USING LIMESTONE DUST AND SUPERPLASTICIZER TO REDUCE PERMEABILITY AND IMPROVE DURABILITY OF CONCRETE EXPOSED TO SULFURIC ACID

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ABSTRACT

The effects of limestone dust and superplasticizer upon the permeability, mechanical properties and durability of concrete exposed to sulfuric acid have been investigated. The properties of admixtured concrete and conventional concrete are compared. The coefficient of permeability of admixtured concrete was lower than that of normal concrete by 91.44%. The results indicated that the mechanical properties (compressive, splitting and flexural) strengths of superplasticized limestone dust concrete were higher than of normal reference concrete at all ages of concrete. The compressive strength of superplasticized concrete containing limestone dust were 46.94%, 49.48% and 47.59% more than that of reference concrete at ages 28, 60 and 90 days, respectively. The decreasing ratios in compressive strength of normal and superplasticized limestone dust concrete were (21.41%, 55.73% and 65.80%) and (20.46%, 43.81% and 54.20%) at 28,60 and 90 days of exposure to sulfuric acid, respectively.

KEYWORDS

Concrete, Concrete Strengths, Permeability, Durability, Superplasticizer, Admixtures, limestone dust.

INTRODUCTION

A permeability is one of the very important properties of concrete relating to its durability and especially when concerned with its use in special applications such as in the isolation waste materials, acid attacks or aqueous structures [1].

Penetration of materials in solution into concrete may adversely affect its durability, for instance when $Ca(OH)_2$ is being leached out or an attack by aggressive liquids takes place. This penetration depends on the permeability of the concrete. The absence of durability may be caused either by the environment to which the concrete is exposed or by internal causes within the concrete itself. The external causes can be physical, chemical or mechanical: They may be due to weathering, occurrence of extreme temperatures, abrasion, electrolytic action, and attack by natural or industrial liquids and gases. The extent of damage produced by these agents depends largely on the quality of the concrete although under extreme conditions any unprotected concrete will deteriorate with different rates [2].

Wallace G.B., and Ore, E.L., found that for a given cement content the compressive strength of the laboratory specimens containing admixture exceeded by an average of about 20% of that the reference concrete [3].

The strength of concrete is basically controlled by the water-cement ratio. In order to achieve high strength in cementing materials, it is necessary to have a low water-cement ratios, whilst maintaining sufficient workability to be fabricated successfully. It is not possible to obtain increased workability via increased paste to aggregate ratio without eventually compromising strength. The most successful method is to utilize superplasticizer there by enabling as low water-cement ratio as possible to be used for a specified workability [4].

Malhotra and Carett, summarized the effect of limestone dust on the strength of concrete. They stated that for mix with water-cement ratio of 0.7, the strength of concrete incorporating limestone dust was generally comparable to or higher than that of the control concrete at all ages, while for mixes with a water-cement ratio of 0.53, the incorporation of limestone dust had no significant effect on the compressive strength of concrete regardless of the percentage of dust used. Also, they found, at 10% replacement, and at water-cement ratio of 0.4, the compressive strength at all ages was lower than that of the control mix, while at 20% replacement, the compressive strength was higher than that of control mix. The increase in the compressive strength of concrete incorporating limestone dust is probably due to the filler effect of the dust. In addition to the filler effect, there may be some contribution to the strength increase from factor such as the accelerated hydration of cement paste [5].

EXPERIMENTAL PROGRAM

Materials

- Cement

Sulfate resisting cement produced by Al-Muthena factory was used throughout this work. The percentage oxide composition and the physical properties of the cement are shown in Table (1) and (2) respectively. The results are conformed to the Iraqi specification No. 5/1984 [6].

- Fine aggregate

Al-Ukhaider natural sand was used throughout this work. The grading of fine aggregate is shown in Table (3). Results indicated that the fine aggregate grading and the sulfate content were within the requirement of Iraqi specification No. 45/1984 [7]. The specific gravity, absorption, sulfate content and material fine than No. 200 (75 µm) sieve of the used fine aggregate were (2.62, 0.95%, 0.21% and 0.8%) respectively.

