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A Non-shrinking & Low-expanding Cement: Part I — Preparation of Cement

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A simplified procedure for the preparation of a non-shrinking low-expanding cement from Portland cement, calcium sulphate and dried hydration products of lime and kaolin has been developed. The optimum proportions for the different constituents have been found to be 75 parts Portland cement and 25 parts of a mixture of gypsum, lime and kaolin, the proportion of dry hydrated reaction product of lime and kaolin to gypsum being 1 : 1. The cement obtained shows *c.* 0·45 per cent expansion after 7-10 days' water curing and satisfactory strength after 28 days.

THE development of a self-stressing cement[1] by Russian scientists has renewed interest in expanding cements[2,3]. The results of an investigation on the suitability of several mixtures for use as expanding cements have been reported by the present authors in an earlier paper[4]. Budnikov and Kosuireva[5] prepared an expanding cement by mixing ordinary Portland cement with calcium sulphate and the dried and ground hydration product of lime-pozzolana reaction. This method has been studied by us and a simplified procedure suggested on the basis of the chemistry of the hydration reactions. Details of the simplified procedure and the properties of the cements prepared by the two methods are reported in this paper.

Materials and methods

The chemical compositions of the raw materials used are given in Table 1. Kaolin was calcined at 800°±10°C. in a muffle furnace to remove all combined water. Dry hydrated lime was prepared by hydrating quicklime prepared from a high calcium limestone (98 per cent $CaCO_3$) with a known quantity of water to convert calcium oxide into calcium hydroxide.

TABLE 1 — CHEMICALS ANALYSIS OF RAW MATERIALS USED

Constituent	Portland cement	Kaolin	Gypsum
Insolubles, %	0·82		
Silica, %	22·03	46·40	6·42
Aluminium oxide, %	5·98	36·20	—
Ferric oxide, %	2·41	2·60	1·14
Calcium oxide, %	62·59	—	30·02
Magnesium oxide, %	0·85	—	—
Sulphur trioxide, %	2·35	—	42·20
Free lime, %	0·65	—	—
Carbon dioxide, %	—	—	0·20
Loss on ignition, %	1·90	14·82	—
Combined water, %	—	—	19·60

TABLE 2 — EXPANSION AND COMPRESSIVE STRENGTH OF EXPANDING CEMENT

Sl No.	SO_3 %	Linear expansion (%) after					Compressive strength (kg./cm.²) after		
		3 days	7 days	10 days	14 days	28 days	7 days	14 days	28 days
E_1	6·36	0·29	0·37	0·37	0·375	0·375	295·7	440·0	467·0
E_2	6·93	0·24	0·37	0·39	0·410	0·420	275·0	369·3	460·0
E_3	7·43	0·28	0·38	0·42	0·460	0·480	264·2	342·1	419·2
E_4	7·93	0·25	0·36	0·50	0·630	0·900	—	—	—
E_5	6·36	0·33	0·35	0·35	0·360	0·360	424·2	455·7	500·7
E_6	6·93	0·33	0·37	0·37	0·370	0·380	369·2	401·4	482·8
E_7	7·43	0·28	0·38	0·42	0·440	0·440	342·1	360·0	510·0
E_8	7·93	0·18	0·28	0·31	0·340	0·370	—	—	—

The hydrate was then dried at 110°C. in CO_2-free atmosphere. Gypsum was dried to remove free water. Ordinary Portland cement conforming to the Indian Standard Specification No. 269-1958 was used throughout this study, unless otherwise stated.

All the raw materials were stored in air-tight drums and ground fresh when preparing any batch of the expanding cement.

Procedure — According to the original method of Budnikov and Kosuireva[5], calcined kaolin and hydrated lime are mixed in quantities satisfying the equation:

$$Al_2O_3+2SiO_2+4Ca(OH)_2+aq. \rightarrow 2(CaO.SiO_2aq.)+2CaO.Al_2O_3.7H_2O \quad \ldots . (1)$$

The mixture is stored in water for 10 days and then dried at 110°C. in CO_2-free atmosphere. The dried product is then mixed with an equal amount of gypsum. In the hydration of the final product, the following reaction is believed to take place:

$$3(2CaO.Al_2O_3aq.)+6CaSO_4+aq. \rightarrow 2(3CaO.Al_2O_3.3CaSO_4aq.)+Al_2O_3aq. \quad \ldots . (2)$$

The final mixture of the dried and ground hydration product of kaolin and lime and gypsum is known as the expanding agent. It is admixed with Portland cement to prepare the expanding cements. Though the exact quantity of the expanding agent to be mixed depends on the ultimate expansions to be achieved, it is seldom more than 25 per cent; otherwise the strengths are very much reduced.

In the present study, the dried and ground hydration product of calcined kaolin and lime was mixed with 0·66, 0·83, 1·0 and 1·2 parts of gypsum. Twenty-five parts of each of the four mixtures were mixed with 75 parts of Portland cement to obtain four samples of the expanding cement E_1, E_2, E_3 and E_4 respectively. The compressive strengths and the expansion characteristics of the cement pastes (at normal consistency) cured under water at 27°±2°C. are given in Table 2.

