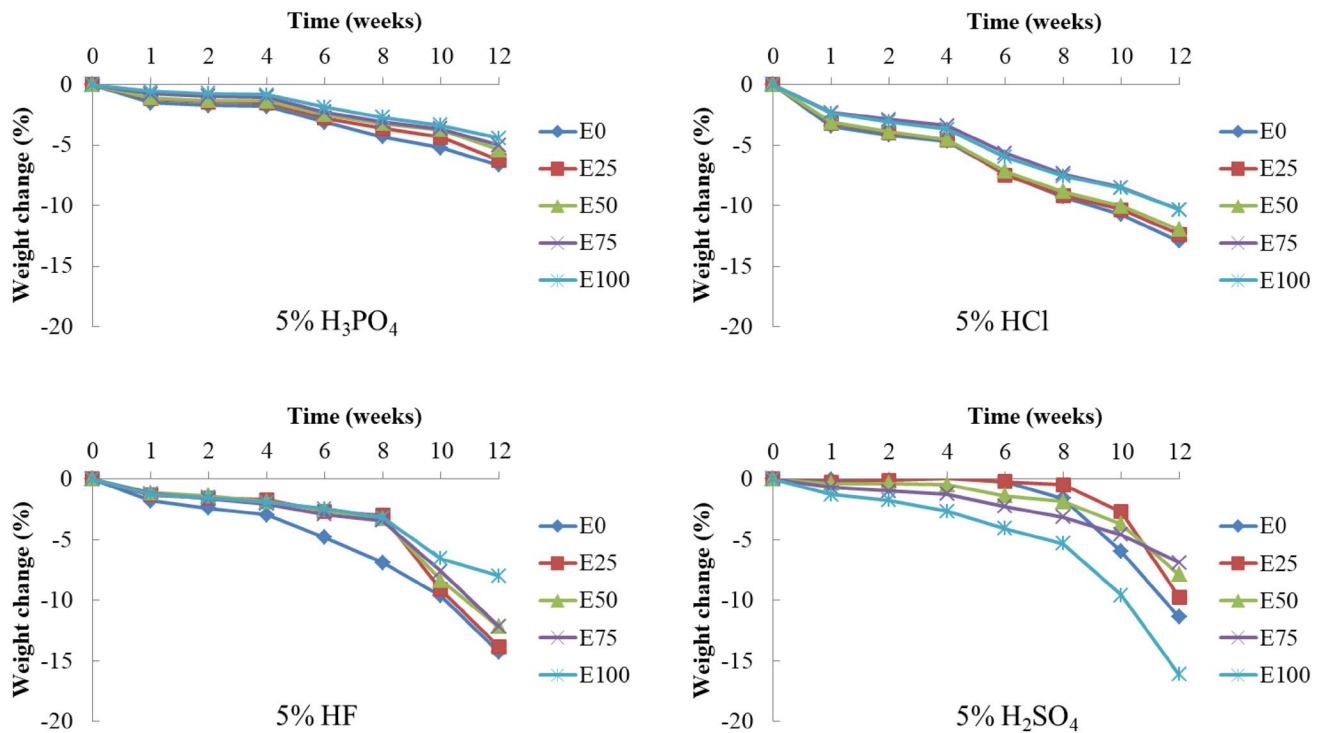
Fig. 6 Weight changes of the samples in the acid solutions

