





## A comparative study on the sodium sulfate resistance of concrete with the supplementary cementitious materials

### Tamamlayıcı çimentolu malzemelerle betonun sodyum sülfat direnci üzerine karşılaştırmalı bir çalışma

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#### Abstract

Sulfate attack is one of the main factors causing durability problems in concrete. In this study, in order to evaluate the physical/chemical interaction of sulfate resistance, concrete mixtures with silica fume, blast furnace slag, fly ash, limestone filler, hydrated lime and Portland cement are investigated by conducting a series of experiments. Five different series of concrete mixtures containing the specified supplementary cementitious materials were developed with a water-binder ratio of 0.33 and a total binder content of 400 kg/m<sup>3</sup>. The concrete samples were exposed to lime-saturated water and sodium sulfate solution of 50 g/l for 365 days. The evaluation of sulfate resistance was done by the determination of compressive strength and change in weight. The improvement of the resistance to sulfate attack is assessed concerning the ratio of the mineral additives and results indicated that using the selected supplementary cementitious materials in the concrete mixtures significantly improves the durability performance.

**Keywords:** Sulfate attack, Sulfate resistance, Compressive strength, Concrete, Durability

#### 1 Introduction

In recent years, there is a great demand to minimize the quantity of Portland cement used in the construction industry because of the significant amounts of CO<sub>2</sub> release. Therefore, a large number of studies have been conducted about how environmental-friendly binders can be an alternative to Portland cement-based binders. For this purpose, the engineering properties of concretes containing different binder materials have received particular attention. Among these properties, concrete durability is a major concern, especially for structural design.

Sulfate attack is a severe and rapid degradation mechanism which may cause durability problems and induce critical damage in concrete structures [1]. The ingress of sulfate ions from the environment induces the sulfate attack. It results in expansion, weight loss, cracking, spalling and as a consequence, decrement in the mechanical properties of the Portland cement concrete. Sulfate resistance depends on many factors like cement composition, permeability of concrete, water/cement ratio, exposure conditions and period [2-9]. In order to improve the resistance of concrete to sulfate attack, permeability reduction is identified as the major parameter. One of the most common ways to achieve lower permeabilities is replacing cement with supplementary cementitious materials [10-12]. By the use of adequate amounts of supplementary cementitious materials as cement

#### Özet

Sülfat etkisi betonda dayanıklılık sorunlarına neden olan ana faktörlerden biridir. Bu çalışmada, sülfat direncinin fiziksel/kimyasal etkileşimini değerlendirmek için silis dumanı, yüksek fırın çürüfö, uçucu kül, kalker filleri, kireç ve Portland çimentosu ile elde edilen beton karışımları bir dizi deney yapılarak araştırılmıştır. Belirtilen tamamlayıcı çimentolu malzemeleri içeren, beş farklı seri beton karışımı, su/bağlayıcı oranı 0.33 ve toplam bağlayıcı içeriği 400 kg/m<sup>3</sup> alınarak üretilmiştir. Beton örnekleri, 365 gün boyunca kirece doymuş suya ve 50 g/l sodyum sülfat çözeltisine maruz bırakılmıştır. Sülfat direncinin değerlendirilmesi, numunelerin basınç dayanımı ve ağırlık değişiminin belirlenmesi ile yapılmıştır. Sülfat etkisine karşı direncin iyileştirilmesi, mineral katkı maddelerinin oranına göre değerlendirilmiş ve sonuçlar, beton karışımlarında seçilen tamamlayıcı çimentolu malzemelerin kullanılmasının, dayanıklılık performansını önemli ölçüde geliştirdiğini göstermiştir.

**Anahtar kelimeler:** Sülfat etkisi, Sülfat direnci, Basınç dayanımı, Beton, Dayanıklılık

replacement material, the amount of calcium aluminate (C<sub>3</sub>A) and calcium hydroxide (CH) decreases which plays a significant role to prevent the formation of destructive compounds such as gypsum and ettringite [13]. Therefore, in order to mitigate the potential durability problems related to sulfate attack and serve as green cement, supplementary cementitious materials usage is proposed. Accordingly, there are investigations on the assessment of sulfate attack induced Portland cement concretes, geopolymer-based concretes and mortars produced with supplementary cementitious materials [14-18]. These evaluations are usually based on such criteria as changes in compressive strength, length, weight, and microstructure.