The results show the optimum proportion of the dry hydrated reaction product of lime and kaolin to

TABLE 3 — X-RAY POWDER DATA FOR THE REACTION PRODUCT OF LIME AND KAOLIN

d A.	I/Io	Characteristic constituent
5·080	vw	A_3†
4·920	vw	CH
3·580	vvw	A_2
3·100*	vw	S
3·050	vvvw	C
2·870	vvw	A_2, T
2·810	vvw	A_3
2·650	vvs	CH, A_2, T
2·510	vvw	A_2
2·390	vvw	A_2, T
2·295	vw	C, A_3
2·120	vvw	A_2
2·045	vvw	T
1·948	s	CH, A_2, T
1·820	m	S, A_2, T
1·708	vw	A_3
1·680	vvw	T
1·505	vw	A_2
1·470	vvvw	A_2, A_3
1·336	vw	A_2

*Not sharp.
†A_2, dicalcium aluminate hydrate; A_3, tricalcium aluminate hydrate; T, tetracalcium aluminate hydrate; CH, calcium hydroxide; S, calcium silicate hydrate gel; C, calcite.
Except for calcium hydroxide and calcite the other phases are present in poorly crystalline state.

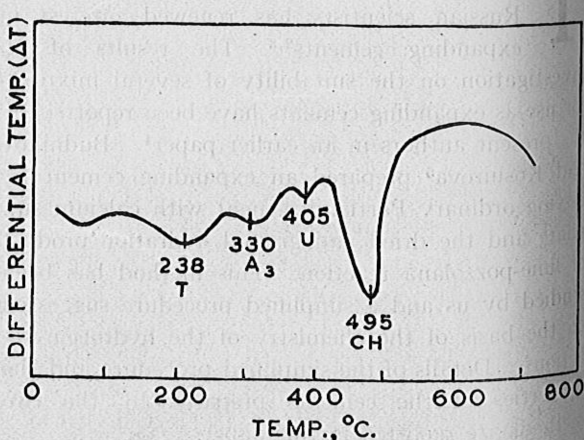

Fig. 1 — Thermogram of reaction product of lime and kaolin [T, tetracalcium aluminate hydrate; A_3, tricalcium aluminate hydrate; U, unidentified, probably calcium hydroxide obtained in earlier dehydration of aluminate hydrate or hydrogarnet; CH, calcium hydrate]

TABLE 4 — LINEAR EXPANSION OF PORTLAND CEMENT AND GYPSUM MIXES

Mix No.	Composition		Linear expansion, %					
	Cement %	Gypsum %	Curing period, days: 3	7	10	14	28	42
1	95	5	0·23	0·26	0·27	0·28	0·31	0·60
2	75	25	0·22	0·30	0·34	0·42	0·60	0·80

gypsum to be 1: 1, thereby confirming the earlier findings[5].

Theoretical basis of the proposed method

The reaction between calcined kaolin and lime is pozzolanic and hence cannot be expected to proceed to completion within the stipulated period of curing, i.e. 10 days. This is borne out by the mineralogical examination of the hydration products of the reaction of calcined kaolin with lime. The endothermic peak at 495°C. in the thermogram (Fig. 1) shows the presence of unreacted calcium hydroxide. The thermogram (Fig. 1) and the X-ray powder data (Table 3) show the presence of higher calcium aluminates besides dicalcium aluminate hydrate and calcium silicate hydrate as envisaged in equation (1). In fact, tetracalcium aluminate hydrate ($4CaO.Al_2O_3$. aq.) was found to be the largest constituent. This is in agreement with the findings of the previous investigators[6,7]. It follows that equations (1) and (2) do not hold good and probably no initial reaction between lime and kaolin takes place. The various constituents of the expanding cement, i.e. calcined kaolin, lime, gypsum and Portland cement, could as well be mixed simultaneously in the dry state and the resulting mixture used as an expanding cement. Therefore, four more samples of expanding cement, E_5, E_6, E_7 and E_8, were prepared by mixing calcined kaolin, dry hydrated lime, gypsum and Portland cement in proportions corresponding to those of E_1, E_2, E_3 and E_4 respectively. The expansion characteristics and strengths of these cements are also given in Table 2.

The expansion characteristics and strengths of the cements of the two series are comparable at all ages, the cements prepared by the dry mix method possessing higher strengths. In both the series the cements with the proportions of kaolin and lime mix to gypsum as 1: 1 show the highest expansions. Therefore, this proportion can be considered as optimum.

