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EFFECTS OF SULPHATES ON ELASTIC MODULUS OF CONCRETE SAMPLES MADE FROM BLENDS OF CEMENT WITH OIL SHALE ASH

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Concrete is a material both weak and strong. Its durability decreases under negative impact of several chemicals. In particular, when some sulphates in sea and ground waters react with cement paste, concrete expands and cracks; therefore, concrete has a very short life span. In that case, either the effects of sulphates should be suppressed as much as possible, or the performance of concrete should be increased. To increase the performance of concrete, some studies are in progress by adding some mineral additives to cement paste in predetermined ratios. In this study, the changes in moduli of static elasticity of the concrete (mortar) samples, produced by using Portland cement which contains 0, 15 and 30% oil shale ash by mass, and cured in Na_2SO_4 *and* $MgSO_4$ *solutions, were examined. Concrete containing 15% ash in cement gave optimum results.*

Introduction

The main constituents of Portland cement are lime (CaO = C), silica (SiO_2 = S), alumina (Al_2O_3 = A), and iron oxide (Fe_2O_3 = F). Various cement specimens are obtained by mixing these raw material constituents. The process of manufacture of cement consists essentially of grinding the raw materials, mixing them thoroughly in certain proportions and burning in a large rotary kiln at a temperature of up to about 1450 ºC when the material sinters and partially fuses into balls known as clinker. The clinker is cooled and ground to a fine powder, with some gypsum added, and the resulting product is the commercial Portland cement which is widely used throughout the world [1–3].

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Four compounds are usually regarded as the major constituents of cement. They are: tricalcium silicate ($C_3S = 3CaO·SiO_2$), dicalcium silicate ($C_2S = 2CaO·SiO_2$), tricalcium aluminate ($C_3A = 3CaO·Al_2O_3$), and tetra-calcium aluminoferrite ($4CaO·Al_2O_3·Fe_2O_3 = C_4AF$) [4].

Concrete expands when cement paste reacts with sea water or underground waters containing Na_2SO_4 and $MgSO_4$, and eventually weakens. Researchers have conducted experiments on additives used with cements to reduce the damage caused by sulphates [5–10]. The effects of Na_2SO_4 and $MgSO_4$ on cement paste are higher than those of $CaCO_3$ compounds (lime) [11] and calcium aluminates [1–3].

The content of dissolved sulphate in water and active and passive condition of water affect concrete strength. If sulphate concentration in water is < 0.10 g/l, 0.15 g/l – 1.00 g/l, 1.00 g/l – 2.00 g/l, and over 2.00 g/l, the effect of sulphate in waters is considered harmless, less harmful, harmful and severe harmful, respectively. Generally, it is considered that harmful effects appear when the content of dissolved sulphate in one liter water exceeds 210 mg. In swamp waters, this value is 225 mg/l. Reaction between SO_4^{-2} and cement does not continue for long compared to their reactions in active waters. This indicates that calm waters are less harmful than active ones. The numbers should be increased up to 50% for calm waters. The numbers given above should be divided to half for $MgSO_4$ since the negative effect of $MgSO_4$ is twice higher than that of $CaSO_4$, Na_2SO_4 and K_2SO_4 [3, 7].

Pozzolanic effects on the main compounds and characteristics of cement are very important. There are many kinds of pozzolanas. Oil shale ash (OSA) is one of them. Effects of sulphate on cement and main characteristics of the process should be known when different amounts of OSA have been added to cement. There are many studies on the resistance of cement and concrete to sulphate made by Raado and Hain [12], Bellman [13], Moon [14], Lee [15] etc. However, no research on the resistance of mixed cement and concrete to sulphate has been found, thus making this study more important.

Static methods of measuring modulus of elasticity can be applied to investigate the decrease in compressive strength of concrete induced by chemical factors with time. There is a relation between modulus of elasticity and strength of hardened cement [2, 7].

Changes in cement quality and thus modulus of elasticity can be caused by different factors. It should be necessary to produce concrete samples of the same quality for observing the static modulus of elasticity. Thus, it can be possible to compare different moduli of elasticity of concretes, affected and unaffected by chemical factors [16].