- Coarse aggregate

Crushed gravel from Al-Nibaey region was used, throughout this work. The grading of coarse aggregate is shown in Table (3). The specific gravity, absorption, sulfate content and materials fine than No, 200 (75 µm) sieve of the used coarse aggregate were (2.65, 0.64%, 0.08% and 0.3%) respectively.

Results indicated that the fine aggregate grading and the sulfate content were within the requirement of Iraqi specification No. 45/1984 [7].

- Water

Ordinary potable water was used for mixing and curing purposes in this work.

- Limestone dust

A limestone dust from north of Iraq with maximum size 0.6-mm was used throughout this work, as a partial replacement 20% (by weight) for fine aggregate. It is contains 96% of $CaCO_3$. The specific gravity and absorption of the used limestone dust were 2.68 and 1.2 % respectively.

- Superplasticizer (high range water reducing admixture (HRWRA)):

A sulphonated melamine formaldehyde condense which is known commercially as Melment L10, was used throughout this work as a high range water-reducing admixture. It was brought from Baghdad Company for building chemicals, Ltd. (Baghdad-Iraq).

Melment L10 provides workable concrete with very low water-cement ratio while maintaining the workability. In this work a 26% water reduction was obtained by adding 6.5% Melment L10 as a percentage by weight of cement.

Mix Design

The concrete mix was designed according to the 1986, British standard method. The reference concrete mix designed to have a 28 days, compressive strength of about 30 MPa and a slump of a bout 50±5mm. The maximum size of the used crushed aggregate was (20 mm). According to the mix design procedure, concrete mix with a weight proportions of (1:1.73:2.82) and water-cement ratio of (0.52) was used as reference concrete mix. Table (4) shows the details of mixes with and without admixtures (limestone dust and superplasticizer-Melment L10).

Mixing Procedure

The mixing of concrete is important to obtain the required workability and homogeneity. A mechanical mixer of (0.16) m^3 capacity was used. The interior surface of the mixer cleaned and moistened before placing the materials. For reference concrete, the raw materials of gravel, sand and cement were first mixed dry for about one and half minutes then the water was added to the mixer. After that mixing continued for about three minutes until a homogenous concrete mix was obtained. For concrete containing superplasticizer and limestone dust, the raw materials of gravel, sand, limestone dust and cement were first mixed dry for about one and half minutes then the water with superplasticizer (Melment L10) were added to the mixer. After that mixing continued for about three minutes until a homogenous concrete mix was obtained.

Casting, Compaction and Curing

The mixed concrete was poured into the mould in two layers for cubes and beams and into three layers for cylinders. Each layer was vibrated by using a vibrating Table until no air bubbles emerged from the surface of the concrete. Then they were covered with polyethylene sheet in the laboratory for about 24 hours, and then demolded and kept in water for 28 days. After that, the specimens were stored in open air (in the laboratory) until tested. But, for specimens were exposed to sulfuric acid, the specimens were demolded and then immersed in H_2SO_4 (20% concentration) until tested.

Testing of Hardened Concrete

Compressive Strength Test

Based on B.S. 1881: part 116 [8], the compressive strength was carried out on 150 mm cube specimens. The compressive strength was taken as the average value of three specimens. The rate of loading was about 15 N/mm^2 per minute.

Splitting Tensile Strength Test:

The splitting tensile strength was conducted on cylinders of 150-mm diameter and 300 mm height. The average of three test specimens was taken. The test was carried out in accordance with ASTM C 496-86 [9], using the compression testing machine at stress rate of about 1.5 N/mm^2 per minute.

Flexural Tensile Strength Test

This test was conducted on prisms of (100 x 100 x 500) mm. This test was done according to ASTM C 78-84 [10]. The rate of loading was about 1.5 N/mm^2 per minute. The flexural tensile strength was taken as the average value of three specimens.

Permeability Test

Permeability apparatus was used to measure permeability of concrete. It is used for specimens of 38 mm in diameter and 50 mm in thickness. The maximum size of coarse aggregate used 8 mm. All specimens were tested after 90 days, 28 days kept in water and 56 days in open air. Darcy's equation was used to calculate the coefficient of permeability.

