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EFFECT OF EXTERNAL SULPHATES ON PROPERTIES OF LIME-POZOLANA CONCRETE

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Abstract: This study aims to evaluate the resistance of Lime-Pozzolana concrete mixtures to external sulfate attack, represented by studying their effect on compressive strength, splitting tensile strength, dynamic modulus of elasticity, and weight loss. Three types of pozzolanic materials used in concrete mixtures; Silica fume (as LS mix), Silica fume-Fly ash (LSF) and Metakaolin (LMK). LS and LSF mixture were exposed to 5% concentration of $MgSO_4$ solution, while LMK mix was exposed to 5% concentration of $NaSO_4$ solution until 210 days after a moist curing in tap water until 14 days age. Results indicate that specimens of mixtures (LS and LSF) didn't disintegrate when subjected to the very harsh environment of $MgSO_4$ solution until 210 days age. There was not visual sign of deterioration nor a significant loss in specimens weight of the two mixes at the end period of exposure of 210 days age. While LMK mix specimens disintegrate at 180 days age due to exposure to Na_2SO_4 solution.

Keywords: *Lime-Pozzolana Concrete, External Sulfate Attack*

تأثير الكبريتات الخارجية على خواص خرسانة الجير- بوزولانا

الخلاصة: تهدف هذه الدراسة إلى تقييم مقاومة خلطات خرسانة الجير- بوزولانا إلى هجوم الكبريتات الخارجية، ممثلة بتأثيرها على مقاومتي الانضغاط وشد الانفلاق، معامل المرونة الديناميكي، وفقدان الوزن. تم استعمال ثلاثة انواع من المواد البوزولانية شملت ابخرة السليكا (برمز خلطة خرسانية LS)، خليط ابخرة السليكا ورماد الفحم (LSF)، اضافة الى الميتاكاؤلين(LMK). تم تعريض نماذج خلطات LS و LSF الى محلول حاوي على كبريتات المغنيسيوم بتركيز 5%، بينما عرضت نماذج الخلطة LMK لمحلول حاوي على كبريتات الصوديوم بتركيز 5% لغاية عمر 210 يوم بعد معالجتها بماء الاسالة لغاية عمر 14 يوم. بينت النتائج بينت النتائج بان نماذج الخلطات LS و LSF لم تتفتت عند تعرضها الى الظروف القاسية من محلول كبريتات المغنيسيوم لغاية عمر 210 يوم. كما لم يلاحظ اي تلف او فقدان مهم في الوزن ولغاية عمر 210 يوم. بينما تفتت نماذج الخلطة LMK بعمر 180 يوم من التعرض لمحلول كبريتات الصوديوم.

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1. Introduction

Lime-Pozzolana (LP) is a building material that had been used in the masonry construction for a long time [1]. The slow strength gain of this material led to use Portland cement. Nowadays, the increase of pollution by CO2 comes from the manufacture of Portland cement, encourage the researchers to think of other types of binding materials. One of those materials is by returning to lime-Pozzolana. LP cause lower pollution due to the production of lime at 1000 C while cement produce at 1450 C, in addition to the existence of huge amount of Pozzolanas as wastes from industry, such as fly ash. This make LP cheap and more sustainable material compared to Portland cement [2].

Lime-Pozzolana is one of a number of low-carbon emission cements being developed to cross demand for concrete in the construction. At the present time, researches focus on production of economic binder by using the industrial by-products (blast furnace slag, fly ash in addition to silica fume) and the natural resources (natural Pozzolana, Limestone and calcined clay) to reduce the blemish recorded during the manufacture of Portland cement. Using of mineral admixtures in cementing materials mixes would help to overcome these problems and would also result in the improvement of the workability, strength and durability of cementing materials. This would also results in additional benefits in terms of cost reduction, energy savings; reduce CO2 emissions promoting ecological balance and conservation of natural resources etc. [3]. Extensive testing has proven that Lime-Pozzolana binder displays similar strength characteristics as Portland cement. The Lime-Pozzolana concrete can be batched and cast into molds in exactly the same way as Portland cement based concretes.

Grist *et al*. [4] and other researchers prepared and development LPC mixes with binders consisted of 50% hydraulic lime and 50% pozzolanic materials used to produce mixes of Lime-Pozzolana concrete. This Lime-Pozzolana Concrete had a compressive strength at 28-day more than 20 MPa.

