



ALKALIS IN CEMENT

by H E Vivian*

SYNOPSIS

Alkalis have different and sometimes undesirable effects on freshly mixed and hardened cement paste. The paper examines these effects paying particular attention to the role of cyclic wetting and drying and to the effects of uncombined lime.

SAMEVATTING

Die uitwerking van alkalië op pasgemengde en verharde sementbry is verskillend en dikwels ongewens. In die referaat word hierdie uitwerking ondersoek met besondere aandag aan die rol van die sikliese benatting en droging en die uitwerking van ongebonde kalk.

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Secretariat: NBRI of the CSIR
P O Box 395, Pretoria 0001, South Africa
Telephone (012) 86-9211 Telegrams Navorsbou
Telex SA 3-630

Sekretariaat: NBNI van die WNNR
Posbus 395, Pretoria 0001, Suid-Afrika
Telefoon (012) 86-9211 Telegramme Navorsbou
Teleks SA 3-630

* formerly Division of Building Research, CSIRO, Melbourne, Australia.

1. SUMMARY

Alkalis are important minor components of clinker. Since they are readily soluble and form strongly alkaline solutions they may have several different and sometimes undesirable effects on both freshly-mixed and hardened cement paste, mortar and concrete. They may modify the solubilities and reactivities of clinker components and the physical state of freshly-mixed cement paste, they may react with certain aggregate components and modify the corrosion rates of metals, and in addition alkali metal ions in combination with appropriate anions may promote surface staining and efflorescence and cause scaling deterioration. Alkalis also modify the physical state of hydration products and increase the magnitude of drying shrinkage of hardened cement paste.

2. INTRODUCTION

Portland cement consists of a mixture of finely-ground clinker and gypsum. Clinker is composed essentially of lime, silica, alumina and iron oxide combined to form the compounds, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetra calcium aluminoferrite (C_4AF) which occur as crystalline or amorphous (glassy) phases. Clinker may also contain small amounts of oxides such as uncombined lime (CaO), magnesia (MgO), alkalis ($Na_2O + K_2O$), manganese dioxide (MnO_2), phosphorous pentoxide (P_2O_5) and titanium dioxide (TiO_2). These minor components may sometimes occur as separate phases or as simple compounds but are usually present in solid solutions or in complexes with one of the major clinker compounds. The quantity of these oxides is generally so small that they have very little effect on the properties of cement and concrete. In some instances, however, uncombined lime, magnesia and alkalis, especially when present in sufficiently large quantities, may induce certain deleterious effects which reduce the durability of hardened cement paste and concrete.

The general occurrence and behaviour of alkalis in clinker and cement and their damaging effects on hardened cement paste and concrete have been discussed earlier¹. In contrast to other ions and hydrating compounds in cement, the high solubility of alkalis in water and their strongly alkaline solutions can have far-reaching effects on the hydration of cement and on its reactions with other materials with which it may be in contact. In hardened cement paste and concrete alkalis may be present in solution in relatively high concentrations and, by modifying the nature of the hydration products, may in turn modify the properties and performance of the hardened paste. The present paper aims primarily to discuss the effects of alkalis on the drying shrinkages of hardened cement paste and mortar specimens which are subjected to dry-wet cycling exposure conditions. It will also indicate that alkalis have a modifying effect on the deleterious, delayed expansion which is caused by uncombined lime which is not detected by the usual standard tests on clinker and cement.

3. EXPERIMENTAL RESULTS

Linear movements of cement paste and mortar specimens relative to their initial measurements were obtained by subjecting specimens to cycles of drying and wetting. These specimens were made from an ordinary Portland type A cement which contained 0,09 per cent K_2O and 0,45 per cent Na_2O . The cement was modified prior to making the different specimens by (a) adding amounts of finely-ground clinker compounds namely (i) tricalcium silicate (C_3S), (ii) tricalcium aluminate (C_3A), (iii) tetracalcium aluminoferrite (C_4AF) and (iv) an inert compound, iron oxide (Fe_2O_3) in amounts equivalent to 10 per cent by mass of cement and (b) by additions of sodium hydroxide equivalent to 5 per cent by mass of cement, dissolved in the mixing water. The paste specimens therefore consisted of (a) Portland cement without any additions, (b) cement with additions of each of the finely-ground compounds, (c) cement with added sodium hydroxide and (d) cement plus each of the finely-ground compounds plus added sodium hydroxide.

