Environmental Effects of Sulphate on Conventional Concrete Based on Portland Composite Cement

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Abstract*—Concrete performances have weaknesses; one of those weaknesses is that it is significantly affected when put in a high sulfate and chloride environment. This study aims to investigate sulfate's effect on PCC concrete's performance. In this research, PCC concrete was immersed in water for 28 days and conducted after the casting. After being soaked in water, three immersed specimens were removed and immersed in magnesium sulfate solution for 24 days and 84 days. In contrast, three others were removed and immersed in natrium sulfate solution for 24 days and 84 days. The observation showed that PCC concrete's average compressive strength test with water immersion was 42.17 Mpa. It meets the SNI 2847:2019 Indonesian standard for sulfate classification S1. The specimens decreased to 30.74 Mpa after being soaked in the magnesium sulfate solution for 28 days and again reduced to 25.39 Mpa at 84 days. The average compressive strength of specimens bathed in the sodium sulfate solution for 28 days was 32.19 Mpa. It decreased to 28.03 Mpa at the age of 84 days. The results of this study show that the compressive strength of PCC concrete soaked in sodium sulfate meets the SNI 2847:2019 standard for sulfate classification S1, which is more than 28 Mpa. The compressive strength of PCC concrete immersed in magnesium sulfate for 1 month (28 days) is more than 28 MPa. It meets the standard as well. Yet, the compressive strength of PCC concrete soaked in magnesium sulfate for 3 months (84 days) does not meet the standard.

***Keywords*—Portland composite cement, Concrete, Mechanical properties, Durability**

I. INTRODUCTION

Concrete is in great demand in the market due to its advantages compared to other construction materials. Globally, Portland cement contributes production of about 1.35 billion tons of CO2 per year, about 7% of the total greenhouse to the earth [1]. Concrete provides some advantages, such as it is easy to form when it is fresh, fireproof, and most importantly, its relatively high compressive strength. Further, concrete development is very rapid, starting from how it is made from concrete to the technology of its implementation. Concrete is obtained from mixing water, cement, coarse aggregates, and fine aggregates that involve mechanical and chemical interaction [10-20]. High-quality concrete has strength, durability, and effective serviceability [21-42]. Based on Indonesian standard SNI-03-6468-2000**,** high-strength concrete is defined as concrete that fulfills the requirement of required compressive strength of more than 41.4 MPa. The use of cement provides many advantages for the environment. The application of concrete is easy and familiar in fieldwork, and it is easy to form various cross-sections. The calculation is relatively easy, too, because it is commonly used. And this study applied Sika Viscocrete 3115 N Superplasticizer, which was used consistently with a content of 0.6%. [18-32].

Conventional concrete is generally used with a mixture of water, cement, sand, and gravel with an adjusted ratio according to the function and purpose of the concrete making. Concrete is glued together with cement and mixed with water to bind coarse or fine aggregates. Concrete is a material that cannot be removed in the construction process. Concrete also has an essential role in determining the age and strength of a building. It happens because concrete has its advantages and disadvantages. In 1994, Omar et al., n.d. researched magnesium and sodium sulfate attacks in plain and blended types of cement. The study investigated the influence of magnesium and sodium sulfate on two plain cement and three mixed types of cement, explaining the mechanism of sulfate exposure to cement mixed with magnesium and sodium. After two years of exposure, the damage is observed from all cement. The study showed that cement with mixtures such as silica fume, furnace slag mixture, and fly ash suffered the most severe damage compared to ordinary cement without a mixture. In 2000 [10] studied the distributions of bound sulfates and chlorides in concrete subjected to mixed NaCl, MgSO4, and Na_2SO_4 attacks. This study was a typical phenomenon of an observation of concrete that was exposed to sulfates and had undergone sulfates exposure. Since high permeability was a distinctive feature of the inspected concrete, a large amount of sulfate accumulated near the upper surface of the concrete forming gypsum, exposed concrete. Due to its high permeability, using sulfate-resistant cement alone was insufficient to protect this concrete from sulfate attack. In 2014 [20-21] conducted another study on the resistance of concrete and mortar against a combined attack of chloride and sodium sulfate. This research examined the mutual influence of Cl and SO_4 for four mixtures, using Ordinary Portland Cement, High Sulfate Resistant (HSR) Cement, and Blast-Furnace Slag (50% and 70% cement replacement). Measurements of the changes in length and mass were carried out to test the effect of Cl exposure on MgSO4. It can be concluded that chloride penetration increases when the sulfate content increases at a short immersion period, except for HSR concrete. Regarding sulfate attacks, the presence of chlorides has a mitigating effect.

