

Evaluation of blends tincal waste, volcanic tuff, bentonite and fly ash for use as a cement admixture

Y. Abali^a, S.U. Bayca^{b,*}, S. Targan^a

^a Department of Chemistry, Faculty of Science and Art, Celal Bayar University, Manisa, Turkey

^b Soma Technical Vocational School, Celal Bayar University, Soma, Manisa, Turkey

Received 8 June 2005; received in revised form 30 August 2005; accepted 10 September 2005

Available online 28 November 2005

Abstract

The evaluation of blends tincal waste (TW), fly ash (FA), bentonite (BE), volcanic tuff (VT) for use as a cement admixture was investigated. The properties examined include setting time, expansion, water requirement, specific surface and compressive strength of cement mixtures. The results revealed that the early compressive strength decrease with increasing tincal waste, due to tincal waste increasing initial setting time of the cement. The tincal waste and volcanic tuff of cement mixtures increased and there was reduction in compressive strength. The more the tincal waste increased the greater retardation there was initial setting time this may be attributed to containing high amount B₂O₃ and MgO content. The tincal waste and fly ash increased with expansion increased. Water requirement increased as the Blaine fineness of the cement mixtures increased. The results obtained were compared with standards and five batches were advised as suitable for the standard.

© 2005 Published by Elsevier B.V.

Keywords: Compressive strength; Setting time; Tincal waste; Admixture; Reuse waste

1. Introduction

Turkey is the second producer following the United States with 1.72 million tonnes boron minerals and compounds production. The most important boron ores in Turkey are colemanite, ulexite and tincal. Products, such as borax, boric acid and sodium perborate are obtained from these ores. But, the trommel sieve waste forms in the reactor during the borax production from tincal. The amount of this waste is about 250,000 tonnes/year [1].

FA is a waste of coal-burning power plants. It is widely used as a cementitious material and a pozzolanic ingredient in concrete. The use of FA in concrete is constantly increasing because it improves the properties of concrete [2]. FA is also an abundant waste material, i.e. Turkey utilities generate 10 million tonnes of FA each year [3]. Tuffs, which are used as admixtures in cement, are very important economically. They are cheap raw materials and its utilization leads to considerable savings in the unit cost of concrete [4].

In recent years, various types of materials such as fly ash, tincal waste, bentonite, volcanic tuff and slag have been investigated as Portland cement additives. Borate wastes, (i.e. tincal waste, colemanite waste, ulexite waste, borogypsum) have investigated by many researches [5–8]. The addition of borate wastes has been found to increase the setting time of the cement. The presence of B₂O₃ in the colemanite ore waste has remarkable effect on the mechanical properties of cement apart from increased replacement of colemanite waste with Portland cement results higher setting time and specific surface [8].

Concrete containing the ground coarse fly ash replacement between 15 and 50% can produce high concrete and 25% cement replacement gave the highest compressive strength [2]. The inclusion of natural pozzolan at replacement levels of 5% resulted in an increase in compressive strength of the specimens compared with that of the control concrete [9]. It can be concluded that certain natural pozzolan-silica fume combinations can improve the strength of mortars more than natural pozzolan or silica fume alone [10].

Most of the fly ash and bottom ash mixtures show compressive strength values better than that of the reference mixture [11]. The degree of the increase of the bend strength was influenced by water content and SiO₂/CaO mass ratio of the coatings on

* Corresponding author. Tel.: +90 236 612 0063; fax: +90 236 612 0063.

E-mail address: salih.bayca@bayar.edu.tr (S.U. Bayca).

the interface. Higher SiO₂ and lower CaO contents of the additives were preferred in the experimental range. The strength of concrete with 40, 45 and 50% fly ash content, even at 28 days is sufficient enough for use in reinforced cement concrete construction [12]. Certain cement containing pozzolans with high activity or low alumina content improve resistance to sulfate attack, although the amount of pozzolan in the cement is important [13].

The effects of one or two additives in Portland cement were investigated by many researchers. The influence of combined action of volcanic tuff, bentonite, fly ash, tincal waste on the properties of cement was examined in this paper. The main aim is to find the best combinations of these mixtures and evaluate volcanic tuff, bentonite, fly ash, tincal waste. Therefore, the various combinations of cement containing volcanic tuff, bentonite, fly ash, tincal waste and Portland cement were prepared.