A similar series of mortar specimens was made from these cements and an inert quartz sand from Leighton Buzzard and mixed in the proportions 1 : 2 by mass. The water/cement ratios for pastes were 0,30 and for mortars 0,50 by mass. After curing for 24 hr, all the specimens were demoulded and measured; some were then dried at $100^\circ C$ while others were cured in a moisture saturated atmosphere for 28 days before commencing drying. After drying for 7 days the specimens were cooled, measured and then immersed in water at atmospheric temperature for 3 months to ensure their complete re-wetting and specimens have since been subjected to this dry-wet cycle. The shrinkage and swelling movements of these specimens relative to their initial measurements after various dry-wet cycles are recorded in Table 1, (page 2).

Although the linear movements of mortars are different in magnitude from those of pastes, it is apparent that comparable specimens are behaving consistently and in accordance with a common pattern. While the initial drying shrinkages of pastes were invariably much greater than those of mortars the shrinkages of both were increased significantly by added sodium hydroxide. As cycling proceeded both mortars and pastes which contained no added sodium hydroxide developed earlier and larger expansions than those of comparable specimens which contained added sodium hydroxide. The initial drying shrinkages of specimens cured in moisture saturated air for one day were generally smaller than those of comparable specimens cured in moisture saturated air for 28 days. All dried specimens swelled and expanded when re-wetted. Those specimens which contained no added sodium hydroxide tended to recover a greater proportion of their shrinkage movement than those which contained added sodium hydroxide. The differences between dry and wet length measurements after different numbers of cycles have been recorded in Table 2, (page 3). Although these differences between dry and wet length measurements, which are largest in specimens containing no added sodium

hydroxide, are increasingly affected by positive expansions as cycling progresses, they indicate that added sodium hydroxide reduces the capacity of dried specimens to swell when re-wetted. In addition, while increased curing time in moisture saturated air increases initial drying shrinkage, it appears on subsequent cycling to retard or repress expansion in specimens containing added sodium hydroxide and to promote expansion in specimens containing no added sodium hydroxide.

4. DISCUSSION

The cement used in this study was tested in accordance with the Australian Standard Specification for Portland Cement (AS1315-1973) and was found to comply with specified requirements. It showed no unsoundness tendencies in these tests or in the Autoclave Expansion Test for Portland Cement (ASTM C151-54). Data recorded in this paper indicate that the unexpected delayed expansions, which occur in both paste and mortar specimens, are probably caused by the delayed hydration of uncombined lime in clinker.

The addition of sodium hydroxide generally but not invariably inhibits the early onset of expansion, increases drying shrinkage and tends to reduce the swelling of dried specimens when re-wetted. These changes in the behaviour of hardened cement paste are caused by a change in the nature of the hydration products. The pertinent induced modification involves a change in the relative amounts of crystalline and colloidal (gelatinous) products in the hydrated cement paste rather than compositional changes, the formation of new or different compounds or the suppression of clinker hydration. In the presence of sodium hydroxide the hydration products tend to be more gelatinous and less coarsely crystalline than those produced by very low alkali cements. Consequently the overall drying shrinkage of a high alkali paste will increase. Moreover the gelatinous hydration products form surface coatings which closely invest the clinker particles and retard their continued hydration. Drying induces large shrinkage movements in the gel coatings which, on account of their diffuse distribution throughout the paste, undergo extensive rupturing and the presence of alkalis tends to retard the complete re-wetting and swelling of the dried gel coatings

TABLE 2 : Differences between the dry and wet length measurement of cement paste and mortar specimens after dry-wet cycling