There is no doubt that the modulus of elasticity increases with an increase in the compressive strength of concrete, but there is no agreement on the precise of the relationship. This is not surprising, given the fact that the modulus of elasticity of concrete is affected by the modulus of elasticity of the aggregate and by volumetric proportion of aggregate in concrete. The former is rarely known, so that some expressions, for example that of ACI 318-95, allow to characterize the modulus of elasticity of an aggregate by a coefficient which is a function of density of concrete, usually density raised to power 1.5. All that can be said reliably is that the increase in the modulus of elasticity of concrete is progressively lower than the increase in compressive strength raised to power 0.5. The expression for the secant modulus of elasticity of concrete, E_c in pounds per square inch, recommended by ACI 318-89 (Revised 1992) for structural calculations, applicable to normal weight concrete, is $E_c = 57\,000(f'_c)^{0.5}$ [7]. Modulus of elasticity for normal weight concrete is 14 000–42 000 N/mm^2 and for lightweight concrete – 10 500–17 500 N/mm^2 [17].

In the study, changes in static modulus of elasticity for concretes containing 0, 15, and 30% OSA added to cement and cured in aggressive solutions such as Na_2SO_4 and $MgSO_4$ for 90 days were investigated.

Materials and methods

Materials

Cement

The ordinary Portland cement (OPC) (CEM I) used in this study was provided by Elazig Cement Factory. Chemical composition of OPC and OSA is given in Table 1.

Table 1. **Chemical composition of OPC and OSA, %**

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		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	–	–
Specific gravity g/cm^3		2.7		3.15	3.11	3.11
Cement activity days [19] compression strength N/mm^2	2	15.3		–	–	–
	7	23.9		–	–	–
	28	29.5		–	–	–
Compression strength (Flexural strength) (days) [19] N/mm^2	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 (OSA) is a pozzolonic material made of oil shale rocks processed at very high temperatures (500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1030 °C). Oymael [18] has used OSA processed at 700 °C for 90 min, with varying the percentage of Portland cement added in concrete samples. Compression tests showed that the optimum success was obtained with Portland cement containing 15% OSA.

Superplasticizer

Superplasticizer (SP), obtained from Sika, was used as an additive in amount of 0.9% of cement weight. Sikament-FF-N naphthalene formaldehyde sulphone) was the superplasticizer 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% (Table 2).

Standard Sand

Sand used in the research program was of standard Rilem Cembureau type according to TS 819 [21], and it was produced in Pinarhisar. The amount of SiO_2 in standard sand (SS) is 90% (Table 2).

Table 2. **Material quantities, solutions, oil shale ash (OSA), superplasticizer (SP) water/cement (W/C) ratio and slump values in production of concrete samples**

No	Content of substitute	Water, solutions	kg/m^3			Ratios, %		
			OPC 32.5	OSA	SS	SP	W/C	Flow
1	0%	Water –1 Na_2SO_4-1 $MgSO_4$-1	330	–	1000	–	0.57	105
2	0% (SP)	Water -2 Na_2SO_4-2 $MgSO_4$-2	330	–	1000	0.9	0.46	106
3	15%	Water -3 Na_2SO_4-3 $MgSO_4$-3	280	50	1000	–	0.62	108
4	15% (SP)	Water -4 Na_2SO_4-4 $MgSO_4$-4	280	50	1000	0.9	0.51	106
5	30%	Water -5 Na_2SO_4-5 $MgSO_4$-5	230	100	1000	–	0.67	105
6	30% (SP)	Water –6 Na_2SO_4-6 $MgSO_4$-6	230	100	1000	0.9	0.55	107

Solutions

Na_2SO_4 and $MgSO_4$ obtained from Merck company are characterized in Table 3. 70% solutions of Na_2SO_4 and $MgSO_4$ were prepared in the laboratory. Concentration of sulphate solution was 33.800 mg $MgSO_4$/l, and pH was varied between 6 and 8 [22–24]. The aggressive (corrosive) volume *versus* sample volume ratio was maintained constant at less than 1 cm^3 cement in reply to 1 ml solution [25].

Table 3. **Impurities in Na_2SO_4 and $MgSO_4$**

Chemical composition (weight %)		
	Na_2SO_4	$MgSO_4 . 7\, H_2O$
NaOH	–	< 0.008
H_2SO_4	–	< 0.01
Cl	< 0.002	< 0.014
Pb	< 0.001	< 0.0005
As	< 0.0002	< 0.0002
Ca	< 0.005	< 0.01
Fe	< 0.001	< 0.001
Mg	< 0.01	–
Se		< 0.001

Methods

It is known that the value of static elasticity modulus changes with stress applied on samples. In order to avoid this, the experiment procedure proposed by RILEM [26] was used. According to the procedure, static modulus of elasticity is computed as follows:

$$\varepsilon_s = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

where: A – sample cross-section area, P – breaking load, P_1 – initial load which produces 0.5 N/mm^2 stress, P_2 = P/3 – final load, $\sigma_1 = P_1/A$ – initial stress, $\sigma_2 = P_2/A$ – final stress, $\varepsilon_1$ve ε_2 – initial and final strains (average of three readings).