2. Materials and methods

FA was supplied from Soma SEAS Thermal Plant (Manisa, Turkey); clinker (C) and gypsum from the Baticim Cement Plant (İzmir, Turkey); TW from Eti Maden Borax Plant (Kirka, Eskisehir, Turkey); VT from Gökçeören (Kula, Manisa, Turkey) and BE from EMKO Mining Industry (Ayvacık-Çanakkale, Turkey). Chemical analyses of these materials were done by using gravimetric and volumetric methods. Table 1 shows chemical properties of used materials.

Sixteen batches were prepared according to TS 24 [15]. The batch A₁ was used as a control cement in this study. The mixing proportions are summarized in Table 2. A laboratory ball mill was used for the grinding process. The preparation of specimens was carried out at room temperature. The specimens were ground to a fineness of 26% mass residue on a 32 µm size mesh. The fineness of the mixtures was measured by Blain's specific surface test. Physical characteristics of mixtures are shown in Table 2.

Table 2
Physical characteristics of cementitious mixes

Symbol	VT (%)	BE (%)	FA (%)	TW (%)	PC (%)	Fineness (wt.%)		Blaine fineness (cm ² /g)	Specific gravity (g/cm ³)
						+32 µm	+90 µm		
A ₁ control	0	0	0	0	100	27.5	2.1	3010	3.17
A ₂	0	2	5	2	91	18.7	1.3	3970	3.10
A ₃	0	6	10	6	78	15.7	1.5	4780	3.01
A ₄	0	10	15	10	65	12.9	1.8	5580	2.93
B ₁	6	0	5	6	83	13.3	1.5	4870	3.07
B ₂	6	2	10	10	72	16.6	2.1	4950	3.00
B ₃	6	6	15	0	73	13.4	1.9	4910	2.98
B ₄	6	10	0	2	82	18.1	1.7	4880	3.08
C ₁	12	0	10	0	78	18.3	1.5	3910	3.03
C ₂	12	2	15	2	69	13.3	2.3	4960	2.97
C ₃	12	6	0	6	76	18.0	2.7	5170	3.06
C ₄	12	10	5	10	63	19.0	2.1	5370	2.97
D ₁	20	0	15	6	59	16.0	1.8	5060	2.93
D ₂	20	2	0	10	68	21.0	1.8	4900	3.03
D ₃	20	6	5	0	69	16.5	2.5	5060	3.01
D ₄	20	10	10	2	58	15.8	2.3	5580	2.93

Table 1
Chemical characteristics of used material

	Weight (%)				
	Clinker (C)	TW	FA	BE	VT
SiO ₂	20.58	16.50	40.83	57.83	50.79
Al ₂ O ₃	4.92	1.94	19.41	13.55	20.53
Fe ₂ O ₃	3.75	0.31	5.03	5.94	7.45
CaO	65.12	17.45	25.81	3.97	6.56
MgO	0.90	17.42	2.01	2.44	3.74
SO ₃	1.00	–	4.40	0.08	0.08
Na ₂ O	0.34	5.46	0.15	–	–
K ₂ O	0.99	0.86	1.43	1.59	2.74
B ₂ O ₃	–	10.0	–	–	–
LOI	–	30.06	0.92	10.17	3.69
Others	2.4	0.0	0.01	4.43	4.42

The mixture proportion of the specimens corresponded to 450 g cement content, 1350 g of fine aggregate (Rilem Cebu-reau standard sand) and 0.5 water water-to-content ratio. The cement–water mixtures were stirred at low speed for 30 s then, with the addition of sand, the mixtures were stirred for 5 s. Sixteen batches were prepared and cast into 40 mm × 40 mm × 160 mm moulds for strength tests. After 24 h of curing at 20 °C with 95% humidity, the samples were demolded and immersed in a tap water and cured up to 28 days.

Compressive strength measurement was tested with a Tony technique compression machine at the loading rate 20–40 N/mm²/s according to TS 19. The setting times of mixtures were determined according to TS 24 using a Vicat apparatus at room temperature.