Number of dry-wet cycles completed	Added clinker compound	% Linear movement of:							
		Paste specimens				Mortar specimens			
		which contained:							
		No added NaOH		Added NaOH		No added NaOH		Added NaOH	
		and cured for:							
1 day	28 days	1 day	28 days	1 day	28 days	1 day	28 days		
1	Nil	0,45	0,54	0,46	0,44	0,10	0,20	0,09	0,12
5	"	0,42	0,48	0,27	0,32	0,15	0,59	0,17	0,15
10	"	0,44	0,47	0,30	0,31	0,28	0,32	0,42	0,30
1	10% C ₃ S	0,39	0,46	0,58	0,49	0,12	0,14	0,10	0,13
5	"	0,42	0,49	0,32	0,32	0,15	0,38	0,14	0,17
10	"	0,41	0,44	0,32	0,33	0,33	0,99	0,34	0,29
1	10% C ₄ AF	0,44	0,51	0,35	0,47	0,12	0,18	0,12	0,14
5	"	0,43	0,55	0,28	0,31	0,18	0,42	0,15	0,16
10	"	0,46	0,55	0,26	0,28	0,34	0,52	0,22	0,27
1	10% C ₃ A	0,41	0,51	0,43	0,55	0,13	0,15	0,11	0,13
5	"	0,42	0,60	0,24	0,31	0,22	0,41	0,14	0,15
10	"	0,88	1,42	0,26	0,31	0,57	1,15	0,39	0,25
1	10% Fe ₂ O ₃	0,45	0,59	0,34	0,48	0,12	0,19	0,12	0,13
5	"	0,38	0,54	0,25	0,31	0,14	0,58	0,17	0,16
10	"	0,37	0,50	0,08	0,29	0,44	0,41	0,26	0,28

TABLE 1 : Percentage linear movements of cement paste and mortar specimens when subjected to cyclic dry-wet exposure conditions. The specimens contained additions of finely-ground clinker compounds and iron oxide, with and without added sodium hydroxide

Cycle (D1 = First dry) (W1 = First wet)	Added clinker compounds	% Linear movement of:							
		Paste specimens				Mortar specimens			
		which contained:							
		No added NaOH		Added NaOH		No added NaOH		Added NaOH	
		and cured for:							
1 day	28 days	1 day	28 days	1 day	28 days	1 day	28 days		
D1	Nil	- 0,50	0,59	- 0,65	- 0,78	- 0,11	- 0,17	- 0,18	- 0,22
W1	Nil	- 0,05	- 0,05	- 0,19	- 0,34	- 0,01	0,03	- 0,09	- 0,10
D5	Nil	- 0,57	- 0,45	- 0,56	- 0,80	- 0,12	- 0,04	- 0,26	- 0,28
W5	Nil	- 0,15	0,03	- 0,29	- 0,48	0,03	0,55	- 0,09	- 0,13
D10	Nil	- 0,54	- 0,27	- 0,76	- 0,81	0,13	0,77	0,04	- 0,26
W10	Nil	- 0,10	0,20	- 0,46	- 0,50	0,41	1,09	0,46	- 0,04
D1	10% C ₃ S	- 0,43	- 0,46	- 0,65	- 0,83	- 0,12	- 0,13	- 0,22	- 0,24
W1	"	- 0,04	±0,00	- 0,07	- 0,34	±0,00	0,01	- 0,12	- 0,11
D5	"	- 0,57	- 0,47	- 0,66	- 0,82	- 0,18	- 0,03	- 0,39	- 0,35
W5	"	- 0,15	0,02	- 0,34	- 0,50	- 0,03	0,35	- 0,25	- 0,18
D10	"	- 0,43	- 0,26	- 0,63	- 0,81	0,01	1,12	- 0,27	- 0,39
W10	"	- 0,02	0,18	- 0,31	- 0,48	0,34	2,11	0,07	- 0,10
D1	10% C ₄ AF	- 0,49	- 0,59	- 1,09	- 1,07	- 0,12	- 0,17	- 0,30	- 0,39
W1	"	- 0,05	- 0,08	- 0,74	- 0,60	±0,00	0,01	- 0,18	- 0,25
D5	"	- 0,55	- 0,47	- 1,19	- 1,06	- 0,11	- 0,01	- 0,45	- 0,46
W5	"	- 0,12	0,08	- 0,91	- 0,75	0,07	0,41	- 0,30	- 0,30
D10	"	- 0,45	0,03	- 1,25	- 1,06	0,30	1,38	- 0,53	- 0,46
W10	"	0,01	0,58	- 0,99	- 0,78	0,64	1,90	- 0,31	- 0,19
D1	10% C ₃ A	- 0,46	- 0,53	- 0,72	- 0,95	- 0,14	- 0,14	- 0,24	- 0,27
W1	"	- 0,05	- 0,02	- 0,29	- 0,40	- 0,01	0,01	- 0,13	- 0,14
D5	"	- 0,49	- 0,33	- 0,74	- 0,93	- 0,06	0,16	- 0,39	- 0,34
W5	"	- 0,07	0,27	- 0,50	- 0,62	0,16	0,57	- 0,25	- 0,19
D10	"	- 0,10	0,49	- 0,69	- 0,93	0,97	1,41	- 0,24	- 0,36
W10	"	0,78	1,91	- 0,43	- 0,62	1,54	2,56	0,15	- 0,11
D1	10% Fe ₂ O ₃	- 0,51	- 0,66	- 0,72	- 0,99	- 0,13	- 0,17	- 0,27	- 0,31
W1	"	- 0,06	- 0,07	- 0,38	- 0,51	0,01	- 0,02	- 0,15	- 0,18
D5	"	- 0,51	- 0,41	- 0,50	- 0,96	- 0,12	0,05	- 0,36	- 0,38
W5	"	- 0,13	0,13	- 0,25	- 0,65	0,02	0,63	- 0,19	- 0,22
D10	"	- 0,47	0,05	- 0,38	- 0,96	0,51	1,69	- 0,43	- 0,38
W10	"	- 0,10	0,55	- 0,30	- 0,67	0,95	2,10	- 0,17	- 0,10