Bakharev [8] stated that the weight loss of FA-based geopolymer materials exposed to 5% H_2SO_4 solution for 150 days was between 1.96 and 12.43%. Sata et al. [17] reported that all of the bottom ash geopolymer mortars were less affected by H_2SO_4 attack than the PC mortars. The weight loss of the bottom ash geopolymer mortars was found to be less than 3.6%. Ariffin et al. [9] found that the weight loss of geopolymer concrete exposed to 2% H_2SO_4 for 18 weeks was 8%. Ganesan et al. [13] stated that adding steel fiber to FA-based geopolymer concrete exposed to 3% sulfuric acid solution for 180 days increased the weight loss in geopolymer concrete. Deb et al. [14] reported that the average weight losses of the geopolymer mortars immersed in 3% H_2SO_4 for 90 days decreased from 6 to 1.9% as a result of 2% added nanosilica. Djobo et al. [15] reported that the decrease in weight loss of volcanic ash-based geopolymer mortars in 5% H_2SO_4 solution was 3.51% and 3.1% for geopolymer mortar samples cured at 27 °C and 80 °C, respectively. Mehta and Siddique [16] stated that as the ratio of PC replacement in geopolymer concretes exposed to 2% H_2SO_4 solution increased, weight loss of samples increased. Kwasny et al. [19] stated that the weight losses in the samples exposed to HCl solutions were between 1 and 5% and the weight losses in the samples exposed to H_2SO_4 solutions were between 2 and 8%. When the results of the studies given in the literature are examined, it is seen that there were weight losses in geopolymers exposed to acid. Consistent with the results in the literature, weight losses were also observed in geopolymer concretes exposed to acid in this study.

3.5 Length Change

Samples completing the curing time were immersed in acid solutions for 12 weeks and the length changes of the samples were examined during this process. Length changes of the samples immersed in acid solutions are given in Fig. 7. As shown in Fig. 7, expansion occurred in the samples immersed in H_2SO_4 and HF solutions and shrinkage in the samples immersed in HCl and H_3PO_4 solutions. It is seen that when the length changes of the samples are compared, length changes of samples exposed to H_3PO_4 and HCl solutions were very small. In particular, it is known that H_2SO_4 produced ettringite in the microstructure of the geopolymer concrete [15]. Because ettringite is an expanding material in concrete, it causes volume expansion in concrete. It can be said that the reason for the greatest expansion of the geopolymer concrete samples in 5% H_2SO_4 is ettringite formation.