This work is part of project studying lime-Pozzolana concrete (LPC) began in the University of Technology by Kadum et al [5]. They used three types of pozzolanas with hydrated lime to produce and studied the properties of the produced concrete mixture in fresh and hardened state. This research aims to study the effect of external sulfates (5% Na_2SO_4 and $MgSO_4$) on properties of LPC.

2. Experimental Work

2.1. Materials

2.1.1. Cement

(Al-mass) Iraqi ordinary Portland cement is used in this work. The compliance of the cement is done conformity to the Iraqi Standards No.5 (IQS 5) [6]. Chemical and physical properties for ordinary Portland cement shown in Table 1.

2.1.2. Lime

A commercial hydrated lime of comparatively was used. Blaine fineness and chemical composition of the hydrated lime were specified in accordance to ASTM C 25[7] and C204 [8]. The suitability of the hydrated Lime was estimated in conformity to the ASTM C821 [9]. Table 1 shows the physical and chemical properties of the hydrated lime.

2.1.3. Silica Fume

Silica fume, SF from Sika company used in this work. It satisfy the chemical and physical requirements of the ASTM C1240 [10], as shown in Table 1.

2.1.4. Fly ash

The chemical composition and properties of Fly ash used in this study are shown in Table 1. The results display that the fly ash is in accordance with the requirements of ASTM C 618 [11].

2.1.5. Metakaolin

Metakaolin, (MK) is produced by burning kaolin clay at temperature of 700°C at a rate of 2°C/min. The chemical and physical properties of MK are shown in Table 1.

Table 1: Chemical and physical properties for all materiales

Chemical composition					
Oxides (Content percent)	Lime	Silica fume	Fly ash	Metakaolin	Portland Cement
SiO_2	-	88.74	58.13	48.7	21.93
Al_2O_3	-	1.03	18.89	29.4	4.98
Fe_2O_3		0.03	5.98	2.3	3.1
MgO	3.25	0.01	0.72	0.17	2.00
Na_2O	-	0.22	1.27	-	-
K_2O	-	0.15	1.46	-	-
CaO	87.90	1.09	1.60	3.00	66.11
SO3	-	0.21	0.21	0.15	2.25
L.O.I	-	2.46	3.28	7.8	2.39
Physical properties					
Fineness (Blaine method) m^2/kg	1200	20000	773	1100	367
Specific gravity	-	0.5± 0.1 (kg/l)	2.26	2.48	-
Strength Activity Index(7 day)	-	128.3	112.5	105.8	-

2.1.4. Fine Aggregate

Al Ukhaider natural sand,with fineness modulus 2.52 , is used according to the IQS No. 45 [12]. Table 2 show grading of fine aggregate.

Table 2. Grading and physical properties of fine aggregate

Sieve size (mm)	percentage passing	Limits of Iraqi spec. No. 45/1984/Zone 2
10	100	100
4.75	97	90-100
2.36	88	75-100
1.18	77	55-90
0.6	59	35-59
0.3	22	8-30
0.15	5	0-10
Sulphate content = 0.19 percent		max.= 0.5 percent
Specific gravity,SSD = 2.62		

2.1.5. Coarse Aggregate

Crushed gravel used with 5-14 mm grading conforms to the Iraqi Standard IQS 45 [12], as shown in Table 3.

Table 3. Grading and physical properties of coarse aggregate

Sieve size, mm	Passing percent	Limits of Iraqi spec.No.45/1984
20.0	100	100
14.0	93	90-100
10.0	60	50-85
5.0	5	0-10
Specific gravity, SSD	2.64	-
Sulfate content, percent	0.06	≤ 0.1 percent
Absorption, percent	0.05	-
Bulk Density, kg/m^3	1565	-

2.1.6. High range water reducing admixture (Superplasticizer)

A high performance superplasticizer admixture of aqueous solution of modified polycarboxylate basis (Viscocrete-5930) [13] was used. It conforms to ASTM-C-494 types F [14].

2.2. Concrete Mix Proportions

Three concrete mixtures of lime-Pozzolana concrete (LS, LSF and LMK) were selected from previous research [5], with two modification.