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II. METHOD

A. Specimens

This study applied an experimental method using Portland Composite Cement Type V as the primary material for making high-quality conventional concrete. The materials used in this study were portland composite cement, water, sand, and gravel. These materials had to be examined first to determine the mix design. PCC concrete was molded on a 100 mm x 200 mm cylinder using the composition shown in Table 1.

TABLE 1.
COMPOSITION OF THE DESIGNED MIX KG/M^3

Dry Method		
PCC concrete	661.21	Kg/m3
Sand	424.95	Kg/m3
Gravel	933.84	Kg/m3
Water	235.53	Kg/m3
Superplasticizer (SikaViscocrete 3115 N)	3.31	Kg/m3

In this study, the value of Viscrocrete 3115 N type F based on *polycarboxylic ether* used was 0.6%. The ratio between Na_2SO_4 and $MgSO_4$ was 1: 1, and the content of Na_2SO_4 and $MgSO_4$ used was 50 grams/liter

B. Materials

The excellent quality of concrete is determined by the materials used to manufacture concrete. The basic materials used for the concrete manufacture in this study are as follows:

1) Cement

The cement employed in this study came from PT. Semen Gresik (Persero), a type of Portland Composite Cement Type V. Portland compounds consist of various mixtures such as lime (CaO), alumina oxide (Al_2O_3), silica oxide (Sio_2), and iron oxide (Fe_2O_3). The combination content of the four oxides was approximately 90% of the weight of cement. The combination is commonly called major oxides. The arrangement of oxides above forms the following compounds:

TABLE 2.
CHEMICAL COMPOUNDS OF PORTLAND CEMENT

Compound	Chemical formula	Symbol
Tri Calcium Silicate	3CaO SiO_2	C_3S
Di Calcium Silicate	2CaO SiO_2	C_2S
Tri Calcium Aluminate	3CAO Al_2O_3	C_3A
Tetra Calcium Alumina Ferrite	3CAO Al_2O_3	C_4OF

Source: Neville, 1981

2) Aggregate

The aggregate content in concrete mixtures is usually very high. The aggregate composition ranges from 60% - 70% by weight of the concrete mix. The most important properties of an aggregate are the crushing resistance and toughness, which affects its bonding with cement paste, porosity, and characteristics for water absorption affecting the resistance to freezing processes and chemical aggression as well as resistance to shrinkage.

By grain size, the aggregate was distinguished into two types; fine aggregate and coarse.

a. Fine Aggregate

Fine aggregate is aggregate, which particles pass through on a 4.8 mm perforated sieve (ASTM C33-99, 1999) [3]. Fine aggregate for concrete can be natural sand, fragments from natural stone, or artificial sand produced by a machine used to crush stones, called a crusher. Fine aggregates should not contain more than 5% sludge as well as not contain organic substances that can damage concrete. The sand material used in this study was Lumajang sand.

TABLE 3.
THE RESULTS OF THE FINE AGGREGATE TEST

Parameter	Content	Unit
Fine Modulus	2.25	%
Volume Weight	1.60	tone/m^3
Moisture	0.57	%
Specific Gravity	2.82	tone/m^3
Absorption	0.68	%

b. Coarse Aggregate

Coarse aggregates are aggregates that grains retain on a sieve of 4.8 mm (ASTM C33-99, 1999) [3]. Coarse aggregate for concrete was gravel from natural stone and crushed by crushed stones obtained from stone fragments. Coarse aggregate should consist of hard, non-porous particles. Coarse aggregates should not contain more than 1% sludge as well as not contain substances that cause damage to concrete, such as alkaline reactive substances. The coarse aggregates used in the study came from PT. Eternal Calvary.

TABLE 4.
COARSE AGGREGATE TEST RESULTS

Parameter	Content	Unit
Coarse Modulus	3.59	%
Volume Weight	1.30	tone/m3
Moisture	0.52	%
Specific Gravity	2.72	tone/m3
Absorption	2.19	%

3) Water

Water is one of the essential materials in the manufacture of concrete. Water used for concrete making must be non-greasy, which does not contain alkaline acids, salts, and organic materials or materials that can damage concrete.