DISCUSSIONS

The superplasticizer (Melment L10) was used for reducing the water-cement ratio while maintaining equal workability to reference mix. The results indicated that, the optimum dosage of superplasticizer required to attain maximum water reduction 26% was 6.5% by weight of cement content for concrete containing 20% by weight limestone dust as a partial replacement of fine aggregate.

The effect of sulfuric acid on the compressive strengths of normal concrete and superplasticized limestone dust concrete mixes are presented in Table (5) and plotted in Figure (1). The results indicated that, the compressive strength of superplasticized limestone dust concrete was higher than of normal reference concrete at all ages of concrete. The compressive strength of superplasticized concrete containing limestone dust were 46.94%, 49.48% and 47.59% more than that of reference concrete at ages 28, 60 and 90 days, respectively.

Table (5) and Figure (1) also shows that, the compressive strength of superplasticized limestone dust concrete was higher than that of normal reference concrete at all periods of exposure to sulfuric acid. The compressive strengths of superplasticized limestone dust concrete were 38.86 MPa, 30.26 MPa and 25.72 MPa at 28, 60 and 90 days of exposure to acid, respectively. While they were 26.13 MPa, 15.95 MPa and 13.01 MPa for normal reference concrete after the same periods of exposure to sulfuric acid.

The superplacticized limestone dust concrete was suffered less reduction in compressive strength due to exposure to acid compared with normal reference concrete at all periods of exposure to acid. The percentage losses in compressive strength of superplacticized limestone dust concrete were 20.46%, 43.81% and 54.20% at 28, 60 and 90 days of exposure to acid, respectively. While they were 21.41%, 55.73% and 65.80% for reference concrete after the same periods of exposure to acid.

The less reduction in compressive strength of superplasticized limestone dust concrete was due to the good acid resistance of such type of concrete compared with normal concrete.

Tables (6 and 7) and Figures (2 and 3), show the effect of sulfuric acid on the splitting and flexural strengths of superplacticized limestone dust and normal reference concrete after 28, 60 and 90 days of exposure to acid. The splitting tensile strength of superplasticized limestone dust concrete was 43.77% more than that of reference concrete at 28 days of exposure to sulfuric acid, while it were 76.40% and 68.84% more compared with reference concrete at 60 and 90 days of exposure to acid, respectively. The flexural strength of superplasticized limestone dust concrete were 4.66 MPa, 3.99 MPa and 3.06 MPa at 28, 60 and 90 days of exposure to acid, respectively, while they were 3.33 MPa, 2.89 MPa and 2.10 MPa for normal reference concrete after the same periods of exposure to acid.

The results of coefficient of permeability (K) are reported in Table (8) and plotted in Figure (4). The coefficient of permeability of superplasticized limestone dust concrete mix decreases with duration of test until it reaches a steady state flow after about (4-5) days. Also, the coefficient of permeability of superplasticized limestone dust concrete was lower than that of normal reference concrete by 91.44%.

This reduction in coefficient of permeability for superplasticized limestone dust concrete may be attributed to the effect of superplasticizer on water content of fresh concrete mix, and consequently it reduces the size and number of pores within the concrete matrix, in addition to the effect of fine materials of limestone dust as filler particles leading to a denser and less permeable concrete.

CONCLUSIONS

Depending on the results of this investigation, the following conclusions can be drawn:

1. At optimum dosage of high range water reducing agent of 6.5% by weight of cement, the maximum percent of water reduction was 26% for normal concrete containing 20% by weight limestone dust as a partial replacement of fine aggregate.
2. The incorporation of 20% by weight of limestone dust as a partial replacement of fine aggregate with the optimum dosage of superplasticizer (Melment L10) 6.5% by weight of cement in concrete led to reduce permeability and improve mechanical properties (compressive, splitting and flexural strengths) of concrete at all ages.
3. The coefficient of permeability of superplasticized limestone dust concrete mix decreases with duration of test until it reaches a steady state flow after about (4-5) days. Also, the coefficient of permeability of

superplasticized limestone dust concrete was lower than that of normal reference concrete by 91.44%.