First, addingcertain amount (5% binder weight) of ordinary Portland cement to accelerate setting the mix, and second, decreasing w/b ratio to satisfy the requirements of the durability according to ACI 201[15]. The details of concrete mix proportions are shown in Table 4.
All mixes were designed to attain 25 MPa as compressive strength at 28 days ago.

Table 4. Details of concrete mixes

Designation	Binder, kg/m^3					Fine aggregate kg/m^3	Coarse aggregate kg/m^3	S.P by weight of binder percent	W/Binder by weight	Binder/ Aggregate by weight
	Cement	Lime	Silica fume	Fly ash	Metakaolin					
LS	16.5	166.5	166.5	0	0	680	1020	3.5	0.40	1:5
LSF	20	190	110	80	0	640	960	1.5	0.35	1:4
LMK	20	190	0	0	190	640	960	1.5	0.38	1:4

2.3 Mixing Procedure

A pan tilting draw mixer of about 0.07 m^3 capacity has been used to mix up the ingredients with the following with special procedure.
The binder (lime and Pozzolanic materials) need to be mixed very well before addition of aggregate, so it was decided to adopt the following method of mixing [16]:

- **a.** The dry fine aggregate, lime and Pozzolana have been mixed together in the mixer for about 3 minutes.
- **b.** The dry coarse aggregate is added to the mixture (fine aggregate, Lime and Pozzolana) and mixing continued for another 1 min.
- **c.** Mixing the ingredients with 60 percent of the required water for 3 minutes.
- **d.** After that, the remained water and the superplasticizer are added and mixing continues for 3 minutes.

2.4 Curing of concrete specimens

Reference specimens (LS-R, LSF-R and LMK-R) were immersed in tap water until the age of test. While the other specimens, immersed in tap water until 14 days age, and then submerged partially in aggressive solution containing 5% concentration of either ($MgSO_4$ for LS-Ex and LSF-Ex) mix specimens or Na_2SO_4 for (LMK-Ex mix specimens), until test age. Table 5 shows exposure conditions for all mixes.

Table 5. Exposure conditions for all mix.

Mix	Exposure Conditions
LS-R	immersed in tap water
LSF-R	immersed in tap water
LMK-R	immersed in tap water
LS-Ex	submerged partial in 5% $MgSO_4$ solution
LSF-Ex	submerged partial in 5% $MgSO_4$ solution
LMK-Ex	submerged partial in 5% Na_2SO_4 solution

3. Result and Discussions

3.1 Compressive Strength

All reference mixes, except for the mix LMK-R have attained the targeted compressive strength, 25MPa at 28-day age.

Table 6 and Figure 1 show the compressive strength of LPC mixtures under different exposure conditions. It can be seen that using silica fume or a combination of silica fume and fly ash with hydrated lime form good binding material which can produce concrete having structural strength of about 26 MPa at 28 days age (mixes LS-R and LSF-R), while reaction Metakaolin with hydrated lime in concrete produce poor quality concrete (LMK-R) that cannot be recommend.

Table 6 and Figure 1 show that when LP mixtures (LS-Ex and LSF-Ex) subjected to $MgSO_4$ solution, their compressive strength continued to increase until 90 days age with a small reduction in strength reaching 7.7% and 6.2% respectively at 90 days compared with reference mixes.

But after 90 days age, higher reduction in strength, of LS-Ex and LSF-Ex mixes due to the aggressive solution the difference between their strength and the reference mixes 25.3% and 22.5% respectively at 210 days age.

This might be due to the attack of Portland cement compound by $MgSO_4$ [17], also due to the growth of crystal salts entered to the concrete in the matrix voids and so exerting a gradual internal stress affecting concrete strength. Figure 2 shows the LS-Ex mix specimens expose to external $MgSO_4$ Solution at 180 day age.

The effect of Na_2SO_4 solution on the weak LMK-Ex mixture specimens was more pronounced, where the strength of those mix specimens begin to drop after 28 days age to reach a reduction in compressive strength of 57.7% at 120 day compared to mix LMK-R and break down at 180 days age, as shown in Figure 3. This behavior could be explained by that Metakaolin has higher alumina content than silica fume and fly ash and that leads to reaction between this phase and SO_3 ions .This reaction is the cause for the faster disintegration of LMK mixes.