4) Portland Composite Cement (PCC)

There are several types of cement, and Portland Composite Cement type V is one of those types. Composite cement is produced by crushing and grinding portland cement powder with other inorganic materials that have pozzolan characteristics containing high silicate, lime, and slag from burning iron. The materials are added to cement as much as 6-35% of the cement (SNI 15-7064-2004, 2004). The use of the additive in PCC cement aimed to provide suitable quality enhancers, speed up the hardening time, improve the ease of manufacture process, lower porosity, and increase the resistance towards destructive substances in aggressive environments.

5) Superplasticizer

Superplasticizer is an additive used in concrete mixtures. Adding a superplasticizer aims to reduce water content but maintain constant workability in the strength and durability of concrete. The effective use of superplasticizers is 0.8% - 2% of the number of binders. The binder used in this study was Portland Composite Cement, which modifies the concrete properties according to the research plan.

This study used a polycarboxylic ether-based F-type superplasticizer (Sika Data Sheet, n.d.) Sika ViscoCrete-3115 N is a third-generation superplasticizer for concrete and mortar, mainly developed for producing high-flow concrete with outstanding flow retention properties. Sika ViscoCrete-3115 N works by surface adsorption on cement particles resulting in a steric separation effect. Concrete made with Sika ViscoCrete-3115 N exhibits the following properties:

1. Excellent flowability (resulting in highly reduced placing and compacting efforts)
2. Strong self-compacting behavior.
3. Extremely high water (resulting in high density and strength)

Sika ViscoCrete-3115 N does not contain chlorides or other materials that cause corrosion in steel. Therefore, it can be used for reinforced and pre-pressed concrete construction without restrictions.

C. Resistance of Concrete to Sulfates

Concrete durability is the ability of concrete to withstand weathering action caused by chemical attacks, abrasions, or other concrete processing processes (Morshed et al., 2021). The durability of the concrete maintains its desired engineering properties when exposed to the surrounding environment, such as environmental aggressiveness, abrasion, weather action, and chemical attacks affecting the durability of concrete through the alternative of drying and wetting processes in coastal areas. Chemicals such as sulfates and chlorides in soil and water react with cement pastes and form some undesirable but harmful compounds that gradually hinder the development of the compressive strength of concrete. Thus, it causes deterioration, such as lack of durability of concrete leading to premature cracking in concrete, and corrosion of reinforcement in a short time (Bosunia & Choudhury, n.d.)

D. Conventional Concrete Testing

This study was carried out through several processes applied to the specimens. The first stage was conducted by treating the specimens (curing) in clean water for 28 days. The second one was done by immersing the specimens in magnesium sulfate and sodium sulfate solution, and each process was conducted for 28 days and 84 days. Two solutions were used for immersion: sodium sulfate and magnesium sulfate, acting as the research control. These two solutions were the proper immersion medium for the specimens to determine the performance of high-quality concrete in acidic and alkaline environments. The degree of acidity (pH) was the main indicator of this study. The degree of values of base and acidity of the immersion were as follows; magnesium sulfate 5% pH = 6.00 – 8.00; sodium sulfate 5% pH = 6.00 – 8.00; and ordinary water pH = 7.00. This research investigated PCC concrete compressive strength values, mass changes, and pH solution values

TABLE 5.
SPECIMENS

Testing	Age	Number of Samples		
		Air-ambient Curing	Na_2SO_3 Immersion	$MgSO_4$ Immersion
Compressive Strength Test	28 days	3	-	-
	28 days	-	3	3
	84 days	-	3	3
Mass Change Test	0, 1, 3, 7, 14, 21, 28, 56, 84 days	-	3	3

1. Slump Test

This test was carried out on fresh concrete, aiming to determine the ease level in concrete work. This test was applied to plastic concrete with a maximum coarse aggregate size of up to 37.5 mm (1 1/2 in.) Based on (SNI 1972:2008, 2008), concrete with a slump value of < 15 mm may not be plastic enough, and concrete whose slump is > 230 mm may not be cohesive sufficient for this test. The mold for the slump test should be a hooked cone with a base diameter of 203 mm, an upper diameter of 102 mm, and a height of 305 mm.