Central static compression tests were conducted on 70×70×70-mm cubic concrete samples with or without OSA additives to measure the values of static elasticity modulus (E_s). Deflections were measured in ± 0.002 mm range error. A metal ring covering the sample was mounted on the bottom plate and the dial indicator measuring device on top of the metal ring. Constant strain rate of 0.24 N/mm^2 was used in the testing procedures.

Experimental

Curing of Specimens

The admixture was premixed with total amount of water before application, and this solution was used for preparation of concrete mortars. Concrete mortar mixtures were prepared in accordance with ASTM C 109 [19]. The samples were cured in 95% humidity at 20 ± 2 °C in the laboratory for 24 hours, and then put into the water bath for 14 days 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 ($MgSO_4$ and Na_2SO_4) solutions.

Test Performed

The flow test of mortars was conducted to determine water content necessary for the desired workability. Flow test of fresh mortar was carried out using a flow table and cone immediately after mixing. The amount of water necessary for each mix was determined using flow table expounded in ASTM C 109 for maintaining a constant flow. The flow table was applied to get a flow of 105–115 mm, according to ASTM C 109 [19].

As stated previously, three samples in each treatment were prepared from cement substituted with 0, 15 and 30% OSA additive. Three samples were used in compression strength tests, and other three were used for determining the elasticity modulus values.

Results and Discussion

The measured and calculated scales are given in Table 4 and shown in Fig. 1 and 2. The unit weight of the samples placed into $MgSO_4$ solution was higher than that of samples placed into water bath for standard cure. Similar findings were obtained for the values of elasticity modulus of concrete samples. Samples in $MgSO_4$ solution were significantly wearied out, micro textures were developed on the surfaces, the samples started to dissolve, and the unit weight started to decrease due to an increase in the void ratio. Naturally, the values of elasticity modulus decreased. Similar findings, but less severe damages occurred in Na_2SO_4 solution. 15% OSA added to concrete gave optimum results for strengths and modulus of elasticity. This was attributed to the OSA's pozzolonic effect at 15% additive [27]. Concrete used in the experiments were named as microconcrete because their aggregate size were less then 4 mm. The results from the tests conducted on microconcrete can be generalized for concretes [28, 29].

If the values of modulus of elasticity were accepted as 100% for 0% OSA-substituted cement (control samples) in water, values of modulus of elasticity for 15% and 30% OSA-substituted cement decreased to 71% and 36%, respectively. When concrete samples were examined in $MgSO_4$ solution, higher % of OSA caused the decrease in the value of modulus of elasticity. This situation is also valid for concrete in Na_2SO_4 solution. Comparison of the

Table 4. **Calculation procedure for modulus of elasticity of samples (cured in water, $MgSO_4$ and Na_2SO_4 solutions) with respect to their substitute ratios and superplasticizer**

Content of OSA	Sample area, mm^2	Breaking load, kN	Initial load, kN	1/3+7* P Peak load, kN	P_2/A N/mm^2	P_1/A N/mm^2	$\frac{\Delta \ell_2}{\ell}$ $*10^{-3}$	$\frac{\Delta \ell_1}{\ell}$ $*10^{-3}$	$\frac{\Delta\ell_2 - \Delta\ell_1}{\ell}$ $*10^{-3}$	$E_s = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$ N/mm^2
	A	P	P_1	P_2	σ_2	σ_1	ε_2	ε_1	ε_2-ε_1	Es
Samples in water										
0%	4900	112.21	2.45	37.40	7.633	0.5	4.07	3.94	0.13	54869
15%	4900	81.83	2.45	27.28	5.567	0.5	5.27	5.14	0.13	38977
30%	4900	45.08	2.45	15.03	3.067	0.5	6.60	6.47	0.13	19746
30% (SP)	4900	54.88	2.45	18.29	3.733	0.5	6.14	5.99	0.15	21553
Samples in $MgSO_4$ solution										
0%	4900	94.08	2.45	31.36	6.400	0.5	6.27	6.07	0.20	29500
15%	4900	67.62	2.45	22.54	4.600	0.5	6.67	6.43	0.24	17083
30%	4900	35.28	2.45	11.76	2.400	0.5	7.10	6.92	0.18	10556
30% (SP)	4900	50.47	2.45	16.82	3.433	0.5	6.83	6.60	0.23	12752
Samples in Na_2SO_4 solution										
0%	4900	104.86	2.45	34.95	7.133	0.5	6.77	6.61	0.16	41456
15%	4900	80.36	2.45	26.79	5.467	0.5	5.69	5.56	0.13	38208
30%	4900	39.69	2.45	13.23	2.700	0.5	4.64	4.43	0.21	10476
30% (SP)	4900	51.94	2.45	17.31	3.533	0.5	6.37	6.14	0.23	13187