Table 6. Compressive strength of LPC mixes under different exposure conditions

Mix	Compressive strength MPa at age of						
	14 day	28 day	56 day	90 day	120 day	180 day	210 day
LS-R	21.2	29.3	35.5	41.8	42.3	43.5	43.8
LS-Ex	21.2	29	34.8	38.6	36.8	33.2	32.7
LSF-R	17.6	26.2	32.7	40.2	41.5	42.7	43.5
LSF-Ex	17.6	25.8	31.7	37.7	36.6	34.4	33.7
LMK-R	6.4	8.3	8.9	9.1	9.7	10.2	10.3
LMK-Ex	6.4	8.1	6.4	4.8	4.1	Failure	Failure

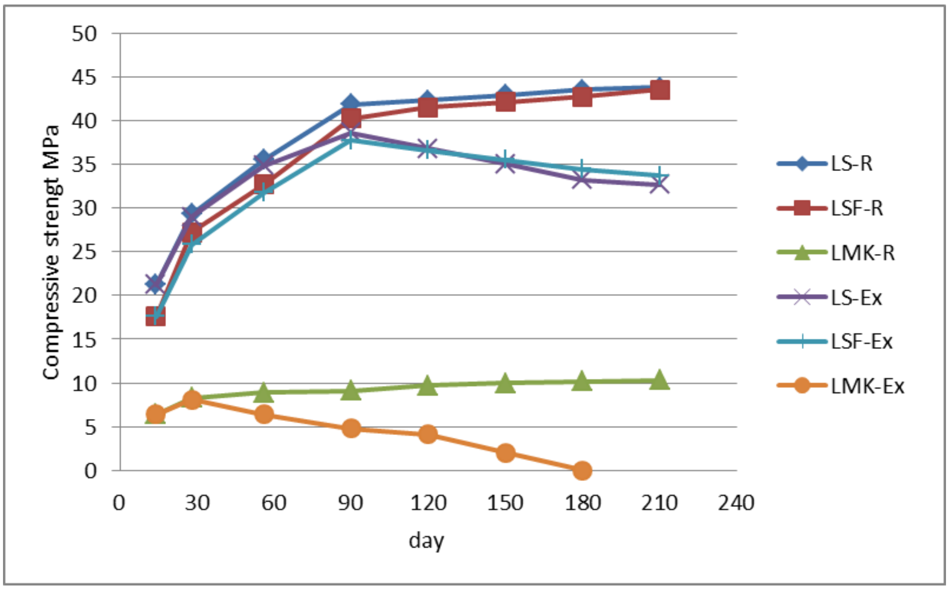

Figure 1. Effect of exposure condition on compressive strength for all mixes

Figure 2. LS-Ex mix specimens expose to external MgSO4 Solution at 180 day age

Figure 3. LMK-Ex mix specimens expose to external NaSO4 Solution at 180 day age

3.2 Splitting Tensile Strength

Table 7 and Figure 3 show that when LPC mixtures (LS-Ex and LSF-Ex) subjected to $MgSO_4$ solution, their splitting tensile strength, performed on 100 × 200 mm cylinder specimens, decrease at an increasing rate reach 26.3 and 23.1% respectively at 210 days age with respect to reference mixes (mixes LS-R and LSF-R). This is because of the same reasons mentioned in the previous article.

The effect of Na_2SO_4 solution on the weak LMK-Ex mixture specimens was more pronounced, where the strength of those mix specimens drop sharply after 28 days age to reach a reduction in compressive strength of 55.6% at 120 day compared to mix LMK-R and break down at 180 days age.

Table 7. Splitting tensile strength of LPC mixes under different exposure conditions

Mix	Splitting tensile strength, MPa at age of						
	14 day	28 day	56 day	90 day	120 day	180 day	210 day
LS-R	1.8	2.5	3.1	3.6	3.7	3.8	3.8
LS-Ex	1.8	2.5	2.8	3.1	3.2	2.9	2.8
LSF-R	1.6	2.4	3.1	3.6	3.7	3.8	3.9
LSF-Ex	1.6	2.3	2.8	2.9	3.0	3.1	3.0
LMK-R	0.5	0.7	0.8	0.8	0.9	1.0	1.1
LMK-Ex	0.5	0.6	0.6	0.5	0.4	failure	failure