3. Results and discussions

3.1. Compressive strength of mortars

The 2-day compressive strength of the cement mixtures (except A₄, D₂) is suitable for the standard [14]. The 28-day

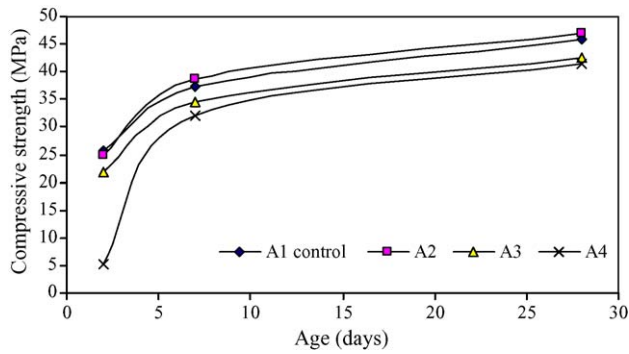


Fig. 1. Compressive strength of A₁ control, A₂, A₃ and A₄ cement mixtures.

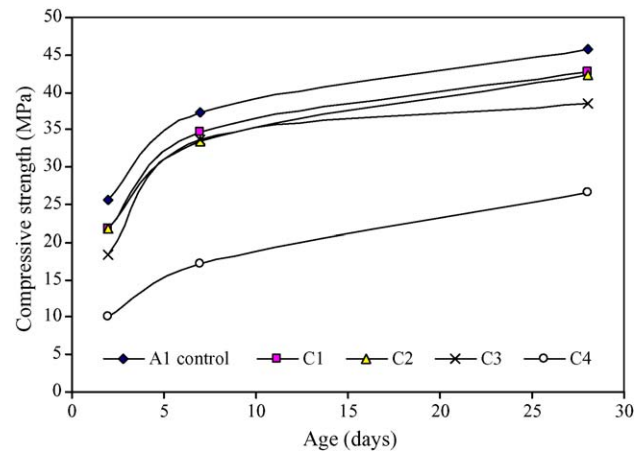


Fig. 3. Compressive strength of C₁, C₂, C₃, C₄ and control cement mixtures.

compressive strength of the cement mixtures (except C₄, D₂, D₄) are suitable for the standard [14].

The 2-day compressive strength of batches A₂, A₃ and A₄ was about 3.1, 14.8 and 79.8% less than control (A₁) concrete, respectively (Fig. 1). The 28-day compressive strength of batches A₃ and A₄ was about 7.2 and 9.6% less than control (A₁) concrete, respectively but the 28-day compressive strength of batch A₂ was about 2.4% more than control concrete.

The 2-day compressive strength of batches B₁, B₂, B₃ and B₄ was about 17.1, 58.0, 5.8 and 9.7% less than control (A₁) concrete, respectively (Fig. 2). The 28-day compressive strength of batches B₁, B₂, B₃ and B₄ was about 3.9, 9.6, 3.9 and 19.9% less than control (A₁) concrete, respectively.

The compressive strength of batches at 2-day C₁, C₂, C₃ and C₄ was about 15.6, 15.6, 28.4 and 61.1% less than control (A₁) concrete, respectively (Fig. 3). The 28-day compressive strength of batches C₁, C₂, C₃ and C₄ was about 6.6, 7.6, 15.9 and 41.9% less than control (A₁) concrete, respectively.

The compressive strength of batches at 2-day D₁, D₂, D₃ and D₄ was about 59.1, 68.5, 17.1 and 34.2% less than control (A₁) concrete, respectively (Fig. 4). The 28-day compressive strength of batches D₁, D₂, D₃ and D₄ was about 24.7, 38.0, 8.7 and 41.3% less than control (A₁) concrete, respectively.

Generally, the 2-day compressive strength of batches was very low when compared with control concrete. While the pozzolanic materials increase, compressive strength of cement mixture decreases. This may be attributed to the fact that pozzolanic materials were low at early compressive strength. Shannag [16]

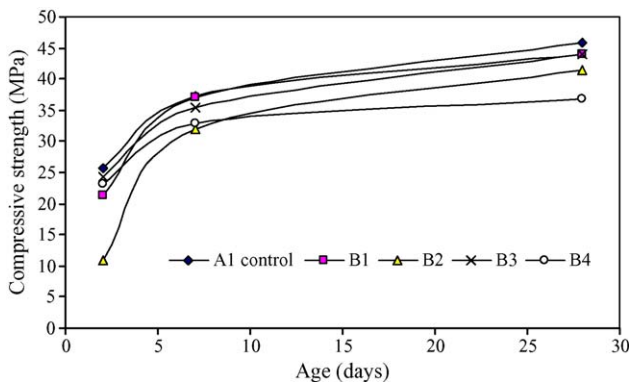


Fig. 2. Compressive strength of B₁, B₂, B₃, B₄ and control cement mixtures.

reported that the appearance of the strength was slowed in the early curing period by adding pozzolanic material. Because the overall pozzolanic reaction was slow.

