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THE EFFECT OF SULPHATE ON LENGTH CHANGE OF CONCRETE

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Sulphates usually affect calcium aluminates in cements. Sulphate ions might have negative effects on cement hydration and it would be a reason of decrease in cement strength. In this study, the effects of Na_2SO_4 solution on the concretes made from OPC with oil shale ash (OSA) addition (0, 15 and 30%) were investigated. Concretes with 15% OSA gave the lowest value of Length Change Factor (LCF). Addition of an optimum amount of superplasticizer increases positive properties of the concrete with 15% OSA addition, binds free $Ca(OH)_2$ in OPC, makes its composition more effective, prevents massive alkali-aggregates reactions showing that this addition rate is proper.

Introduction

In general, sulphate solutions affect cement mortars more aggressive than lime solutions. This indicates that cement mortars behave like a semipermeable material [1–3].

Sulphate affects generally calcium aluminates in cement. However, SO_4^{-2} ions affect less than sulphate. Sulphate affects concentrate more on calcium aluminates. It is reported that cements containing more C_3A are more durable to sulphate attacks [4–7].

The solubility of calcium sulphate ($CaSO_4$) or gypsum is used as the standard for comparing solubility of salts that are more soluble than gypsum. Table 1 gives the data on different salts and their solubility. Pro-corrosion risk might occur in cement affected by soluble salts. Sodium (Na^+) is a positively charged component or cation of salts. Sodium problems are due to its behavior when attached to clay (Al_2O_3) particles. Examples are sodium sulphate or Glauber's salts [8].

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Table 1. **Composition and solubility of some common soluble minerals [8]**

Mineral	Compound	Solubility, mol/l
Calcite	$CaCO_3$ (calcium carbonate)	0.00014
Gypsum	$CaSO_4 \cdot 2H_2O$ (calcium sulphate)	0.0154
–	$CaCl_2 \cdot 6H_2O$ (calcium chloride)	7.38
Magnesite	$MgCO_3$ (magnesium carbonate)	0.001
Hexahydrite	$MgSO_4 \cdot 6H_2O$ (magnesium sulphate)	4.15
Epsomite	$MgSO_4 \cdot 7H_2O$ (magnesium sulphate)	3.07
Bischofite	$MgCl_2 \cdot 6H_2O$ (magnesium chloride)	5.84
Washing soda	$Na_2CO_3 \cdot 10H_2O$ (sodium carbonate)	2.77
Mirabilite	$NaSO_4 \cdot 10H_2O$ (sodium sulphate)	1.96
Thenardite	$NaSO_4$ (sodium sulphate)	3.45
Halite	NaCl (sodium chloride)	6.15

Na_2O + K_2O (alkaline) are present in the component of Portland cement, and when aggregates used in production of concrete contain reactive silica or carbonate, the reaction between alkaline and aggregate occurs. This reaction causes the concrete to crack and break by dispersing after a few months or years. ASTM standards suggest the amount of alkaline not to exeed 0.6% [9].

Tricalcium aluminate hexahydrate ($Al_2O_3 \cdot 3CaO \cdot 6H_2O$) forms when cement interacts with lime. Ettringite sulphoaluminate salt ($Al_2O_3 \cdot 3CaO \cdot 3CaSO_4 \cdot 30H_2O$) forms when sulphate ($CaSO_4 \cdot 2H_2O$) reacts with tricalcium aluminate hexahydrate. 30 molecules of water in ettringite cause stresses resulting in both a volume increase and decrease in reactions. This situation is relevant to an excess content of C_3A and $CaSO_4 \cdot 2H_2O$ in cement. The content of C_3A and C_3S in cement should not exceed some values to preserve durability of cement to sulphate solutions. The ASTM standards suggest $C_3A+C_3S \leq 58\%$ and $C_3A \leq 8\%$ numbers to be maintained [10].

On the other hand, the content of dissolved sulphate in water and active and passive condition of water affect concrete strength. Generally, it is considered that harmful affects start when the amount of dissolved sulphate in 1 liter water exceeds 210 mg. In swamp waters this number is 225 mg. The reaction between SO_4^{-2} and cement does not continue for a long time compared to their reactions in flowing waters. This indicates that calm waters affect less harmful than flowing waters. For calm waters, these numbers should be increased up to 50%. The numbers given above should be divided to half for $MgSO_4$, since the negative effect of $MgSO_4$ is two times higher than that of $CaSO_4$, Na_2SO_4 and K_2SO_4 [10].