4. The compressive strength of superplasticized concrete containing limestone dust were 46.94%, 49.48% and 47.59% more than that of reference concrete at ages of 28, 60 and 90 days, respectively.
5. Using limestone dust (20% by weight as a partial replacement for fine aggregate) and superplasticizer (Melment L10 6.5% by weight of cement) was leads to increase the resistance of concrete to sulfuric acid (20% concentration). The compress0.ive strength of admixtured concrete were 48.71%, 89.71% and 97.69% more than that of reference concrete at 28, 60 and 90 days of exposure to sulfuric acid, respectively.
6. The decreasing ratios in compressive strength of normal and superplasticized limestone dust concrete were 21.41%,55.73% and 65.80% and 20.46%,43.81% and 54.20% at 28,60 and 90 days of exposure to sulfuric acid, respectively.
7. The splitting strength of concrete containing limestone dust and superplasticizer were 3.81 MPa, 3.14 MPa and 2.23 MPa at 28, 60 and 90 days of exposure to acid, respectively, while there were 2.65 MPa, 1.78 MPa and 1.38 MPa for reference concrete after the same periods of exposure.

8. The flexural strength of admixtured concrete were 39.93%, 38.06% and 45.71% more than that of normal reference concrete at 28, 60 and 90 days of exposure to sulfuric acid, respectively.
9. Improve permeability and mechanical properties of concrete containing admixtures (limestone dust and superplasticizer) may be attributed to the effect of superplastizer on water content of fresh concrete mix, and consequently it reduces the size and number of pores within the concrete matrix, in addition to the effect of fine materials of limestone dust as a filler particles leading to a denser and a less permeable concrete.

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Table (1): Chemical analysis of cement used in this work.

Oxides	Percentage by weight (%)	Limitations of Iraqi specification No. 5/1984
CaO	61.85	-
MgO	2.72	$\leq$ 5.0%
SiO_2	22.32	-
SO_3	2.12	$\leq$ 2.5%
Fe_2O_3	4.57	-
Al_2O_3	5.04	-
Insoluble residue	1.01	$\leq$1.5%
Lime saturation factor	0.83	0.66-1.02
Loss on ignition	1.6	$\leq$ 4.0%
Cement compounds		
C_3S	46.21	
C_2S	30.93	
C_3A	3.11	$\leq$ 3.5%
C_4AF	14.57	

Table (2): Physical properties of cement

Physical properties	Test results	Limitations of Iraqi specification No. 5/1984
Specific surface area Blaine method, (cm^2/gm)	3450	$\geq$ 2500
Soundness Le-chatelier method, (mm)	6.0	$\leq$10
Setting time, Vicat's method (hrs:min)		
Initial setting time (hrs:min)	1:46	$\geq$ 1 hrs
Final setting time (hrs:min)	3:35	$\leq$ 10 hrs
Compressive strength (MPa)		
3-days	20.50	$\geq$ 15
7-days	29.75	$\geq$ 23

Table (3): Grading of Fine and Coarse Aggregates

Sieve size (mm)		Accumulated percentage passing (%)		Limit of Iraqi specification No. 45/1984	
Fine Aggregate	**Coarse Aggregate**	**Fine Aggregate**	**Coarse Aggregate**	**Fine Aggregate , Zone (2)**	**Coarse Aggregate**
4.75	**37.5**	95.2	100	90-100	100
2.36	**20**	74.7	100	75-100	95-100
1.18	**10**	60.6	55.2	55-90	30-60
0.60	**4.75**	45.2	6.8	35-59	0-10
0.30	**-**	18.4	-	8-30	-
0.015	**-**	2.6	-	0-10	-

Table (4): The details of the mixes

Mix designation	Mix proportion (by weight)	Water - cement ratio	Limestone* dust (%)	Superplasti-cizer** (Melment -L10) (%)
Normal reference concrete	1:1.73:2.82	0.52	-	-
Superplasticized limestone dust concrete	1:1.73:2.82	0.38	20	6.5

* Limestone dust content as a partial replacement for fine aggregate.