It is observed that incorporation of beyond to 2% TW resulted in a decrease in 2-day compressive strength compared to the strength of the control concrete. Generally, the 28-day compressive strength of batches was less than control concrete. It is observed that combined action of TW and VT have negative effects on the 2-day and 28-day compressive strength of the cement mixtures. Sugama and Kuckaka [17] reported that the addition of borax to magnesia-ammonium polyphosphate cement led to a loss in early strength.

It is observed that when the ratio of TW increased in the cement mixtures, the compressive strength of concrete 2-day decreased, but their compressive strengths at 28 days approached that of the control concrete. This may be attributed to the fact that the TW was added to the mixtures, the initial setting time of concrete increased with increasing TW content.

3.2. Setting time of mortars

The setting time of the cement mixtures containing different replacement materials is given in Table 3. The setting time of

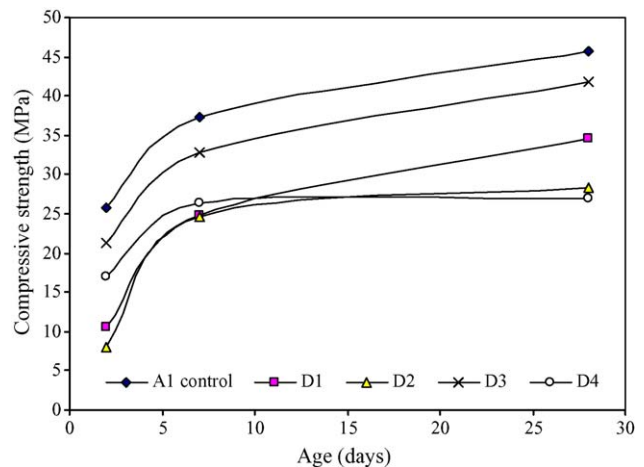


Fig. 4. Compressive strength of D₁, D₂, D₃, D₄ and control cement mixtures.

Table 3
Water percent, setting time and volume expansion test result for cement mixes

Cement mixes	Water (%)	Setting time		Expansion (mm)
		Initial (min)	Final (min)	
A ₁ control	25.5	155	252	1
A ₂	28.0	185	282	2
A ₃	31.2	395	548	3
A ₄	34.2	974	1261	5
B ₁	30.3	513	773	0
B ₂	30.0	922	1232	13
B ₃	31.2	203	305	3
B ₄	29.2	230	323	1
C ₁	27.5	150	280	1
C ₂	30.0	212	322	1
C ₃	30.0	498	662	1
C ₄	33.7	63	1105	2
D ₁	31.3	606	1080	6
D ₂	31.3	52	1108	0
D ₃	28.8	190	243	0
D ₄	32.5	253	357	0
TS 19	–	Minimum 60	Maximum 600	Maximum 10

the batches (except A₄, B₁, B₂, C₃, C₄, D₁ and D₂) is suitable for the standard [14]. The setting time of A₂, A₃, B₃, B₄, C₁, C₂, D₃ and D₄ are near the limit value of the standard.

The initial and final setting time of batch A₃, A₄, B₁, B₂, C₃ and D₁ was higher than the control (A₁). The increase in the setting time can be attributed to the increase B₂O₃ and MgO in the content cement mixtures (Figs. 5 and 6). It was observed that setting time hasn't changed if the cement mixture contained 0.2% B₂O₃. The cement mixture 0.6% B₂O₃ containing shows an increase in the final setting time, but there is no significant change in the initial setting time. The cement mixture containing 1% B₂O₃ caused a significant increase in the both initial and final setting time. Yang [18] and Hall [19] reported that borax is an effective retarder for magnesia-phosphate cement systems. Setting time increased almost linearly with borax content.

The increase in the setting time was resulted out of the standard. The result may be attributed to the combination effect of MgO and B₂O₃ increased setting time more than any single. Zheng [20] and Altun [21] found that the setting time of the cement mixtures increased with increasing MgO content.