Among the traditional supplementary cementitious materials, it is known that slag efficiently improves the sulfate resistance depending on the cement replacement level. On the other hand, the effect of the other mineral additives is an interest. Therefore, the purpose of this study is to discuss the role of the selected supplementary cementitious materials in reducing the sulfate attack in concrete. The results of the resistance to sulfate attack are presented in terms of the change in compressive strength and weight for the concrete mixtures containing different ratios of silica fume, blast furnace slag, fly ash, limestone filler, and hydrated lime.

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## 2 Materials and methods

### 2.1 Materials

In order to investigate the influence of different supplementary cementitious materials on the sulfate resistance of concrete, the following component materials were used in the experiments.

- Cement: Portland cement (PC) CEM I 42.5R used in this study was produced by Istanbul AkcanSA Cement Corp. The physical and chemical properties are given in Table 1.
- Aggregate: In the production of concretes, crushed limestone (4/8 and 8/16 mm) and sea sand (0/4 mm) were used as coarse and fine aggregates. In accordance with TS 706 [19], the aggregate mixing ratio was adjusted remaining between A16 and B16 standard curves.
- Mineral additives: Silica fume (SF), blast furnace slag (BFS), fly ash (FA), limestone filler (LS), and hydrated lime (HL) were used as supplementary cementitious materials in the concrete mixtures. The physical and mechanical properties of each are presented in Table 1.
- Mixing water: Tap water was used.

### 2.2 Method

In order to conduct the experiments to assess the sulfate resistance of concrete mixtures with different supplementary materials, silica fume (SF), blast furnace slag (BFS), fly ash

(FA), limestone filler (LS) and hydrated lime (HL) were replaced with Portland cement (PC). Five different series of concrete mixtures were developed with a water–binder ratio of 0.33 and a total binder content of 400 kg/m<sup>3</sup>. The reference concrete samples composed of ordinary Portland cement were designated as PC and the rest of the mixtures were designated as PC1, PC2, PC3, and PC4. In order to obtain the same workability with the reference samples, PC, 0.9% Glenium 27 was used in the other mixtures. The chemical compositions and mixture proportions of concretes are presented by mass in Table 2 and Table 3, respectively. In Table 3, %H indicates the air content of the specimens.

For each group, 30 concrete specimens were prepared and cast in steel moulds with dimensions of 7/7 cm. The specimens were demoulded after 24 h of casting and cured in lime-saturated water at 20 ± 2 °C for up to 28 days. After 28 days of curing, half of the specimens from each group were immersed in lime-saturated water and half of them were immersed in a Na<sub>2</sub>SO<sub>4</sub> solution of 50 g/l. For all the concrete specimens, the changes in compressive strength and weight were monitored for 365 days. Every 14 days, the specimens were taken out, weighed, and sulfate solutions were renewed. The 28th day was accepted as the curing initiation and the compressive strength and weight changes were determined on the 28th, 56th, 90th, 180th, and 365th days thereafter. Specimens from each mixture were categorized into five series and labelled. Specimens cured in lime-saturated water were labelled with the letter W, specimens cured in Na<sub>2</sub>SO<sub>4</sub> solution were labelled with the letter N.