3.6 Visual Inspection

When the samples that had been immersed in the acid solutions were examined visually, softening, deteriorations and cracks on the surface of the samples, especially in H_2SO_4,
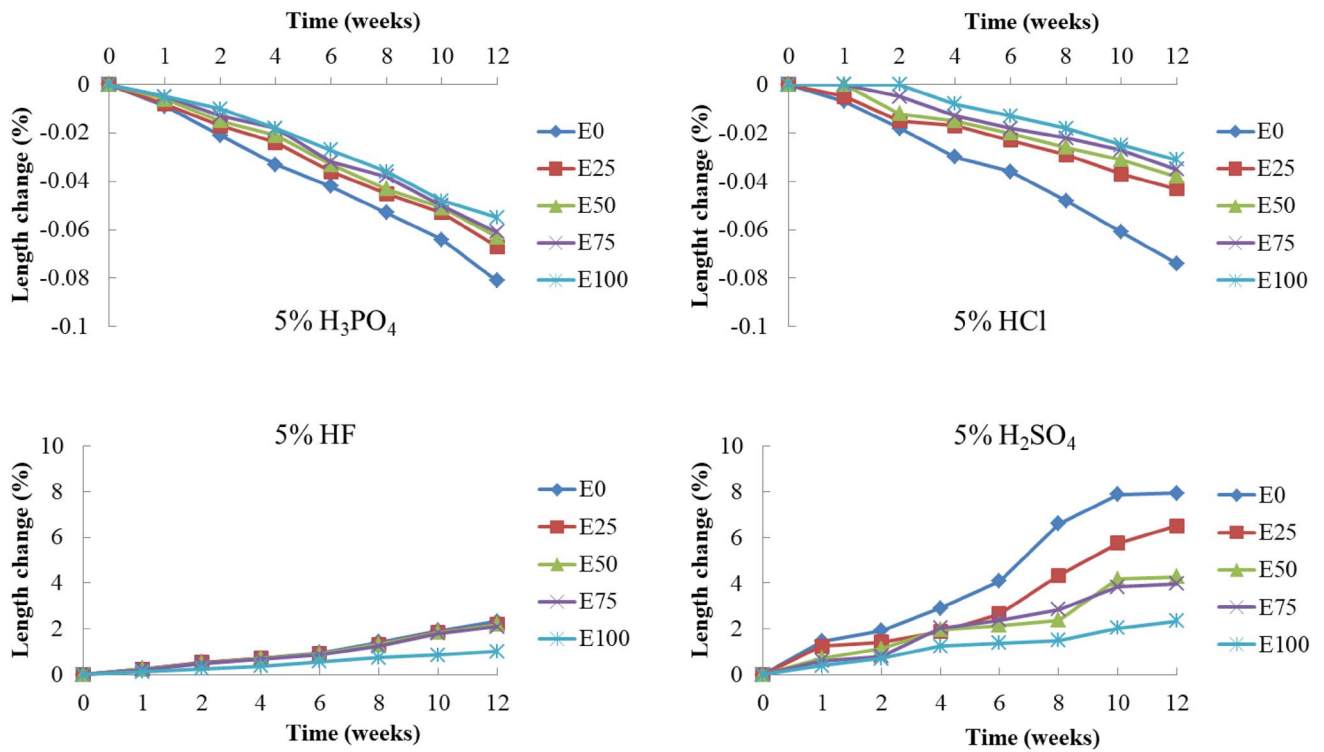
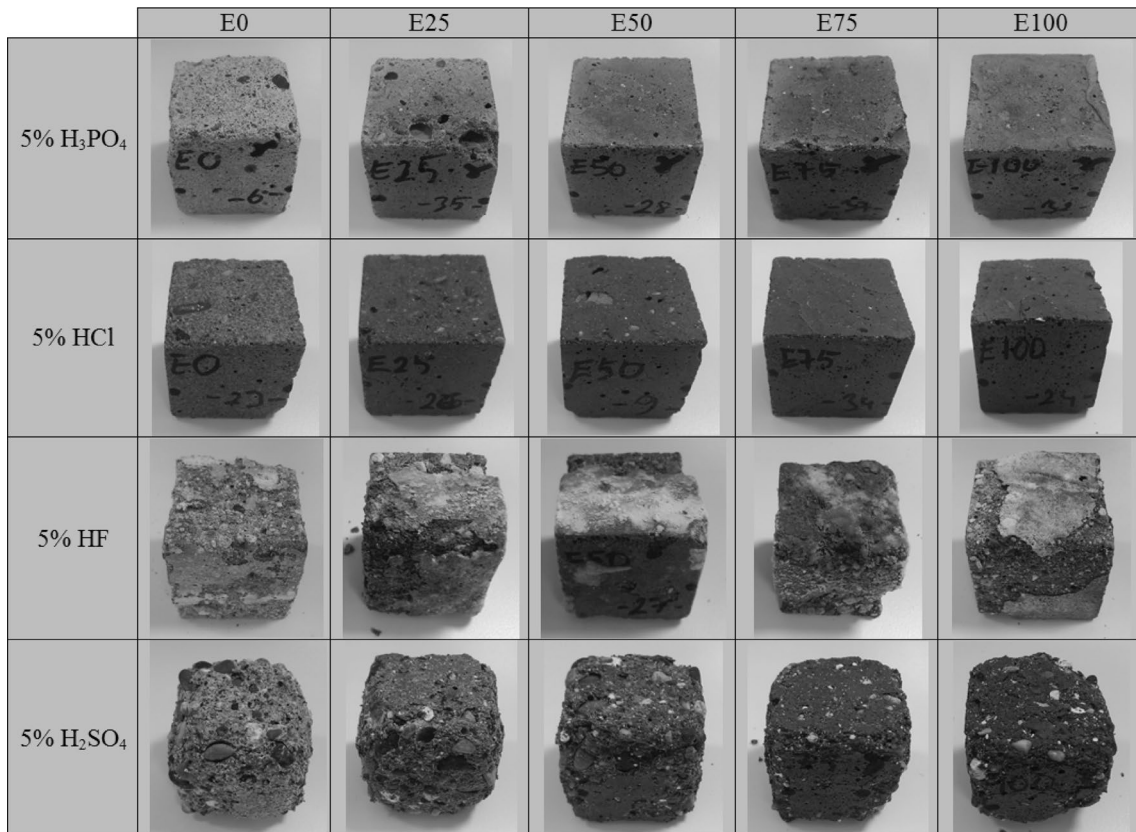**Fig. 7** Length changes of the samples in the acid solutions