2. Compressive Strength Test

Compressive strength is the magnitude of load per unit area that causes specimens to disintegrate when loaded with a specific compressive force generated by the compression testing machine (ASTM C39/C 39M-03, n.d.). In this study, the sample of a cylindrical test object was 10 x 20 cm regarding the ASTM C 39 / C 39M-03 standard or (SNI 1974: 2011, 2011; Yang et al., 2014). The calculation formula for the compressive strength of concrete is as follows:

Compressive Strength of Concrete $=\frac{P}{A}$; declared with MPa

Where:
P = Axial Compressive Force(N)
A = The cross-sectional width of the tested specimens (cm^2)

The standard deviation is also calculated in the results of the compressive strength test with the formula of equation (1) as follows:

$$S = \sqrt{\frac{n\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i}{n(n-1)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Information:
xi = x-i-th value
n = number of specimens

3. Mass Change Test

The cast reacts with C3A or calcium aluminate hydrate existing in concrete to form calcium sulfate aluminate salts, often called ettringite, which have fluffy properties (Wang et al., 2018). Due to the development of larger volumes that exceed their original volume, this chemical process causes inflamed, cracked, and exfoliated concrete (de Weerdt et al., 2019).

Weight Change calculated up to 0.01%, the nearest percentage loss or weight gain of the test object during immersion for each inspection period by taking the weight as 100%(Maes & de Belie, 2017).

Based on (ASTM C 267 – 01), mass change can be calculated by equation (2) as follows :

$$\text{Mass Change (\%)} = \text{x } 100 \, \frac{(W-C)}{C} \quad \ldots\ldots\ldots\ldots (2)$$

Where:
W = weiight of the specimens tested (grams)
C = Initial weight of the specimens tested (grams)

4. Solution pH test

The pH of the solution experienced a significant increase during the early weeks, indicating the presence of alkali migration from concrete specimens. There was a significant increase in the pH value during the first 14 days, but after that, the increase was not significant (Mehmet Burhan Karakoc, et al.; 2015)

TABLE 6.
PH VALUE

pH	Information
Ph < 7	acid
pH = 7	Normal
pH > 7	Base

The purpose of analyzing the pH change of the solution was to determine a difference in the degree of acidity or pH of the specimens soaked in a solution of magnesium sulfate with a concentration of 5%. The pH test conducted was based on (ASTM D1293 2012) ("Standard Test Methods for PH of Water," 2005). The specimens used were PCC concrete with a 10 cm x 20 cm cylindrical mold. The test was performed using a pH meter.

III. RESULTS AND DISCUSSION

A. Slump Test

TABLE 7.
SLUMP TESTING

Casting	Slump Value	Number of Specimens
I	18 cm	9
II	20 cm	9
III	20 cm	9

The first casting was used for concrete with sulfate immersion for 3 months, where the slump value obtained was 180 mm. The second casting was used for concrete with a sulfate immersion for 1 month, where the concrete slump value was 20 cm. The slump results from the two castings have met the workability standards in accordance with the regulations (SNI 1972: 2008) as they are in the range values of 150 - 230 mm.

B. Mass Change

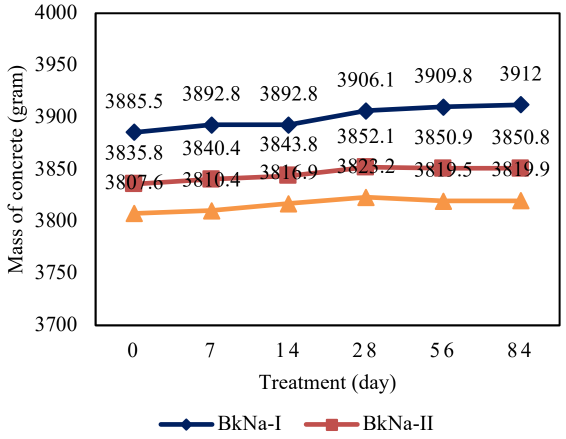

Figure 1. Change in concrete mass in sodium sulfate baths by 5%

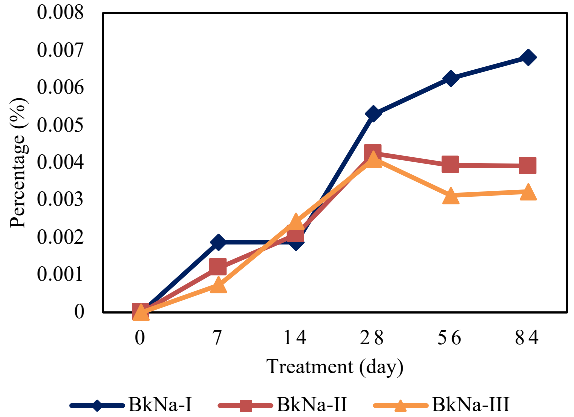

Figure 2. The percentage change in concrete mass in sodium sulfate is as much as 5%

Figure 1 and Figure 2 show that the average mass of the three PCC concrete test objects soaked in sodium sulfate for 7,14,28,56.84 days increases by 0.13%, 0.21%, 0.45%, 0.44%, 0.47% from the original condition.