**Table 1.** Chemical composition and physical properties of Portland cement and cementitious materials

Chemical Properties	PC (%)	SF (%)	BFS (%)	FA (%)	LS (%)	HL (%)
SiO <sub>2</sub>	19.86	83.84	35.80	51.50	0.20	0.19
Al <sub>2</sub> O <sub>3</sub>	5.50	0.46	13.78	23.08	0.13	0.13
Fe <sub>2</sub> O <sub>3</sub>	3.55	1.32	1.17	6.07	0.05	0.06
CaO	64.27	1.35	39.06	10.53	98.7	97.8
MgO	1.19	4.84	5.95	2.42		
SO <sub>3</sub>	2.66	1.30	1.31	1.32		
Na <sub>2</sub> O	0.23	0.53	-	0.77		
K <sub>2</sub> O	0.76	3.63	-	2.54		
CaCO <sub>3</sub> +MgCO <sub>3</sub>	-	0.75	-			
Cl <sup>-</sup>	-	0.14	-	0.0028		
Loss on ignition	1.81	2.47	0.71	1.06		
<b>Physical Properties</b>						
Specific gravity (gr/cm <sup>3</sup> )	3.14	2.21	2.93	2.20	2.62	2.21
SSA (m <sup>2</sup> /g)	0.399	13.855	0.550	4.033	0.360	6.67
Retained on 90µm sieve%	-	-	-	-		
Retained on 45µm sieve%	0.5	-	0.6	0.4		

**Table 2.** Mixture proportions of concrete specimens (%)

Sample Series	PC	BFS	SF	FA	LS	HL
PC	100	-	-	-	-	-
PC1	50	42	8	-	-	-
PC2	50	38	8	-	4	-
PC3	50	38	8	-	-	4
PC4	50	38	-	8	-	4

**Table 3.** Mixture proportions of PC and cementitious materials (kg/m<sup>3</sup>)

Sample Series	PC	Water	Sand	Crushed stone No: I	Crushed stone No: II	SF	BFS	FA	HL	LS	G27	%H
PC	397	131	919	443	644	-	-	-	-	-	3.2	0.6
PC1	195	129	903	435	633	31.2	163.8	-	-	-	3.5	2.3
PC2	192	127	889	428	623	31	146	-	15	-	3.5	3.8
PC3	198.5	131	919	443	644	32	151	-	-	16	3.6	0.6
PC4	198.5	131	919	443	644	-	151	32	-	16	3.6	0.5

### 3 Results and discussions

#### 3.1 Compressive strength change

The change in the compressive strength of the concrete specimens was checked during a period of 365 days. The compressive strength results of the five different series of concrete specimens immersed in lime-saturated water and sodium sulfate solution are presented in Table 4 and 5, respectively.

As can be seen from Table 5, all the concrete specimens exposed to the Na<sub>2</sub>SO<sub>4</sub> solution for 365 days have an increment in the compressive strength compared to the corresponding 28-day compressive strength of the reference specimens, PCN. At the age of 90 days, PC2N and PC3N series showed a slight decrement in compressive strength compared to the same age compressive strength of the reference specimens, PCN.

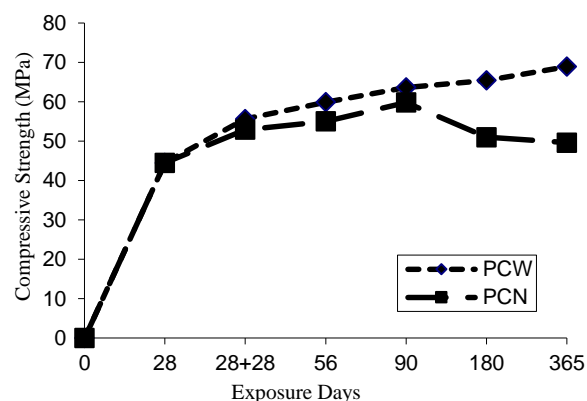
Also, by comparing the results of the compressive strengths of the specimens immersed in lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution, it is observed that all the specimens immersed in the Na<sub>2</sub>SO<sub>4</sub> solution showed a decrement compared to the corresponding specimens immersed in lime-saturated water. After 56 days of exposure to the Na<sub>2</sub>SO<sub>4</sub> solution, all the specimens containing supplementary cementitious materials showed a decrement in compressive strength except PC1N. Specimen series of PC1N showed a decrement after 90 days of exposure to the Na<sub>2</sub>SO<sub>4</sub> solution. After 365 days of immersion in the Na<sub>2</sub>SO<sub>4</sub>, the decrement in the compressive strength of PCN is 28%, PC1N is 2.5%, PC2N is 14%, PC3N is 11% and PC4N is 8.3%. In order to evaluate each group of concrete specimens immersed in lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution, compressive strength results of the reference specimen series and each group containing supplementary cementitious materials during 365 days are presented in Figure 1 and 2, respectively.