values of elasticity moduli of 0% OSA samples cured in water, $MgSO_4$ and Na_2SO_4 shows that in $MgSO_4$ and Na_2SO_4 solutions the value decreased to 54% and 75%, respectively. As for the 15%- and 30%-substituted samples, modulus of elasticity of samples decreased in both $MgSO_4$ and Na_2SO_4. However, all of the 15%-substituted samples are characterized by maximum resistance (Fig. 2). The increase in the elastic modulus of specimens with 30% OSA and superplasticizer have been found insignificant.

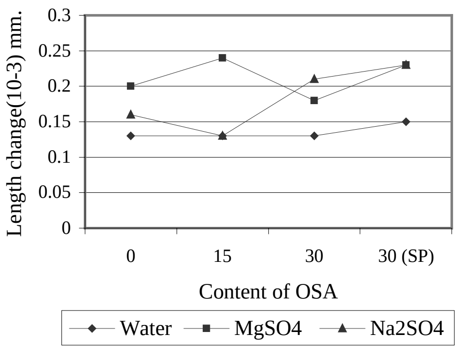

Fig. 1. Length change of samples cured in water, $MgSO_4$ and Na_2SO_4 solutions versus the content of OSA and SP

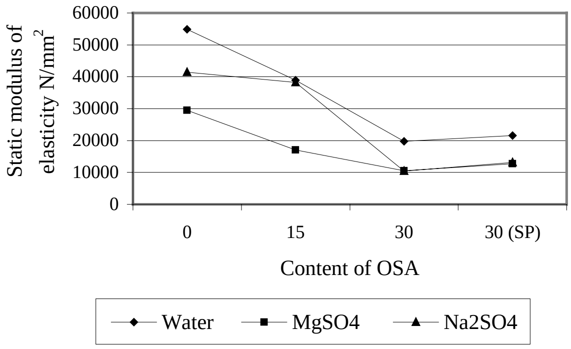

Fig. 2. Modulus of elasticity of samples cured in water, $MgSO_4$ and Na_2SO_4 solutions versus percentage of oil shale ash additive

According to the control samples, decrease in modulus of elasticity for cement substituted by 15% OSA can be related with the effects of C type pozzalans, lower calcareous of OSA and inefficiency of cooling speed after burning. A decrease in modulus of elasticity when the OSA substitution rate was increased to 30% can be related with large amounts of OSA in Portland cement after attaching $Ca(OH)_2$. It can be seen that OSA has weak effects on the values of elasticity modulus (Fig. 2). In this figure the length of the samples hold in $MgSO_4$ has changed substantially.

Conclusions

The 15% OSA additive increased the resistance of Portland cement to sulphate. This increased resistance is less than the increased resistance of 0% OSA. Samples in $MgSO_4$ solution lost more strength than the samples in Na_2SO_4 solution. It is recommended to produce concrete that is water impermeable or insolated from the sulphate effects from 15% OSA-substituted Portland cement (CEM II/B-T), especially for the structures which have no contact with $MgSO_4$.

Recommendations

In this study, oil shale ash was cooled under laboratory conditions. A further research that focuses on different cooling methods and techniques should be undertaken. However, the ability to generalize these results is limited due to scarcity of specified concrete samples and testing procedures. Shortcomings of this study could be overcome by applying tests on different concretes, sample size, and environments including seawaters. Modulus of elasticity of

15% OSA-substituted specimens can, however, be increased by adding superplasticier in suitable amounts.