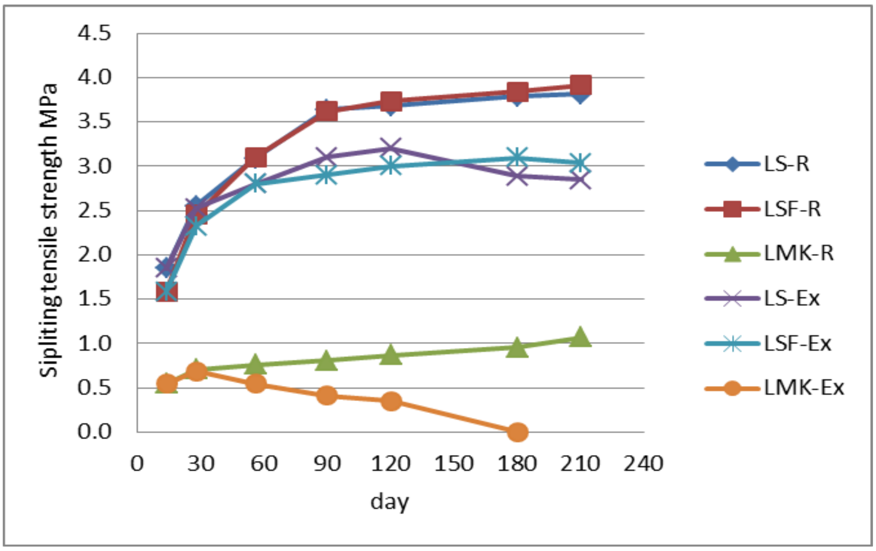

Figure 3. Effect of exposure condition on splitting tensile strength for all mixes.

3.3 Dynamic Modulus of Elasticity

The results of the dynamic modulus are listed in Table 8 and shown Figure 4 to 6. The value of the dynamic modulus were estimated according to equation below:

$$V^2 = E_d (1-\mu) / \rho(1+\mu)(1-2\mu) \qquad (1)$$

Where:
V = Ultrasonic pulse velocity, km/sec.
E_d = Dynamic modulus of elasticity, GPa.
ρ = Density, kg/m^3.
μ = Poisson's ratio (assumed = 0.15)

Table 8 and Figures 4 to 5 show the effect of $MgSO_4$ solution on LP mixtures (LS-Ex and LSF-Ex). Results indicated that a reduction in dynamic modulus of elasticity of LS-Ex mix specimens reaching 8 and 7.6% at ages 90 and 210 days compared to reference mix specimens. These percentages reach 6.7 and 13.5% for LSF-Ex mix specimens. There were not any visual sign of deterioration of the two mix specimens at the end period of exposure of 210 days age. Results shown in Table 8 and Figure 6 indicate that the dynamic modulus of elasticity of LMK-Ex mixture specimens continue to decrease due to exposure to Na_2SO_4 solution until 120 days age to reach 14.2% at 120 days age and then disintegrate at 180 days age.

Table 8. Dynamic modulus of elasticity of LPC mixes under different exposure conditions

Mix	Dynamic modulus of elasticity E_d, GPa				
	28 day	90 day	120 day	180 day	210 day
LS-R	43.59	48.33	48.21	49.20	49.50
LS-Ex	40.68	44.48	45.48	45.50	45.70
LSF-R	48.21	54.23	58.10	59.40	60.14
LSF-Ex	44.17	50.6	52.23	52.43	52.01
LMK _R	44.10	46.13	46.66	46.90	46.61
LMK _Ex	40.85	40.72	40.04	Failure	Failure