** Superplasticizer content by weight of cement.

Table (5): Average compressive strength of concrete at different testing ages and periods of exposure to sulfuric acid(MPa)

Types of concrete	Compressive strength of concrete (MPa) at testing age of		
	28 (days)	60 (days)	90 (days)
Normal reference concrete	33.25	36.03	38.05
Superplasticized limestone dust concrete	48.86	53.86	56.16
Types of concrete	**Compressive strength of concrete (MPa) at period of exposure to sulfuric acid of**		
	28 (days)	**60 (days)**	**90 (days)**
Normal reference concrete	26.13	15.95	13.01
Superplasticized limestone dust concrete	38.86	30.26	25.72

Table (6): Average splitting tensile strength of concrete of different testing ages and periods of exposure to sulfuric acid (MPa)

Type of concrete	Splitting strength of concrete (MPa) at testing age of		
	28 (days)	60 (days)	90 (days)
Normal reference concrete	3.42	3.78	3.93
Superplasticized limestone dust concrete	4.76	5.02	5.14
Types of concrete	**Splitting strength of concrete (MPa) at period of exposure to sulfuric acid of**		
	28 days	**60 days**	**90 days**
Normal reference concrete	2.65	1.78	1.38
Super plasticized limestone dust concrete	3.81	3.14	2.33

Table (7): Average flexural tensile strength of concrete of different testing ages and periods of exposure to sulfuric acid (MPa)

Types of concrete	Flexural strength of concrete (MPa) at testing age of		
	28 (days)	60 (days)	90 (days)
Normal reference concrete	4.25	4.65	4.95
Superplasticized limestone dust concrete	5.80	6.39	6.62
Types of concrete	**Flexural strength of concrete (MPa) at period of exposure to sulfuric acid of**		
	28 (days)	**60 (days)**	**90 (days)**
Normal reference concrete	3.33	2.89	2.10
Super plasticized limestone dust concrete	4.66	3.99	3.06

Table (8): Coefficient of permeability of concrete

Types of concrete	Coefficient of permeability cm/sec * 10^{-10}					
	1 days	2 days	3 days	4 days	5 days	6 days
Normal reference concrete	40.20	22.87	17.88	17.88	17.88	17.88
Superplasticized limestone dust concrete	26.16	18.53	8.11	4.16	1.53	1.53

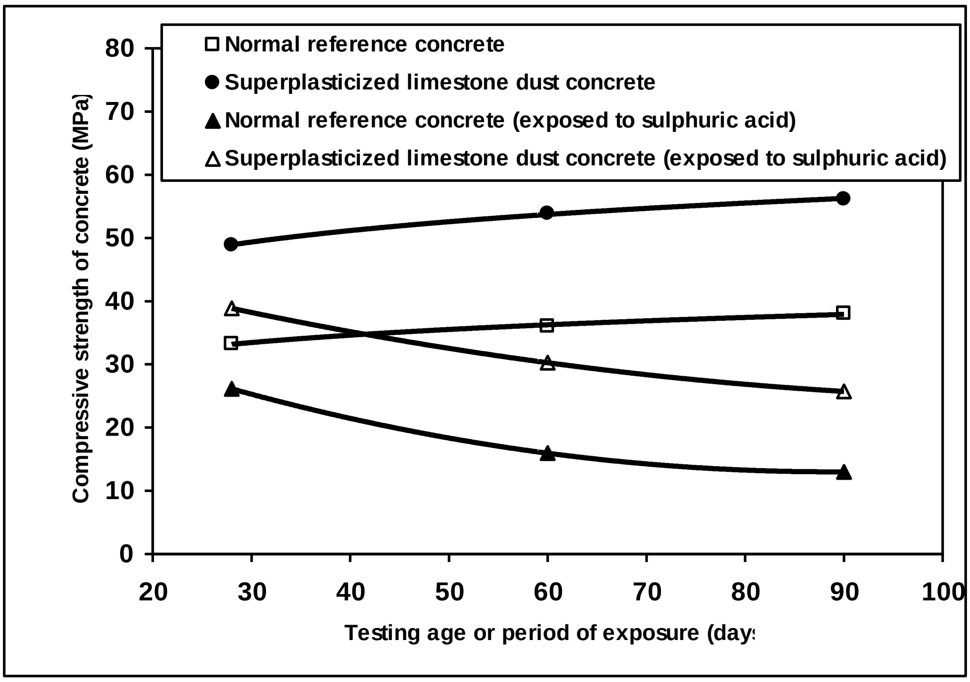

Fig. (1): The relationship between compressive strength of concrete and testing ages or periods of exposure to sulphuric acid.