Shale ash contains round glassy grains made of dry disperse substances 3 µm in size with no more than 0,5% humidity [11]. It is possible to benefit from the energy produced by burning lignite as well as its ash in a thermal power plant equipped with a fluidized-bed boiler. In Germany, oil shale has been burnt in a thermal power plant for 30 years, and 400,000 tons of cement has been produced from its ash. The biggest plant that runs on the fluidized-bed burning system was established in 1986, in Duisburg [12]. In Turkey, the first investigations of OSA were conducted during 1974–1979 in Cayirhan county, Beypazari, Ankara, Turkey MTA. In 1987, some studies were also conducted in the framework of a Turkish-German technical coordination project.

Studies carried out by Kikas [13], Kikas with coworkers [14] and Hanni [15] showed that the addition of about 30% OSA into Portland cement clinker can enhance compressive strength of the ordinary Portland cement. Kikas and coworkers, studying the influence of OSA on the properties of self-stressing shale ash cement, concluded that the concrete made with burnt shale is characterized by high strength, high frost resistance, and low permeability.

In this study, length changes in concrete with OSA addition (0, 15 and 30%) OPC burnt at 700 °C have been investigated. Permeability, expansion or changes in length, sulphate resistance, alkali-aggregate reaction and corrosion of reinforcement of concretes have been determined.

Materials and methods

Cement

The ordinary Portland cement OPC 32.5 used was obtained from Elazig Cement Factory. Chemical and physical characteristics of cement are given in Table 2.

Table 2. **Chemical composition of OPC and OSA [17, 18]**

Components and characteristics		100% OSA (Oil Shale Ash)		0% OSA Substituted Cement (OPC 32.5)	15% OSA Substituted Cement	% 30 OSA Substituted Cement
CaO		26.40		63.0	56.16	50.12
SiO_2		39.12	Limits [20] S+A+F≥70%	19.78	16.79	15.45
Al_2O_3		7.80		5.60	5.44	4.9
Fe_2O_3		4.20		3.35	3.05	3.53
MgO		9.26 (Lim. ≤5%) [20]		3.0	4.87	5.37
SO_3		5.21 (Lim. ≤5%) [20]		2.59	3.04	3.39
Na_2O+K_2O		–		0.15	–	–
Loss of ignition (LOI)		3.82 (Lim. ≤%10) [20]		1.73	4.36	6.2
Cl^-		–		≤0.1	–	–
Blaine surface area, cm^2/g		6000 (Lim. 3000) [20]		3180–3500	3400	3450
Specific gravity g/cm^3		2.7		3.15	3.12	3.11
Cement activity (Leim activity, days) [19]. Compression strength, N/mm^2	2	15.3		–	–	–
	7	23.9 (13.0)		–	–	–
	28	29.5 (8.1)		–	–	–
Compression strength (Flexural strength, days), N/mm^2 [20]	7	–		30.6 (5.7)	30.9 (5.9)	24.5 (4.5)
	28	10 (1.8)		42.6 (6.8)	44.4 (7.0)	37.8 (6.5)

Oil shale ash

Oil shale ash, by its nature, is a pozzolanic material. It contains high amounts of soluble SiO_2 and Al_2O_3 [16] which would react with precipitated calcium hydroxide. Oil shale ash samples used in this study were provided from the Ankara-Beypazari-Cayirhan region. Chemical and physical properties of oil shale ash are given in Table 2. Oymael [17] burnt the oil shale at different temperatures (500, 600, 700, 800, 900 and 1030 °C) and reported that OSA, processed at 700 °C for 90 minutes gives the optimum values of compressive strength for the concrete samples.

Standard sand

The sand used in the research program was of standard Rilem Cembureau type according to TS 819 [21], and it was produced in Pinarhisar, Turkey. The standard sand (SS) contained *ca* 90% SiO_2.

Superplasticizer

Superplasticizer (SP), obtained from SIKA, was used as an additive in amount of 0.9% of cement weight. Sikament-FF-N naphthalene formaldehyde was the superplasticizer (SP) used, and technical information given is as follows: pH 9, liquid, density 1.22 kg/l, proposed amount, of cement weight 0.8–3.0%.