DISCUSSION

Dr P Grattan-Bellew (National Research Council, Ottawa, Canada) asked what symptoms could be seen in concrete when the deterioration was caused by (a) hard burnt lime unsoundness and (b) alkali-aggregate reaction; and how they differed from each other.

Mr Vivian replied that the symptoms were almost identical except in the case of an alkali-aggregate reaction, where microscopical examination would reveal the changes in the aggregate and cracks filled with either sols or gels. These signs were not encountered in deterioration caused by lime unsoundness.

Prof S Diamond (Purdue University, USA) said that he had been intrigued by the distinction between the gel produced by cement hydration processes in the presence of large amounts of alkali and in the absence of alkali. He asked if Mr Vivian had had the opportunity to examine these by scanning electron microscopy or even petrographic microscopy, and what the signs had been.

Mr Vivian confirmed that the gel had been examined with a petrographic microscope. It was difficult to distinguish anything in a great deal of isotropic material. Large alkali contents had purposely been used to enhance the effects and

a reduction in the amount of obviously crystalline material in the hydrated paste had been observed. For example, they had not found large aggregations of crystalline material but had tended to get very much smaller calcium hydroxide crystals. This sort of effect had undoubtedly affected the performance of the paste when it was undergoing shrinkage.

Prof U Ludwig (RWTH, Aachen, West Germany) asked for what length of time the material had been dried at 100 °C. It was known that ettringite was unstable at this temperature; however, at room temperature ettringite formed and expanded sufficiently to crack concrete. This had been found with normal sulphate concentrations, such as occurred in the normal German type 54 cement.

Mr Vivian replied that the material had usually been dried for anything up to a week, although on occasions it had been dried for one day. After about 24 hours most of the water had been lost. The amount of damage caused by ettringite was relatively minor. However, for example, if the sulphate content were increased then of course that problem would be correspondingly enhanced.