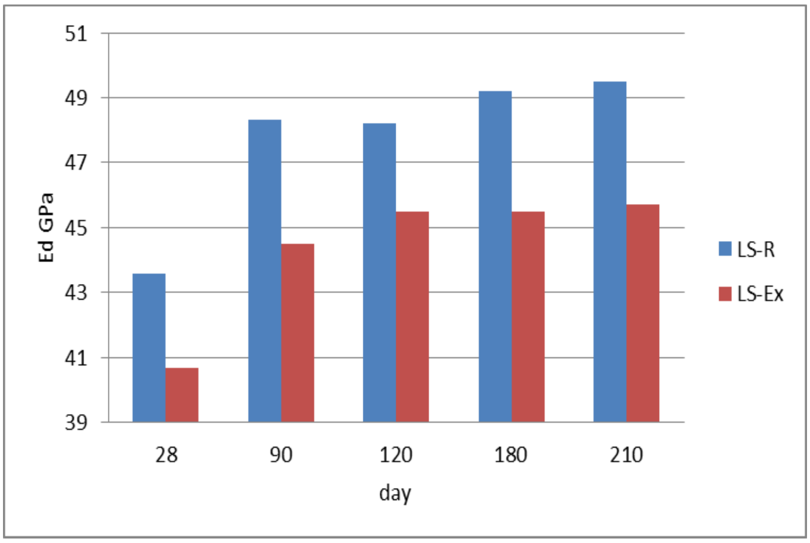

Figure 4. Effect of exposure condition on dynamic modulus for LS mix specimens

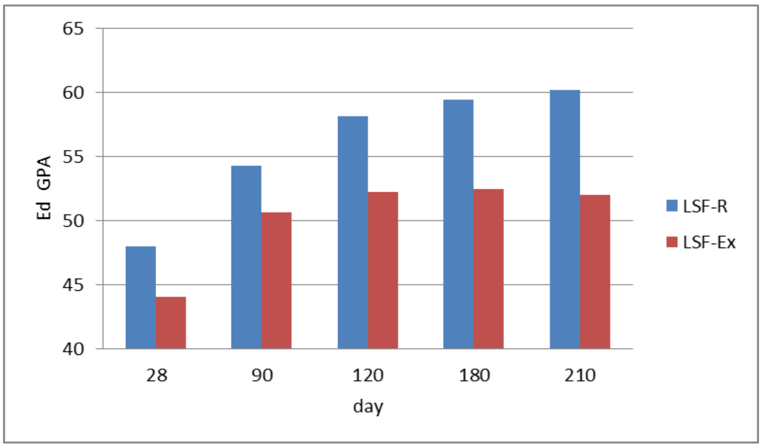

Figure 5. Effect of exposure condition on dynamic modulus for LSF mix specimens

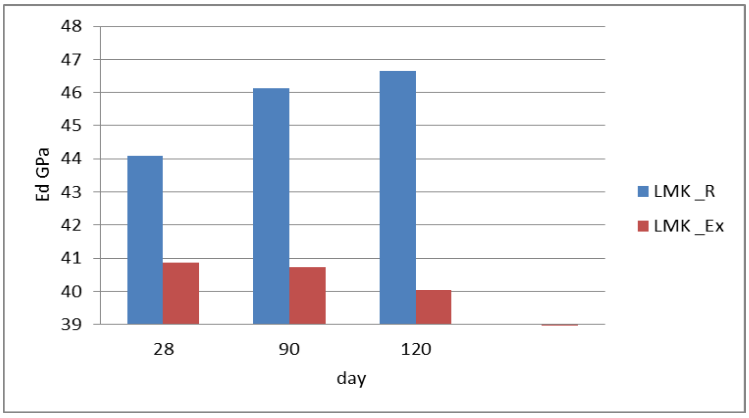

Figure 6. Effect of exposure condition on dynamic modulus for LMK mix specimens

3.4 Weight loss

Table 9 and Figures 7 to 8 show the effect of $MgSO_4$ solution on weight loss of LPC mixtures (LS-Ex and LSF-Ex). Results show that there are not a significant change in weight of those specimens due to exposure to this harsh environment until 210 days age. Meanwhile, LMK-Ex mix specimens subjected to Na_2SO_4 solution showed a continuous weight loss with time of exposure to reach 6.619% at 120 days age and then the specimens disintegrate at 180 days age.