**Table 4.** Change in the compressive strength of concrete specimens immersed in lime-saturated water

Exposure days	Compressive Strength (MPa)				
	PCW	PC1W	PC2W	PC3W	PC4W
0	0	0	0	0	0
28	44.5	44.5	44.5	44.5	44.5
28+28	55.6	50	47.9	48.5	58.6
56	59.9	53.7	56.7	63.5	61.9
90	63.6	60.4	57.5	63.3	65.5
180	65.4	68.7	59.9	68.4	67.9
365	68.9	71.4	60.5	69.9	68.5

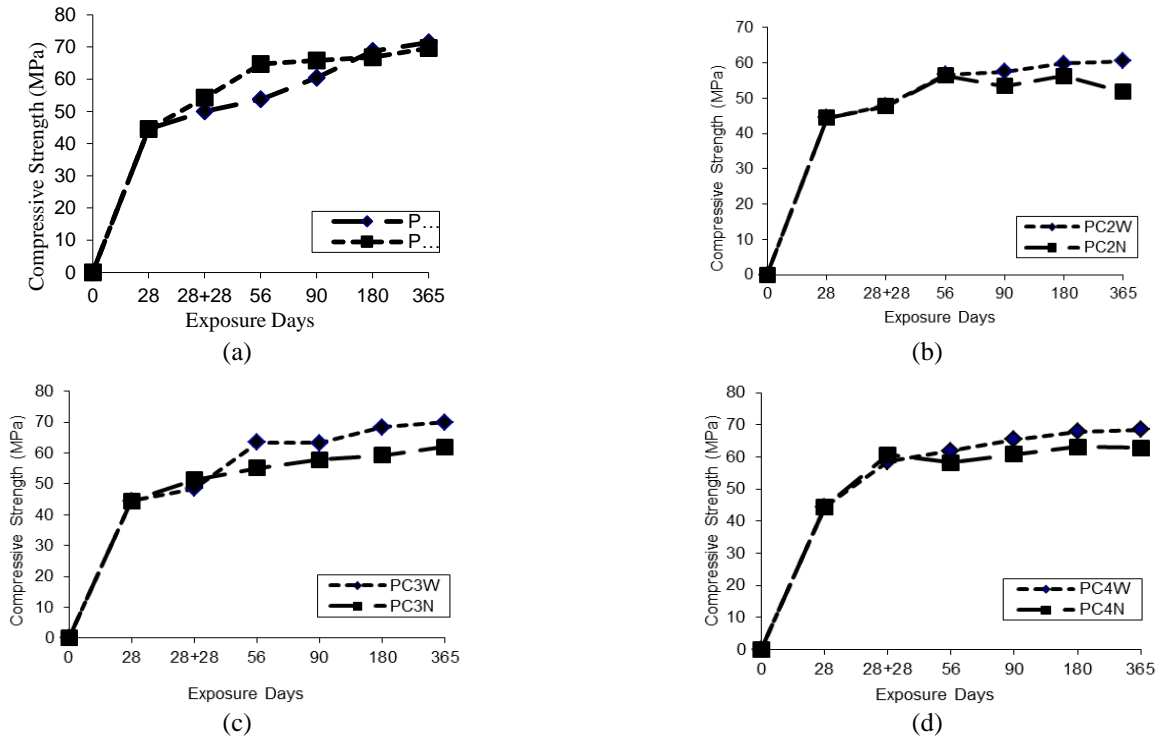
**Table 5.** Change in the compressive strength of concrete specimens immersed in Na<sub>2</sub>SO<sub>4</sub> solution

Exposure days	Compressive Strength (MPa)				
	PCN	PC1N	PC2N	PC3N	PC4N
0	0	0	0	0	0
28	44.5	44.5	44.5	44.5	44.5
28+28	52.9	54.2	47.8	51.3	60.7
56	55	64.7	56.4	55.2	58.2
90	59.8	65.8	53.4	57.9	60.9
180	51	66.8	56.3	59.3	63.1
365	49.6	69.6	51.8	62	62.8