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5. CONCLUSIONS

The experimental work described in this paper constitutes a preliminary study and more extensive and detailed investigations should be made to explore the effects of alkalis on the drying shrinkages of hydrated cement pastes, mortars and concretes. In addition the observed expansions and the fact that their potential occurrence was not detected by the usual standard tests suggest that a searching study should be made not only of methods of test for cement soundness and its uncombined lime content but also of the burning process and the manufacture of clinker. The following conclusions drawn from the present studies seem reasonable.

- (a) Alkalis tend to increase the drying shrinkage movement of hydrated cement paste and are therefore liable to accentuate crack development.
- (b) When hydrating cement has a high alkali content, the hydration products tend to be colloidal (gelatinous) rather than crystalline.
- (c) Although alkalis may modify the rate and total amount of hydration of the different clinker compounds, the overall hydration of cement probably remains unchanged and their major effect is to increase the proportion of colloidal hydration products rather than to produce chemically different products. This suggests that drying shrinkage of hardened cement paste is a function of its proportions of colloidal and crystalline components.
- (d) The hydrated gelatinous product formed in the presence of alkalis retards the hydration rate of clinker which is subjected to continued dry-wet cycling.
- (e) Various procedures, such as increased water/cement ratios and the addition of an inert mineral admixture, which reduce the distribution density of clinker particles in the paste also appear to reduce the density of the gelatinous hydration product and reduce the volume stability of hardened cement paste when subjected to dry-wet cycling.
- (f) A long curing time tends to increase the magnitude of drying shrinkage and simultaneously reduces the volume stability of hardened paste which is subjected to dry-wet cycling because protective gel coatings sustain much damage during drying and do not swell rapidly or completely when specimens are re-wetted.
- (g) Delayed expansion and expansive disruption of hardened cement paste, mortar and concrete when subjected to dry-wet cycling conditions are caused by uncombined lime in clinker.

and the rapid hydration of hard burnt uncombined lime. Moreover, although clinker compounds may undergo further hydration when exposed by the ruptured protective gel coating, extensive hydration is limited by the hydration products rapidly re-forming the protective gel coating. Consequently, alkalis tend to produce large drying shrinkages, low expansion recoveries on re-wetting and delayed uncombined lime expansions.

Differences in the length of the initial curing time before the commencement of drying, in the composition of cement due to the additions of different compounds, and in the constitution of cement paste (water/cement ratio 0,30) and mortar (water/cement ratio 0,50) specimens have also affected the recorded shrinkages and expansions. The length of the initial curing time in moisture-saturated air affects the amount of hydration product that is formed before drying commences and this affects the magnitude of shrinkage. The shrinkage of specimens cured for a very short time in moisture-saturated air, generally increased with continued wet-dry cycling whereas those cured for long times tended to remain relatively constant. The onset of expansion tends to confuse the shrinkage performance of specimens.

Compositional changes produced by adding various compounds to cement have affected the shrinkage and expansion of specimens. The clinker compound (C₄AF) appears to have had the greatest effect on shrinkage. The expansion of specimens indicates that increased amounts of gelatinous hydration products retard the hydration of both clinker and uncombined lime, and that this retardation effect continues even after a large number of wet-dry cycles.

The water/cement ratio of freshly mixed materials affects both the drying shrinkage and expansion tendencies of specimens. Expansion developed more rapidly in mortar specimens (initial water/cement ratio 0,50) than in paste specimens (initial water/cement ratio 0,30) even though the magnitude of the overall drying shrinkage of the former is generally less than one third of those of the latter. The initial water/cement ratio influences the arrangement and packing density of cement particles in the specimen and in turn these factors influence the rate and extent of clinker hydration, the disposition of gel coatings, the movements which can occur during drying and the penetration of water and swelling movements which occur during re-wetting. The degree of internal shrinkage movements, the number of fine cracks induced and the extent of damage sustained by protective gel coatings are all much greater in mortars than in cement paste specimens. These factors promote the continued hydration of clinker particles which, if they contain uncombined lime, will cause specimens subjected to dry-wet cycling to expand significantly.

REFERENCE

1. VIVIAN H E Proc of Symposium on 'The effect of alkalis on the properties of concrete', London, 1976.