Table 9. Weight change of LPC mixes under different exposure conditions

Mix	Weight change, % at age of					
	28 day	56 day	90 day	120 day	180 day	210 day
LS-Ex	0.000	- 0.156	- 0.275	-0.647	-1.078	-1.193
LSF-Ex	0.000	- 0.184	- 0.321	-0.534	-0.748	-0.855
LMK _Ex	0.000	-2.648	-3.972	-6.619	Failure	Failure

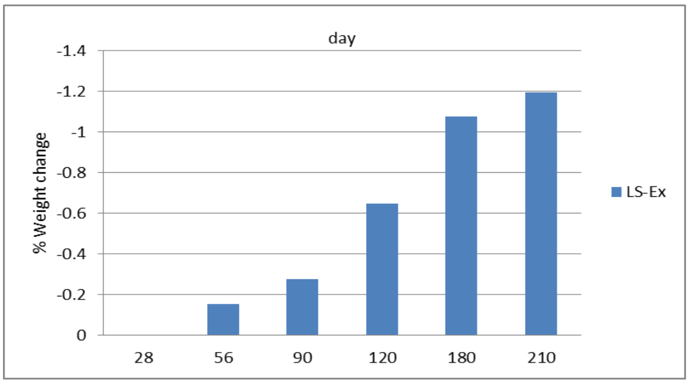

Figure 7. Weight (mass) change of concrete specimens LS-Ex mixes.

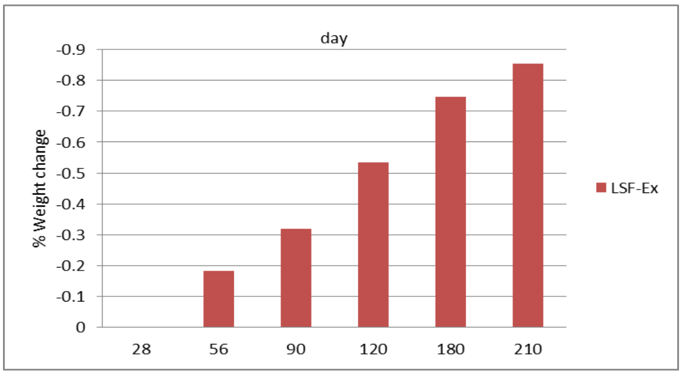

Figure 8. Weight (mass) change of concrete specimens LSF-Ex mixes.

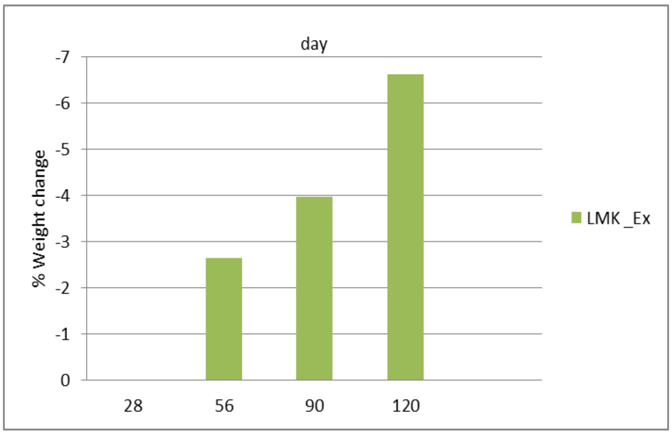

Figure 9. Weight (mass) change of concrete specimens LMK-Ex mixes.

4. Conclusions

1. LPC mixtures, using silica fume or a combination of silica fume and fly ash (mixtures LS and LSF) as a pozzolanic material, didn't disintegrate when subjected to a very harsh environment of 5% concentration of $MgSO_4$ solution until 210 days age. There were not any visual sign of deterioration nor a significant loss in weight of the two mix specimens at the end period of exposure of 210 days age.
2. While LMK mix, using metakaolin as Pozzolan material, disintegrate at 180 days age due to exposure to 5% concentration of Na_2SO_4 solution.
3. The compressive strength of LS and LSF mix specimens continue increasing with time until 90 days age, then begin to drop by 15.3% and 10.6% respectively at 210

days age with respect to that at 90 days age. The effect of Na_2SO_4 solution on the weak LMK-Ex mixture specimens was more pronounced, where the strength of those mix specimens begin to drop after 28 days age, to reach a reduction in compressive strength of 57.7% at 120 day compared to mix LMK-R and break down at 180 days age.

4. The drop in splitting tensile strength of LS and LSF mix specimens due to the $MgSO_4$ solution reached 26.3 and 23.1% respectively at 210 days age with respect to reference mixes (mixes LS-R and LSF-R).
5. The reduction in dynamic modulus of elasticity of LS-Ex mix specimens reaching 8% and 7.6% at ages 90 and 210 days compared to reference mix specimens. These percentages reach 6.7% and 13.5% for LSF-Ex mix specimens.

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