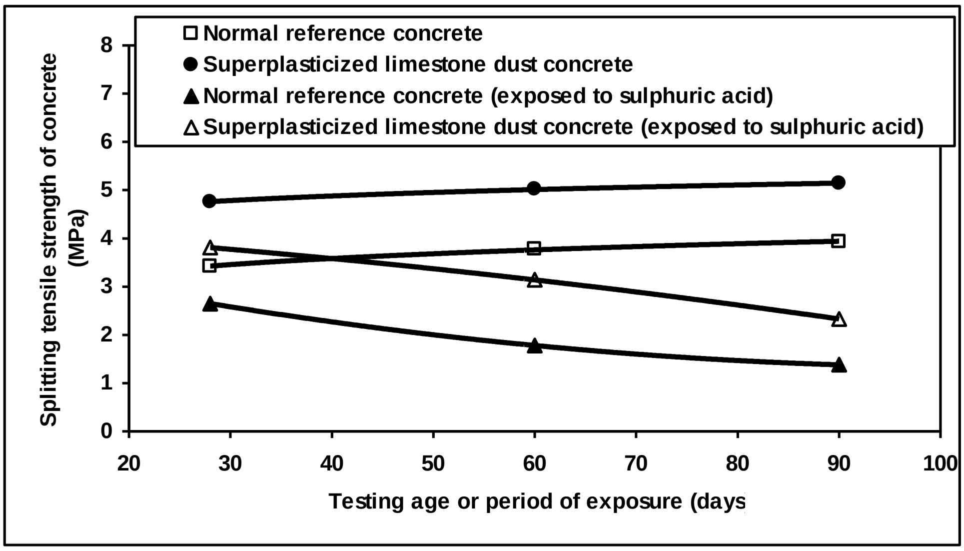

Fig. (2): The relationship between splitting tensile strength of concrete and testing ages or periods of exposure to sulphuric acid.

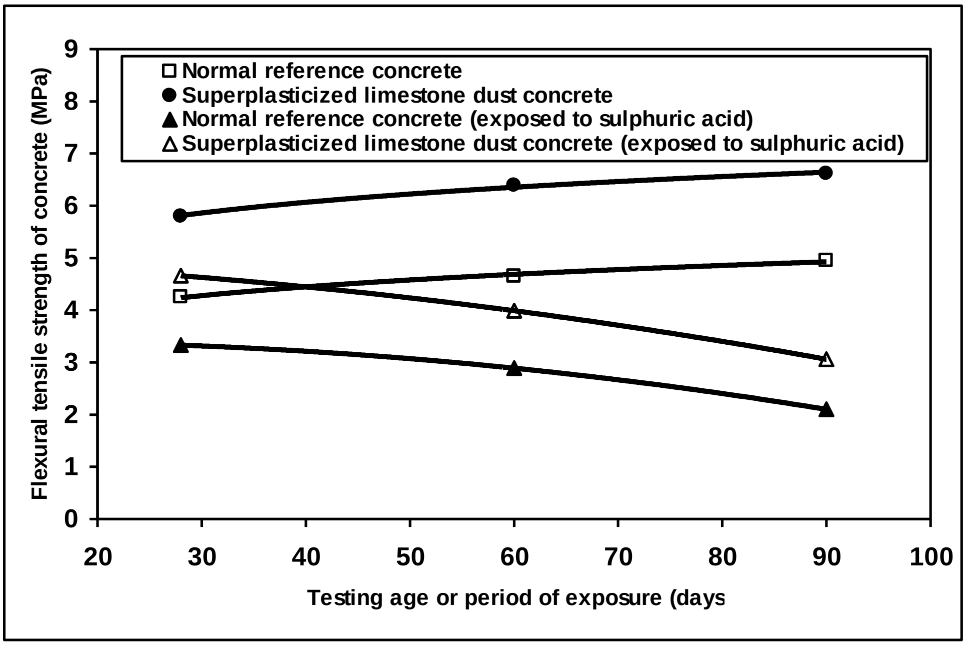

Fig. (3): The relationship between flexural tensile strength of concrete and testing ages or periods of exposure to sulphuric acid.