Effect of variables on strength of expanding cement

Lime, one of the constituents, has a variable composition. Therefore, the effect of purity of lime on the linear expansion of the cement E_7 containing kaolin + lime and gypsum in the proportion 1: 1 was studied. The results showed that for optimum strength of cement, the lime used should be of not less than 95 per cent CaO content. Hydrated lime gives superior cement than slaked lime. From experiments on the effect of fineness of kaolin on the expansion characteristics of cement, it was found that the fraction of kaolin passing 170 mesh B.S. sieve gives best results. The use of Portland cement or clinker, containing tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium alumino-ferrite (C_4AF) in the proportion 48: 27: 10-11: 8 respectively gives a satisfactory product.

TABLE 5 — COMPARATIVE COMPRESSIVE STRENGTHS OF DIFFERENT MORTARS AND CONCRETES

Curing period, days:	Compressive strength, *kg./cm.²* 3	7	28
Portland cement-sand (1: 3) mortar	276	360	373
Expanding cement-sand (1: 3) mortar	125	229	293
Portland cement (75) + gypsum (25) mix-sand (1: 3) mortar	84	98	120
Portland cement concrete	154 (0·034)*	253 (0·034)*	300 (0·034)*
Expanding cement concrete	110 (0·08)*	222 (0·10)*	274 (0·10)*

*Percentage linear expansion.

Portland cement when mixed with an amount of gypsum more than that required for retarding the setting time to the desired extent expands considerably on storage under water. Data on the expansions of the pastes of Portland cement containing 5 and 25 per cent of gypsum given in Table 4 show that the expansions do not get stabilized and are not controllable as against those of the expanding cements (Table 2). Delayed expansions result in the reduction of strength and can also lead to unsoundness. This is evident from the data presented in Table 5. It follows from the data in Tables 2-5 that in the expanding cements (E_5 to E_8), constituents such as kaolin and lime have a positive role in the reactions responsible for stabilized expansions and good strength development. In fact, much of the

TABLE 6 — EFFECT OF ALTERNATE WETTING AND DRYING ON ULTIMATE EXPANSION OF EXPANDING CEMENT AND MORTARS

Sample		Lime used in cement composition	Ultimate expansion, %			
		Curing period, days*:	28	56	70	98
		Curing agent:	Water	Air	Water	Air
Portland cement		—	+0·050	−0·1000	+0·040	−0·100
Expanding cement						
	Sl_1	Slaked lime (comm.)	+0·360	+0·2100	+0·320	+0·220
	Sl_2	Hydrated lime (comm.)	+0·440	+0·2700	+0·410	+0·280
	Sl_3	Slaked lime (analar)	+0·380	+0·2300	+0·340	+0·230
	Sl_4	Hydrated lime (analar)	+0·410	+0·2800	+0·380	+0·270
Portland cement-sand mortar		—	+0·006	−0·0034	+0·006	−0·036
Expanding cement-sand mortar (1 : 3)†		Hydrated lime (comm.)	+0·160	+0·1100	+0·150	+0·110
do		do	+0·140	+0·1000	+0·140	+0·100

*The number of days represent the cumulative number starting from the first day.
†Water curing adopted throughout.
Wet cloth curing adopted throughout.

expansion in the expanding cement prepared occurred within 7-10 days.

Ultimate expansion — An expanding cement can be evaluated only when its ultimate expansion value is known precisely because the design of any structure will always be based on this knowledge. Data on the effect of alternate wetting and drying cycles on the linear expansions of the cement E_7 and 1 : 3 mortar prepared with it, given in Table 6, show that the percentage reduction in length after 28 days' air drying is about 0·15 and 0·05 per cent for the paste and mortar specimens respectively. A further water curing for 14 days followed by air drying for 28 days shows (Table 6) that on the 98th day the net expansion values are practically the same as on the 56th day. The data indicate that the movements occurring during the alternate wetting and drying cycles are primarily due to the Portland cement component (75 parts) of the expanding cement.

The compressive strengths and expansions of 1 : 3 mortar and 1 : 2 : 4 concrete prepared with the expanding cement E_7 and the corresponding values for ordinary Portland cement mortar and concrete are given in Table 5. For comparison, the values for a cement sample containing 75 parts of Portland cement and 25 parts of gypsum are also given in Table 5. It is evident that the compressive strengths of the expanding cement mortar and concrete are *c.* 25 per cent lower than those of the ordinary Portland cement mortar and concrete respectively.

Expanding cements have been used for several purposes such as underpinning of structures, repairs of reinforced bridges, construction of hydrotechnical installations, water-pipes, water reservoirs and tankers, floating docks, railway platforms, etc. In practice, compensating the actual shrinkage in concrete by the use of a non-shrinking and low-expanding cement is more difficult than attaining an overall expansion, because control of curing condition is more stringent in the former application.

Conclusion

A non-shrinking and low-expanding cement has been prepared by mixing 75 parts of Portland cement and 25 parts of a mixture of gypsum, lime and kaolin in dry state. The cement shows about 0·45 per cent expansion after 7-10 days' water curing and satisfactory strength after 28 days. The cement compares favourably with that prepared originally by Budnikov and Kosuireva[5]. The proposed method is simpler and results in savings in equipment and energy.

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