Fig. 8 The appearance of samples immersed in different acid solutions for 12 weeks

H_3PO_4 and HF solutions, were observed. Samples immersed in H_2SO_4 solution had noticeable expansion. Crack formation had not occurred on the samples immersed in HCl solution, but with the increase in the waiting time of the samples, it was observed that the colors of the samples darkened. Softening and visible cracks of the surfaces of the samples immersed in H_2SO_4, HF and H_3PO_4 solutions occurred. Samples exposed to acid solutions for 12 weeks are shown in Fig. 8. It was observed that softening and deterioration of the surfaces of geopolymer concrete samples decreases as the amount of EFS increases, and, therefore, EFS was considered to be more resistant to acid than BFS.

The fracture surfaces of the samples exposed to acid solutions for 12 weeks are shown in Fig. 9. When the fracture surfaces of the samples were examined, it was seen that the acid solutions distort the geopolymer gel structure about 3 mm from the concrete surface (as seen in Fig. 9).

3.7 Microstructure Analysis

SEM images of geopolymer concrete samples which were immersed in 5% H_3PO_4, HCl, HF and H_2SO_4 solutions for 12 weeks are given in Fig. 10. It is seen that geopolymer gel structure in the samples in 5% H_3PO_4 solution was disturbed. There were cracks and gaps in E0 and E100 coded geopolymer concretes immersed in 5% HCl solution. Large cracks occurred in E0 coded geopolymer concrete immersed in 5% HF solution. Geopolymer gel structure of E100 coded geopolymer concrete in 5% HF solution deteriorated and appeared to have gaps in the microstructure of the sample. There were cracks and gaps in the microstructure of the samples and the durability of these decreased due to these cracks and gaps.

It was seen that there were cracks in the microstructure of both E0 and E100 coded geopolymer concretes. As a result of the attack by sulfuric acid, ettringite occurred in the microstructure of the samples. Calcium hydration products are more susceptible to acid attack and if these are found in abundance, it caused degradation of mortar. The reason for the high SiO_2/Al_2O_3 ratio and the low Na_2O/Al_2O_3 ratio after degradation is the dissolution of Na and Al ions from geopolymer structures in the sulfuric acid solution [17]. A strong acid solution can attack the aluminosilicate structure of the geopolymer and cause the aluminates to disappear. This attack leads to the deterioration of Si–O–Al bonds, an increase in the number of Si–OH and Al–OH in the geopolymer and an increase of dimers and silicic acid ions in the solution. Therefore, this process leads to a loss of weight in geopolymer materials. Because of the breakage of Si–O–Si and Si–O–Al bonds in the polymer, crack formation on the aluminosilicate gel in the aggressive medium is
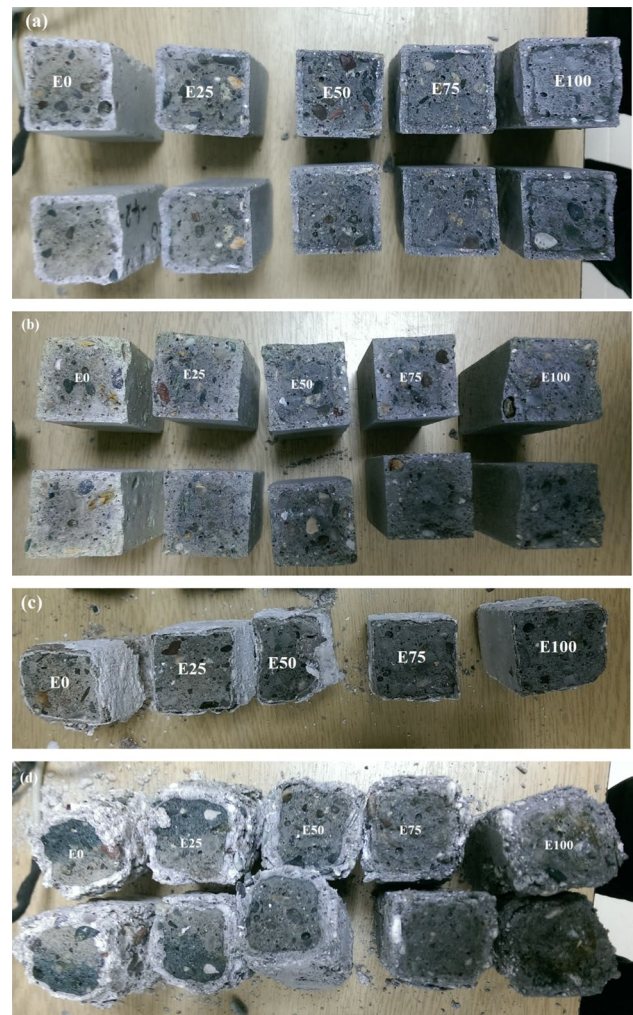