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REFERENCES

1. *Akman, M. S.* Concrete Technology of Marine Structures, ITU Library, No. 1481, Istanbul, 1992. P. 132–206 [in Turkish].
2. *Dreux, G.* Nouveau Guide du Béton, Ed. Eyrolles, Paris 1986.
3. *Durmuş, A.* Aluminous cements in reinforced concrete // Journal of Turkish Engineering News, TMMOB Turkish Chamber of Civil Engineers. 1981. No. 297. P. 23–24 [in Turkish].
4. *Smith, W. F.* Materials Science and Engineering. Literature publishing, Istanbul, 2001. P. 65 [in Turkish].
5. *Al-Dulaija, S. U., Maslehuddi, M., Al-Zahrani, M. M., Sharif, A. M., Shameem, M., Ibrahim, M.* Sulfate resistance of plain and blended cements exposed to varying concentrations of solution sulfate // Cement and Concrete Composites. 2003. Vol. 25. P. 429–437.
6. *Kalousek, G. L., Porter, L. C., Benton, E. J.* Concrete for long-time service in sulfate environment // Cement and Concrete Research. 1972. Vol. 2, No. 1. P. 79–89.
7. *Neville, A. M.* Properties of Concrete. John Wiley & Sons, Inc. New York, 1997.
8. ACI Committee 201, Durability of concrete in service // Journal of ACI. 1962. Vol. 59, P. 57–59.
9. *Gjorv, O. E.* Durability of concrete structures in the ocean environment. Proc. Symp. On Concrete Sea Structures, Tbilisi, 1972. P. 141–145.
10. *Hachani, L., Triki, E., Moussa, D., Raharinaivo, A.* Etude expérimentale de la dégradation du béton armé dans diverses solutions aqueuses. Bull.de Liaison des Lab. Des Ponts et Chaussées. Paris, 1990. No. 169. P. 79–89.
11. *Podvalnyi, A. M.* Phenomenological aspect of concrete durability theory // Materials and Structures. 1976. 9(51), P. 151–162.
12. *Raado, L.-M., Hain, T.* Effect of Portland cement composition on sulphate resistance. I. Scientific Proceedings of RTU Material Science and Applied Chemistry. Book of Abstracts. Riga, Latvia, 2004. P. 15.
13. *Bellmann, F., Möser, B., Stark, J.* The pozzolanic reaction of coal fly ash and its effects on the sulphate resistance of concrete // ZKG. 2003. Vol. 56, No. 10. P. 70–77.

14. *Moon, H. Y., Lee, S. T.* Influence of silicate ratio and additives on the sulphate resistance of portland cement // Advances in Cement Research. 2003. Vol. 15, No. 3. P. 91–101.
15. *Lee, S. T, Moon, H. Y., Swamy, R. N., Kim, S. S., Kim, J. P.* Sulphate attack of mortars containing recyeled fine aggregates // ACI Materials Journal. 2005. Vol. 102, No. 4. P. 224–230.
16. *Erdoğan, T. Y.* Concrete, METU Pres, Ankara, 2003. P. 567–568 [in Turkish].
17. *Mindess, S., Young, J. F.* Concrete, Prentice-Hall, Inc., New Jersey, 1981.
18. *Oymael, S.* The Suitability of Oil Shale Ash as an Admixture in Cement and Concrete, PhD Dissertation, Firat University, Elazig, 1995. P. 163 [in Turkish].
19. ASTM C 109. Test method for compressive strength of hydraulic cement mortars. 1993 Annuel Book of ASTM Standards. Vol. O4.01.
20. Turkish Standards, TS 25 – Trass. Turkish Standards Institution, Ankara, 1975.
21. Turkish Standards, TS 819 – Rilem Cembureau Sand. Turkish Standards Institution, Ankara, 1989.
22. ASTM C 1012-87. Standard test method for length change of hydraulic-cement mortars exposed to sulphate solution.
23. ACI 201. 2R-77, Guide to durable concrete, Chapter 3, Abrasion. ACI Manual of Concrete Practice, Part I, Detroit, 1986.
24. *Tuthill L. H.* Resistance to chemical attack. ASTM Sp. Tech. Publicn. 1978, No. 169 B. P. 369–387.
25. *Madej, J.* Corrosion resistance of normal and silica fume-modified mortars made from different types of concrete, Istanbul Conference, 1992. P. 1189–1196.
26. TMMOB Turkish Chamber of Civil Engineers. Durability of concrete. Proceedings, 5. National congress on concrete, Istanbul, 1–3 October 2003 [in Turkish].
27. *Durmuş, A.* Corrosion of concrete. // Turkish Engineering News, TMMB chamber of civil engineers. Istanbul, 1978. No. 277. P. 20–25 [in Turkish].
28. *Durmus, A., Arnaud, M., Lorrain, M.* Le role des effects transversaux dans la fléxion des planchers nérvures en béton armé: Conséquences sur la sécurité. Annales de 1'ITBTB. Paris, 1979. No. 376 serié EM/173. P. 30–39.
29. *Farran, J.* Contribution minéralogique à l'Etude de l'Adhérence entre les constituents hydratés des ciments et les matériaux enrobes // Rev. des Matériaux de Construction. 1956, No. 490, 491, 492.

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