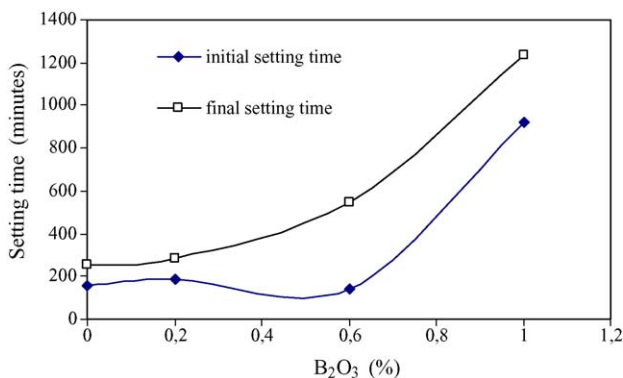


Fig. 5. Effect of B₂O₃ on setting time of mixtures.

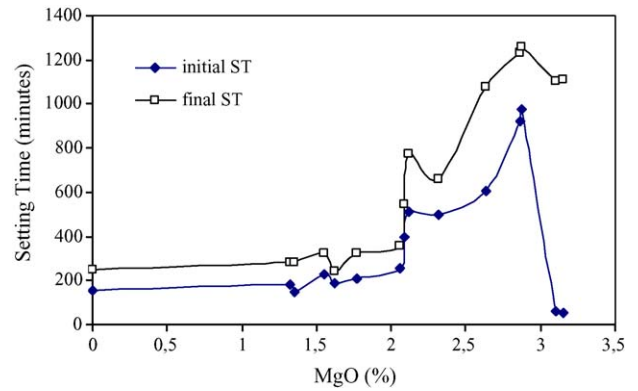


Fig. 6. Effect of MgO on setting time of mixtures.

When the content of MgO exceeds 2.9%, the setting time of the mixtures is sharply decreased (Fig. 6). Liu [24] reported that when content of MgO in the clinker is in a range from 2.0 to 5.0%, the setting time is shortened.

3.3. Expansion of mortars

The mortars resulted in high expansion were prepared by using TW and FA. This may be attributed to the fact both TW and FA have CaO and Na₂O contents. Therefore, the expansion increases as the CaO and Na₂O content of the cement mixtures increases. Shehata [22] found that at a given level of FA replacement, the expansion of concrete prisms generally increased as the calcium or alkali content of the FA increased.

3.4. Water requirement of mortars

The batch A₄ has a Blaine fineness of 5580 cm²/g and water requirement 34.2% whereas the control cement has a Blaine fineness of 3010 cm²/g and water requirement 25.5. As Blaine fineness increased, water requirement increased. Water requirement increased when the ratio of FA and TW were increased. The increase may be attributed to the fact that the more water was needed, the more specific surface of the mixtures increased. When the specific surface of materials increase, the surface require wetting of water also increases. Kula [23] reported that the additions of bottom ash and FA into system increase specific surface that results to an increase in the water requirement.

4. Conclusions

Although the replacement materials were added to Portland cement up to 41% of cement, the compressive strength of cement mixtures is suitable for the standard. When the ratio of TW increased in the cement mixtures, the early strength of concrete decreased, but their ultimate compressive strengths approached that of the control concrete. The setting times of the cement mixture are very sensitive to the ratio of B₂O₃. The mortar containing low amount of B₂O₃ resulted no changing in the setting time, but the mortar containing high amount of B₂O₃ resulted with increasing in the setting time. TW contains high MgO and B₂O₃. Therefore TW must not exceed 2% in the cement mixtures.

As TW and FA contain high amount CaO and Na₂O, expansion of cement mixtures is affected negatively. The batches A₄, B₂ and D₁ have high expansion. Water requirement increased as the Blaine fineness ratio was increased. Water requirement increased when the ratio of FA and TW were increased. The values compressive strength, initial and final setting time and expansion of A₂, B₂, C₁, C₂ and D₃ cement mixtures are suitable for the standard. Through the use of these admixtures, the cost of concrete can be reduced. These composite cements may also used in the nuclear plant for shielding purpose. TW contains boron compounds, which have radiation attenuation properties.

Acknowledgement

The authors gratefully acknowledge Baticim Co. for providing the facilities needed to carry out the experiments mentioned in this paper.