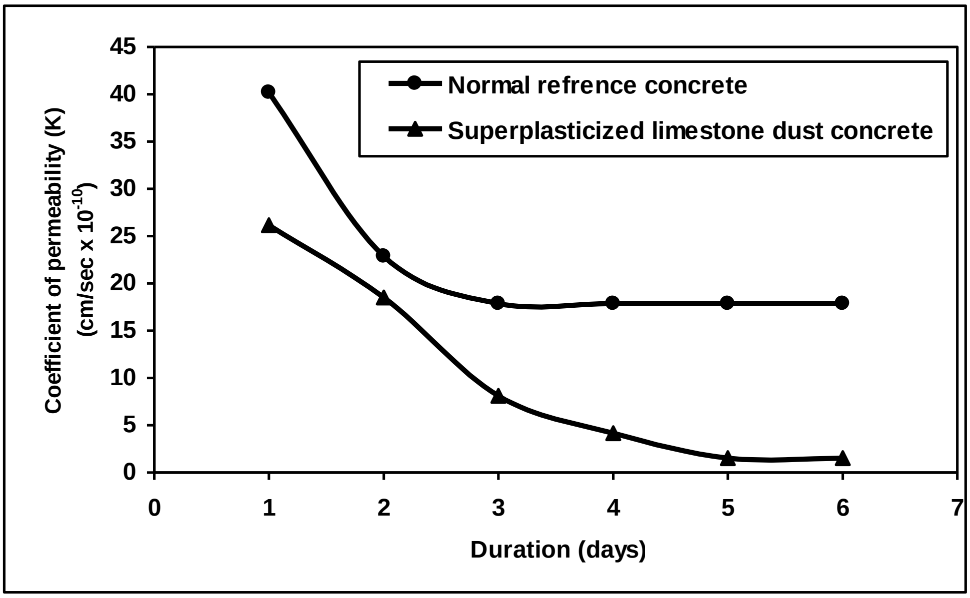

Fig. (4): The relationship between coefficient of test of permeability and duration of test.

استعمال غبار الحجر الجيري والملدن المتفوق لتقليل نفاذية ولتحسين ديمومة الخرسانة المعرضة إلى حامض الكبريتيك

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الخلاصة

تأثيرات غبار الحجر الجيري والملدن المتفوق على نفاذية،الخواص وديمومة الخرسانة الخرسانة المعرضة الى حامض الكبريتيك قد بحثت. خواص الخرسانة الحاوية على المضافات والخرسانة الاعتيادية قد قورنت. معامل النفاذية للخرسانة الحاوية على المضافات كانت اقل من معامل النفاذية للخرسانة الاعتيادية بنسبة 91,44 %.

النتائج أكدت بان الخواص الميكانيكية(مقاومة الأنضغاط،الأنشطار والأنحناء) للخرسانة الحاوية على المضافات كانت أعلى من الخواص الميكانيكية للخرسانة الاعتيادية ولكل الأعمار.

مقاومة الأنضغاط للخرسانة الحاوية على غبار الحجر الجيري والملدن المتفوق كانت 46,94 %، 49,48 % و47,59 % اكثر من الخرسانة الاعتيادية وللأعمار 28،60 و90 يوم على التوالي. نسب النقصان في مقاومة الأنضغاط للخرسانة الاعتيادية والخرسانة الحاوية على المضافات كانت (21,41 %،55,73 % و65,80 %) و(20,46 %،43,81 % و54,20 %) للأعمار 28 ،60 و90 يوم من التعرض لحامض الكبريتيك،على التوالي.

الكلمات الدالة

الخرسانة، مقاومة الخرسانة، النفاذية ، المتانة، الملدن المتفوق،المضافات،غبار الحجر الجيري.