Fig. 9 Fracture surfaces of the samples exposed to acid solutions for 12 weeks, **a** 5% H_3PO_4, **b** 5% HCl, **c** 5% HF, **d** 5% H_2SO_4

likely [8]. In addition, Bakharev [8] stated that FA-based geopolymers exposed to 5% H_2SO_4 solution for 2 months were very porous and brittle. He reported that the Si/Al ratio in geopolymers exposed to sulfuric acid increased. In SEM observations, it was found that new crystals were formed in the matrix of samples exposed to the sulfuric acid solution. Sata et al. [17] stated that low calcium hydration products are more resistant to acid effect than high calcium hydration products in mortar. Djobo et al. [15] reported that microcracks and pores were formed in the microstructure of the geopolymer mortar cured at 80 °C due to the deterioration of the Si–O–Al bond in the geopolymer network as a result of the sulfuric acid attack. Mehta and Siddique [16] stated that the strength loss of samples exposed to acid occurred due to the reaction between the sulfuric acid and calcium ions.
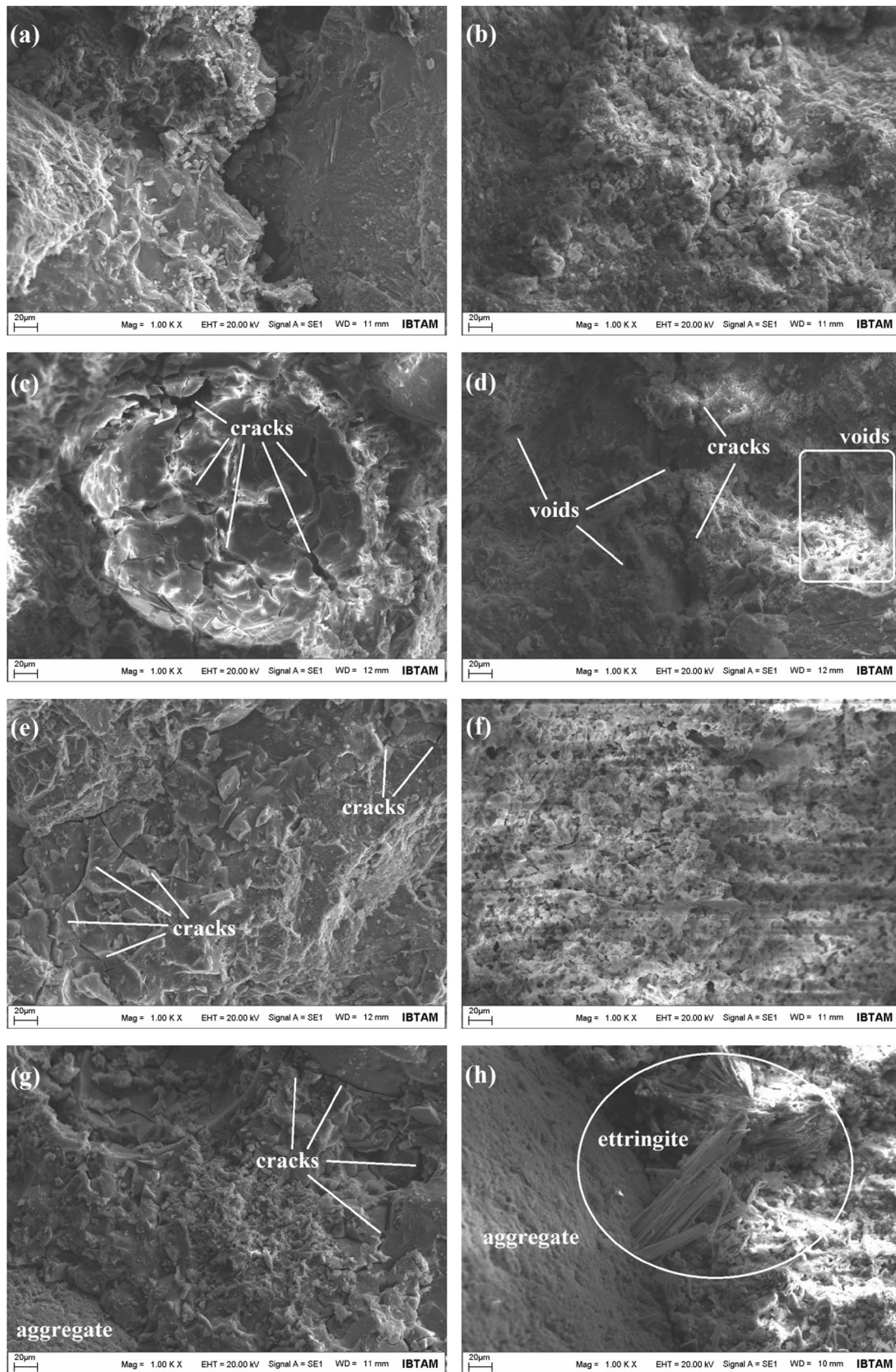
Fig. 10 SEM images of geopolymer concrete exposed to acid: **a** E0 and **b** E100 immersed in 5% H_3PO_4, **c** E0 and **d** E100 immersed in 5% HCl, **e** E0 and **f** E100 immersed in 5% HF, **g** E0 and **h** E100 immersed in 5% H_2SO_4

4 Conclusions

The main conclusions of this study can be listed as follows:

1. As the ratio of EFS in the geopolymer concrete mixture increased, the losses in the compressive strength of the geopolymer concretes exposed to acid decreased.
2. All the samples exposed to acid solutions showed weight loss. The H_3PO_4 solution caused less weight loss in the samples than other acid solutions.
3. The HF and H_2SO_4 solutions caused expansion of geopolymer concretes; H_3PO_4 and HCl solutions caused shrinkage of geopolymer concretes.
4. H_2SO_4, HF and H_3PO_4 solutions caused deterioration of the sample surfaces. The HCl solution only darkened the color of the samples.
5. The H_3PO_4, HCl, HF and H_2SO_4 solutions deteriorated the microstructure of geopolymer concrete. In particular, H_2SO_4 solution led to the formation of ettringite, which negatively affects the mechanical and durability properties of the concrete in the microstructure of the samples. As the ratio of EFS in the geopolymer concrete mixtures increased, deterioration in the microstructure of the samples decreased.
6. The effect of acid on the geopolymer concrete was $H_2SO_4 > HF > HCl > H_3PO_4$ solutions. EFS is more resistant to acid than BFS.

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