References

- [1] R. Boncukcuoğlu, M.T. Yılmaz, M.M. Kocakerim, V. Tosunoğlu, Utilization of trommel sieve waste as an additive in Portland cement production, *Cement Concrete Res.* 32 (2002) 35–39.
- [2] C. Jaturapitakkul, K. Kiattikomol, V. Sata, T. Leekeeratikul, Use of ground coarse fly ash as a replacement of condensed silica fume in producing high-strength concrete, *Cement Concrete Res.* 34 (2004) 549–555.
- [3] B. Bayat, Comparative study of absorption properties of Turkish fly ashes, *J. Hazardous Mater. B* 95 (2002) 275–290.
- [4] A.G. Türkmenoğlu, A. Tankut, Use of tuffs central Turkey as admixture in pozzolanic cements assessment of their petrographical properties, *Cement Concrete Res.* 32 (2002) 629–637.
- [5] M. Özdemir, N.U. Öztürk, Utilization of clay waste containing boron as cement additives, *Cement Concrete Res.* 33 (2003) 1659–1661.
- [6] Ş. Targan, A. Olgun, Y. Erdoğan, V. Sevinc, Effects of supplementary cementing materials on the properties of cement and concrete, *Cement Concrete Res.* 32 (2002) 1551–1558.
- [7] Y. Erdogan, M.S. Zeybek, A. Demirbaş, Cement mixes containing colemanite from concentrator wastes, *Cement Concrete Res.* 28 (1998) 605–609.
- [8] I. Kula, A. Olgun, V. Sevinc, Y. Erdogan, Effects of colemanite waste, coal bottom ash, and fly ash on the properties of cement, *Cement Concrete Res.* 31 (2001) 491.
- [9] Ş. Targan, A. Olgun, Y. Erdoğan, V. Sevinc, Influence of natural pozzolan, colemanite ore waste, bottom ash, and fly ash on the properties of Portland cement, *Cement Concrete Res.* 33 (2003) 1175–1182.
- [10] M. Kuroda, T. Watanabe, N. Terashi, Increase of bond strength at interfacial transition zone by the use of fly ash, *Cement Concrete Res.* 30 (2000) 253–258.
- [11] F. Canpolat, K. Yılmaz, M.M. Köse, M. Sümer, M.A. Yurdusev, Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production, *Cement Concrete Res.* 34 (2004) 731–735.
- [12] R. Siddique, Performance characteristics of high-volume class F fly ash concrete, *Cement Concrete Res.* 34 (2004) 487–493.
- [13] R.E. Rodriguez-Camacho, R. Uribe-afif, Importance of using the natural pozzolans on concrete durability, *Cement Concrete Res.* 32 (2002) 1851–1858.
- [14] TS 19, Turkish National Standards, TSE, Turkish Standard Institution, Ankara, Turkey, 1992.
- [15] TS 24 Turkish National Standards, TSE, Turkish Standard Institution, Ankara, Turkey, 1985.
- [16] M.J. Shannag, High strength concrete containing natural pozzolan and silica fume, *Cement Concrete Res.* 22 (2000) 339–406.
- [17] T. Sugama, L.E. Kuckaka, Characteristics of magnesium polyphosphate cement derived from ammonium polyphosphate solutions, *Cement Concrete Res.* 13 (1983) 499.
- [18] Q. Yang, X. Wu, Factors influencing properties of phosphate cement-based binder for rapid repair concrete, *Cement Concrete Res.* 29 (1999) 389–396.
- [19] D.A. Hall, R. Stevens, B. El-Jazairi, The effect of retarders on the microstructure and mechanical properties of magnesia-phosphate cement mortar, *Cement Concrete Res.* 31 (2001) 455–465.
- [20] L. Zeng, C. Xuehua, T. Mingshu, Hydration and setting time of MgO-type expansive cement, *Cement Concrete Res.* 22 (1992) 1–5.
- [21] İ.A. Altun, I. Yılmaz, Study on steel furnace slags with high MgO as additive in Portland cement, *Cement Concrete Res.* 32 (2002) 1247–1249.
- [22] M.H. Shehata, M.D.A. Thomas, The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction, *Cement Concrete Res.* 30 (2000) 1063–1072.
- [23] I. Kula, A. Olgun, V. Sevinc, Y. Erdogan, An investigation on the use of tincal waste, fly ash, and coal bottom ash as Portland cement replacement materials, *Cement Concrete Res.* 32 (2002) 227–232.
- [24] X. Liu, Y. Li, Effect of MgO on the composition and properties of alite-sulphoaluminate cement, *Cement Concrete Res.*, in press.