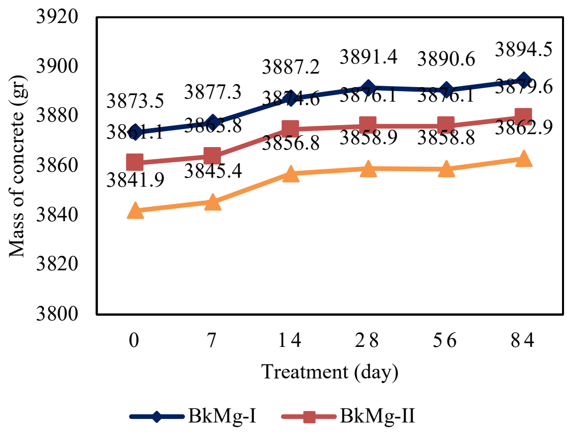

Figure 3. PCC concrete mass change on 5% magnesium sulfate immersion

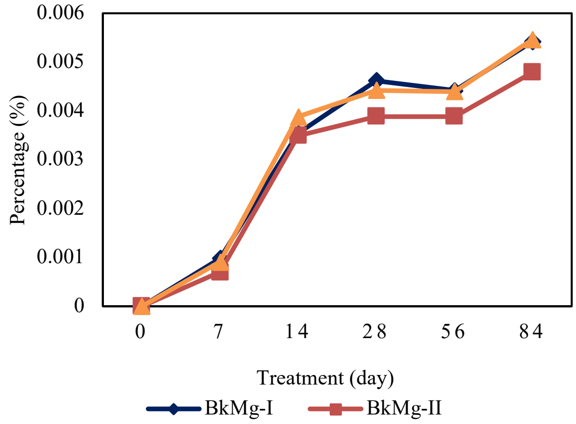

Figure 4. The percentage change in concrete mass in magnesium sulfate is as much as 5%

Figure 4. indicates that the percentage of change in PCC concrete mass in a magnesium sulfate bath is 5%. Figure 3 and figure 4 show that the average mass of the three PCC concrete test objects soaked in magnesium sulfate for 7,14,28,56.84 days decreases by 0.09%, 0.36%, 0.43%, 0.42%, 0.52% from the original condition.

C. Compressive Strength

The specimens made and removed from the mold were treated through water soaking according to the ages planned. The compressive strength test was carried out after the concrete came to the age of 28 days. The compressive strength applied for the specimens was 10x20 cm. The compressive strength tests were carried out when the concrete was 28, 56, and 112 days for concrete with water bath treatment (*curing)*. Concrete affected by magnesium sulfate and sodium sulfate immersion was tested at 28 and 84 days. The concrete began to be soaked in a magnesium sulfate solution and sodium sulfate 28 days after curing. This test was carried out at the Material and Structural Laboratory of the Civil Infrastructure Engineering Building, Faculty of Vocational Studies, ITS Surabaya. Compressive strength test results are presented in Table 8 .

TABLE 8.
COMPRESSIVE STRENGTH TEST

Treatment conditions	Age (day	Sample	Compressive strength (Mpa)	Average (Mpa)	Standard Deviation
Curing with water	28	Bk-Ca-1	47.01	42.17	5.19
		Bk-Ca-2	36.69		
		Bk-Ca-3	42.80		
Magnesium Sulfate	28	Bk-Mg-1	33.50	30.74	5.44
		Bk-Mg-2	28.54		
		Bk-Mg-3	30.19		
Sodium Sulfate	28	Bk-Na-1	25.48	32.19	3.21
		Bk-Na-2	36.56		
		Bk-Na-3	34.52		
Magnesium Sulfate	84	Bk-Mg-1	25.86	25.39	3.38
		Bk-Mg-2	27.90		
		Bk-Mg-3	22.42		
Sodium Sulfate	84	Bk-Na-1	29.04	28.03	4.52
		Bk-Na-2	27.01		
		Bk-Na-3	28.03		

Bk-Ca = Conventional Concrete Water Curing
Bk-Mg = Conventional Concrete Soaked Magnesium Sulfate
Bk-Na = Conventional Concrete Soaked Sodium Sulfate