**Figure 1.** Compressive strength change for PCW and PCN

When Figure 1 is examined, the compressive strength values of the reference concrete specimens immersed in lime-saturated water showed a steady increase with time. After the first 28th day, specimens kept in the sulfate solution showed a steady decrease until the end of curing. In addition to the increase in the decline of the compressive strengths after the 90th day, blisters and spalling were observed on the surface of the reference specimens. On the other hand, the other concrete series exposed to Na<sub>2</sub>SO<sub>4</sub> solution had neither blisters nor spalling on their surfaces. Figure 3 shows the physical condition of the reference specimens and the specimens containing the specified supplementary cementitious materials at the end of 365 days.



**Figure 2.** Compressive strength change for; (a) PC1W and PC1N, (b) PC2W and PC2N, (c) PC3W and PC3N (d) PC4W and PC4N



**Figure 3.** The appearance of the concrete specimens after the immersion in Na<sub>2</sub>SO<sub>4</sub> solution for 365 days

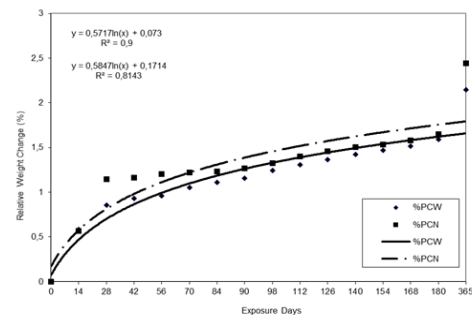
### 3.2 Weight Change

Weight change in the concrete specimens immersed in lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution was monitored for 365 days. At the end of the testing period, it is seen that the specimens exposed to Na<sub>2</sub>SO<sub>4</sub> solution gained more weight compared to the specimens immersed in lime-saturated water. On the other hand, as can be seen from Table 6, the highest weight gain is monitored in the PCW and PCN reference series as %2.14 and %2.44, respectively.

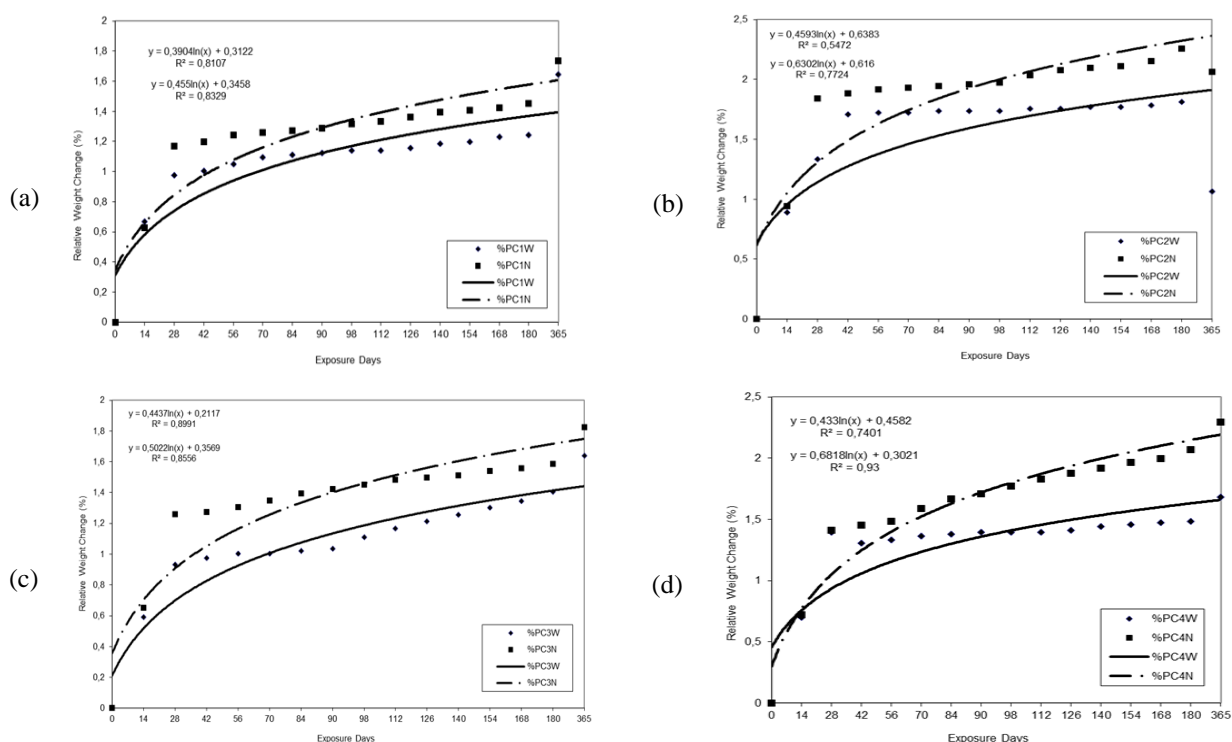
**Table 6.** Change in the weight of concrete specimens immersed in lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution

Sample Series	Weight change (%)	Sample Series	Weight change (%)
PCW	2.14	PCN	2.44
PC1W	1.64	PC1N	1.74
PC2W	1.06	PC2N	2.06
PC3W	1.64	PC3N	1.82
PC4W	1.68	PC4N	2.29

All the concrete specimens immersed in lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution showed a general steady weight gain for the whole testing period. In Figure 4, the relation between the relative weight change and exposure days is given for the reference specimen series in both lime-saturated water and Na<sub>2</sub>SO<sub>4</sub> solution whereas the same relation is presented for all the specimens containing supplementary cementitious materials in Figure 5.



**Figure 4.** Relation between relative weight change and exposure time for PCW and PCN



**Figure 5.** Relation between relative weight change and exposure time for; (a) PC1W and PC1N, (b) PC2W and PC2N, (c) PC3W and PC3N, (d) PC4W and PC4N

#### 4 Conclusion

In this study, the influence of  $\text{Na}_2\text{SO}_4$  solution on the different concrete specimen series prepared by Portland cement (PC) and the specified supplementary cementitious materials (SF, BFS, FA, LS, HL) was investigated for 365 days and evaluated by the comparison with the reference concrete series.

When the results are compared, it is concluded that all concrete specimens containing the specified supplementary cementitious materials have an increase in compressive strength at the end of 365 days of exposure to the  $\text{Na}_2\text{SO}_4$  solution. All mixtures containing supplementary cementitious materials showed good performance in  $\text{Na}_2\text{SO}_4$  solution of 50 g/l for the whole testing period. However, when the compressive strength results are compared, it is seen that among all the other specimens, PC1N showed the best performance. It is observed that the higher levels of cement replacement by BFS appear to be more effective. On the other hand, it is noticed that the PC2N specimen having LS supplement exhibits the lowest compressive strength in  $\text{Na}_2\text{SO}_4$  solution.

When the weight change of the concrete specimens immersed in lime-saturated water and  $\text{Na}_2\text{SO}_4$  solution were compared at the end of 365 days, it is concluded that the specimens exposed to  $\text{Na}_2\text{SO}_4$  solution gained more weight compared to the specimens immersed in lime-saturated water. It can be said that the absorption of the  $\text{Na}_2\text{SO}_4$  solution caused weight gain in the specimens. On the other hand, among the specimens with mineral admixtures immersed in  $\text{Na}_2\text{SO}_4$  solution, the smallest amount of weight gain is observed in PC1N as 1.74% and the highest in PC4N

as 2.29%. Compared to lime-saturated water curing, the weight increment was higher for the concrete specimens containing different types of cementitious materials in different percentages. If the changes in the weight of the specimens both in lime saturated water and  $\text{Na}_2\text{SO}_4$  solution are evaluated separately, it is seen that with respect to the reference series PCW and PCN, all the other series showed weight loss at the end of 365 days.

As a result, in this research, it is seen that the studied supplementary cementitious materials offer properties comparable to those of Portland cement with a much reduced  $\text{CO}_2$  footprint and a potential of a performance advantage over traditional types of cement in certain applications.

#### Conflict of interest:

The authors declare that there is no conflict of interest.

**Similarity rate (iThenticate):** 18%

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