Experimental

Curing of specimens

The samples were cured in 95% humidity at 23 ± 2 °C in the laboratory conditions for 24 hours [22], and thereafter put into the "lime saturated water bath" for standard curing. After the samples have reached the strength 20 N/mm^2, they were taken from the water bath and placed into sulphate solutions (5% Na_2SO_4) for 90 days. Concentration of sulphate ions in the solution was 33.8 mg/l at pH between 6 and 8 [23–25]. To control whether the sample has reached compressive strength 20 N/mm^2 or not, 40×40×160-mm (40×40×40-mm) samples were tested. Cube samples have been found to reach 20 N/mm^2 in 7 days.

The ratio of corrosive (aggressive) volume to sample volume was maintained constant and less than 1 cm^3 cement in reply to 1 ml solution. The evaporation was prevented by covering the solution baths with glass plates as described in [26]. Na_2SO_4 solution is mixed time by time to be not crystallized (Fig. 1).

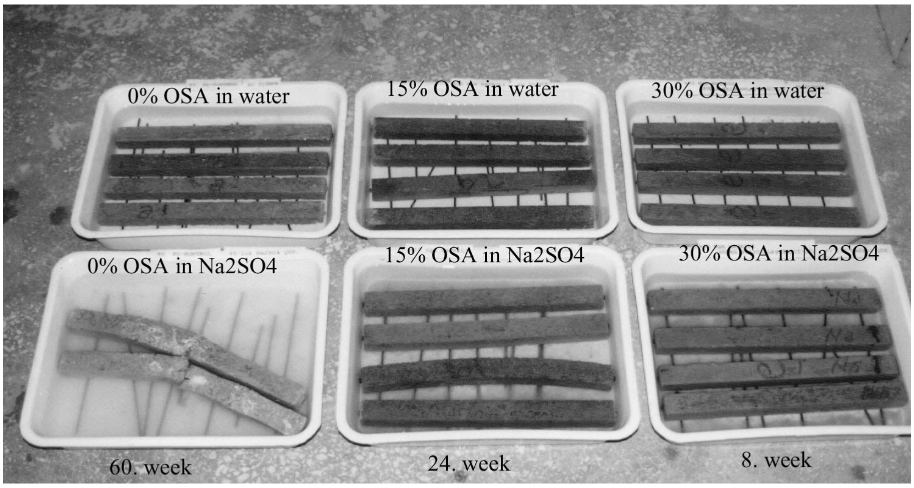

Fig. 1. Cure of mortar bars in water and sulphate colution [13].

Test performed

As stated previously, in each treatment three samples were prepared from cement substituted with 0, 15 and 30% OSA additives. S/B ratio was taken constant value of 0.5 (it is 0.49 according to ACI C1012-87). The amount of optimum flow/water requirement necessary for each mix was determined using the flow table expounded in ASTM C 109, 1993, for maintaining a constant flow.

Concrete mixture design is given in Table 3. The flow test was conducted for 70±1-mm mortars specimen to determine water content necessary for the desired workability, the length change measurements of fresh mortar were carried out on 25×25×285 mm concrete specimen.

Table 3. **Material quantities, solutions, oil shale ash (OSA), superplasticizer (SP) water/cement (W/C) ratio and slump values in production of concrete samples**

No	Substitute Ratio	Water, solutions	Quantity, kg/m^3			Ratios, %		
			OPC 32.5	OSA	SS	SP	W/C	Flow
1	0%	Water -1 Na_2SO_4-1	330	–	1000	–	0.57	105
2	0% (SP)	Water -2 Na_2SO_4-2	330	–	1000	0.9	0.46	106
3	15%	Water -3 Na_2SO_4-3	280	50	1000	–	0.62	108
4	15% (SP)	Water -4 Na_2SO_4-4	280	50	1000	0.9	0.51	106
5	30%	Water -5 Na_2SO_4-5	230	100	1000	-	0.67	105
6	30% (SP)	Water -6 Na_2SO_4-6	230	100	1000	0.9	0.55	107

Table 4 shows compressive and flexural (40×40×160 mm) strengths of mixtures measured after 7, 28 and 180 days, plotted against ash amount in binder. One can see that compressive strength decreases with increasing ash content in the concrete mixtures, and the highest strength of mixtures containing OSA is achieved at the age of 28 days.

Table 4. **Compressive and flexural (40×40×160 mm) strengths of mixtures measured after 7, 28 and 180 days, depending on ash amount in binder**

	days	0% OSA (100% OPC)	15% OSA	30% OSA
Compressive and flexural strength, N/mm^2	7	30.6 (5.7) 28*	30.9 (5.9) 22*	24.5 (4.5) 18*
	28	42.6 (6.8) 36*	44.4 (7) 32*	37.8 (6.5) 27*
	180	51 (7.4)	55.5 (8.5)	52.7 (8.9)

*Measurements by Al-Hasan [27]

Measurement of samples

Samples were formed according to [28], standards and special Ø6 mm noncorrosive bolts were placed at the ends of samples. The distances between the bolts with the formwork were 250±2.5 mm, the length inside the specimen was 7.5±0.5 mm and outside the specimen – 5 mm.