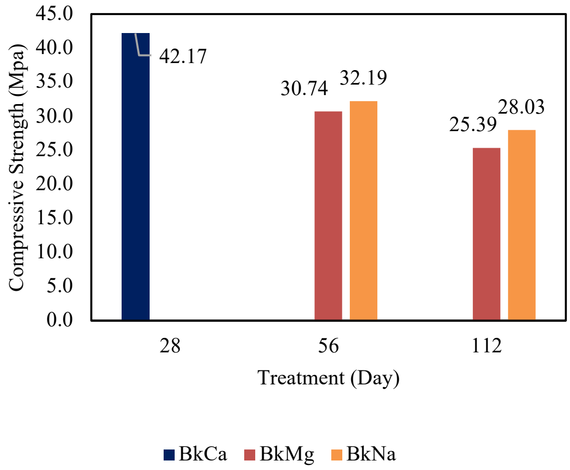

Figure 5. PCC Concrete Compressive Strength Test

Before being soaked in the sulfate solution, the compressive strength of the concrete reached 42.17 MPa. Therefore, it met the standards of SNI 2847:2019 for the classification of exposure to class S1 sulfates of more than 28 Mpa. After 28 days of soaking in magnesium sulfate solution, the compressive strength decreased to 30.74 Mpa, while that of soaked in sodium sulfate decreased to 32.19 Mpa from the original condition. After 84 days of soaking with a magnesium sulfate solution, the concrete compressive strength decreased to 25.39 Mpa, and the compressive strength of concrete bathed in sodium sulfate decreased to 28.03 Mpa from its original condition.

D. Solution pH Test

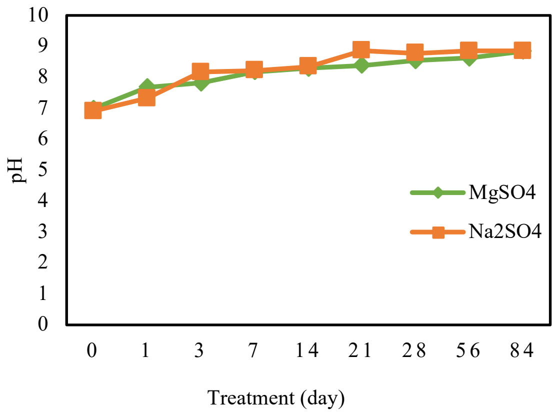

Figure 6. Magnesium pH and sodium pH testing

The results of the test indicated that the pH value of Magnesium sulfate solution at the age of 1, 3, 7, 14, 21, 28, 56, and 84 days increased by 9.9%, 1.8%, 4.6%,1.3%,1.1%, 1.9%, 0.9%, and 2.6%, respectively from the original condition. Meanwhile, the results of the test showed that pH value of sodium sulfate solution at the age of 1, 3, 7, 14, 21, 28 and 56 days increased by 5.6%, 11,6%, 0,6%, 1,5%, 6.2%, 0.9%, and 0.8% from the original condition.

IV. Conclusion

Based on the results of the research on conventional concrete made from Portland composite cement soaked with magnesium and sodium sulfate, it can be concluded from the visual appearance of conventional concrete soaked in magnesium sulfate for 3 months that concrete has formed of several softening layers on the concrete surface. The details results are as follows:

1. The test results of the change in the mass of sodium sulfate dumping for 7, 28, 56, and 84 days show a decrease in mass in conventional concrete after soaking for 12 weeks on sodium sulfate by 0.47% and for magnesium sulfate by 0.52%. This mass change test refers to (ASTM C267-01, n.d.). The mass change is calculated to the nearest 0.01% of the percentage of loss or weight gain of the specimen during the immersion for each inspection period by taking the conditioned weight as 100% (Maes & de Belie, 2017)
2. The compressive strength test results show that the compressive strength value of concrete with the sikaViscocrete 3115 N superplasticizer with a content of 0.6%, with a slump value of 180 mm before being soaked in the sulfate solution for 28 and 84 days was 42.17 Mpa. After 84 days of soaking in magnesium sulfate, the compressive strength of PCC concrete decreases by 25.39 Mpa. Meanwhile, exposure to sodium sulfate for 84 days decreases the compressive strength by 28.03 Mpa. It is due to the development of larger volumes that exceeds their original volume, and this chemical process causes inflamed, cracked, and exfoliated concrete (de Weerdt et al., 2019). And exposure to such a state of concrete decreases compressive crushing strength. Further, the damage spreads to the inside of the concrete, causing corrosion to attack the reinforcement (GP & Tanzil Gunawam, n.d.)

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