The length of the concrete specimens was measured in ±0.002 error range with the device shown in Fig. 2. At the measurements, great pains were taken to calibrate dial indicator and to clean the grooves in which the specimens were put.

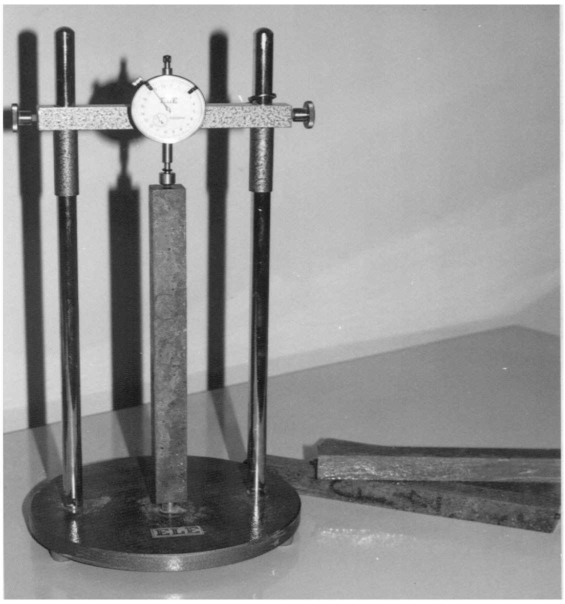

Fig. 2. Measurement of mortar bars with dial indicator.

The samples were measured with a dial indicator within the first ten minutes, thereafter they were taken out of the solution and put back into the solution again.

Length Change Factor (LCF) in prismatic concrete bars, calculated using four-week measurements, are given in Table 5, Figures 3, 4 and 5. LCF was calculated as follows:

$$LCF\ (\%) = L_n - L_0/285 \times 100,$$

where LCF is Length change factor, %

L_0 – length measurement value of four-week prismatic sample, 10^{-3} mm,

L_n – length measurement value at the end of test, 10^{-3} mm.

Table 5. **Length change factor of OSA blended concrete**

No	Compound	Solution	Length Change Factor (LCF), % Week						
			8	12	16	24	36	52	60
1	0% OSA (100% OPC)	water	0.018	0.036	0.056	0.146	0.386	1.343	3.538
	(Contr.) (10^{-3})	Na_2SO_4	0.037	0.199	0.993	1.50	2.012	2.118	4.33
2	15% OSA (10^{-3})	water	0.003	0.072	0.136	0.147	0.512	1.224	1.228
		Na_2SO_4	0.336	0.375	0.445	0.482	0.713	0.945	1.863
3	30% OSA (10^{-3})	water	0.025	0.059	0.072	0.032	0.438	1.308	1.471
		Na_2SO_4	0.021	0.074	0.188	0.200	0.458	1.513	2.134
4	30% OSA (SP)	water	0.015	0.024	0.112	0.151	0.467	0.75	1.047
	(10^{-3})	Na_2SO_4	0.003	0.050	0.092	0.134	0.375	1.303	1.307

Note: Values for the first measurements of samples during the 4th week are not included in this table.

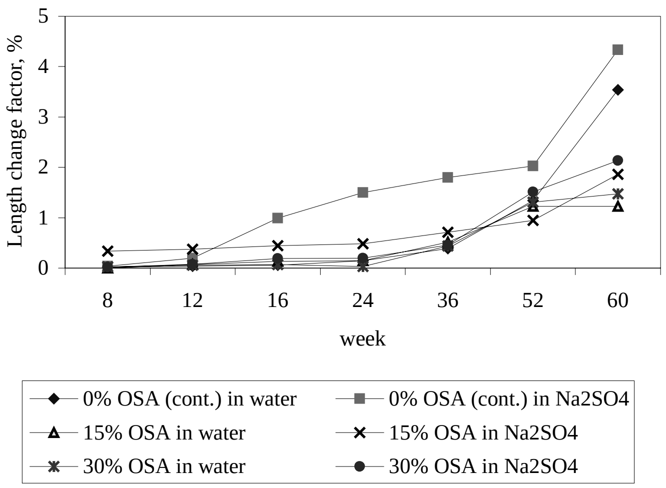

Fig. 3. Expansion of 0%, 15%, 30% OSA added concretes in Na_2SO_4 mixtures and water.

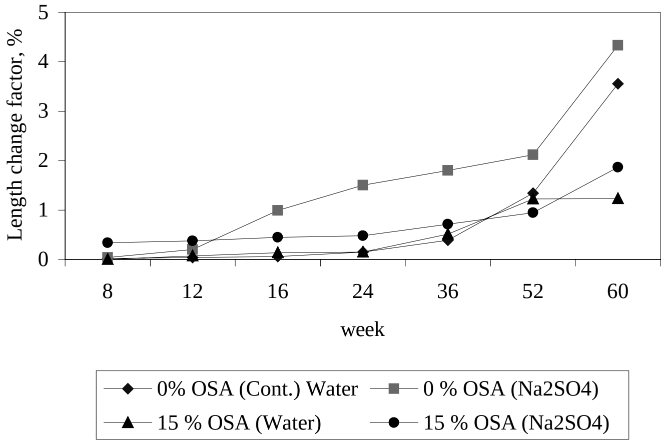

Fig. 4. Expansion of 0%, 15% OSA added concretes in Na_2SO_4 mixtures and water.

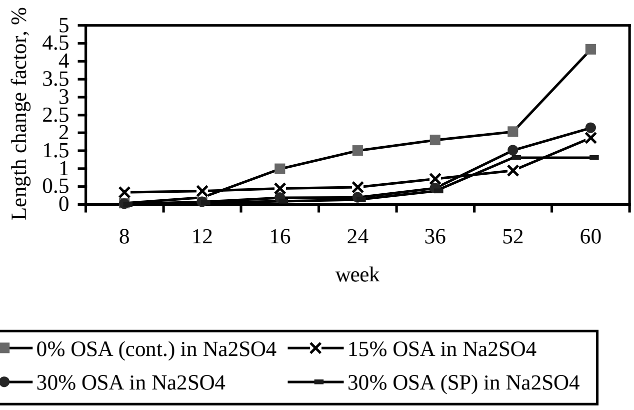

Fig. 5. Expansion of 0%, 15,%, 30% OSA added concretes in Na_2SO_4 mixtures.

Conclusions

This study was carried out in two parts. First, measurement of the compressive strength of 40×40×160-mm samples (3 samples from each mixed total of 54 samples), second, measurement of the length change of 25×25×285-mm concrete specimens (4 samples from each mixed total 72 samples). The length of concrete samples has been measured following the basic rules after 1, 2, 3, 4, 8, 13, 15, 24, 36, 48, 52 and 60 weeks according to ASTM C1012-87. LCF values of concrete in water and Na_2SO_4 solution are given in Table 5 and Figures 3, 4 and 5.

All samples in the solution have demonstrated the characteristics like length extension and shrinkage to be unstable during the initial weeks. However, 4 weeks later the value of length extension for concrete was already stable. Dimensional variability during the initial weeks can be attributed to C-S-H (calcium silicate hydrate), as gels are filling the pores in concrete during hydration.

LCF values of all 0, 15 and 30% OSA-added concrete have been measured within sixty weeks. The lowest value of LCF has been achieved for 15% OSA-added concrete. Deformations of concrete bars of OPC control sample bars according to age are shown in Fig. 4.

Adding SP to concrete exerted positive effect on concrete samples. 30% OSA-blended cement with SP addition demonstrates the same LCF value as 15% OSA-added sample without SP.

The value of length extension for 14 days of samples with OSA addition much below the limits 0.020%, is proper for fly ashes according to ASTM C 618 [29]. According to ASTM C 33 and ASTM C227, 10% expansion limit at the 52nd week is anticipated on the concrete mortar bars. This limit is not passed over by 15% OSA-added concrete sample in water. The addition of 15% OSA into the OPC effectively prevents free $Ca(OH)_2$ and the reactions between alkali aggregates. Oymael [17] has proved the suitability of 15% oil shale ash as an admixture in cement and concrete.

Compression strength values given in the present study to determine length change factor values, are 10–30% higher than those measured by Al-Hassan [27] (Table 4). Differences in the values may be caused by differences in sample dimensions because 40×40×40-mm samples used in the present study are smaller than Al-Hassan's 70±1-mm samples. The shorter the specimen, the higher the value of compressive strength.

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