EVALUATION OF THE EFFECTIVENESS OF MINERAL ADMIXTURES : A QUICK MORTAR BAR TEST AT 150° C.

A.Criaud, C.Vernet and C.Defossé
Technodes SA, Groupe Ciments Français, 78931 Guerville Cédex,
France

In this method, the mortar is made out of the actual components (cement, aggregate(s), pozzolan). The bars are soaked in a model solution, the composition of which matches that of the pore fluids, for 48 hours at 150°C. The expansions are measured. A few assumptions are made regarding the solubility of the alkalis of the mineral additives. The results of the method correlate well with those obtained at 38°C and 60°C, 100% R.H. They allow to sort the pozzolanic materials and determine the minimum proportion for maximum effectiveness.

INTRODUCTION

The effectiveness of mineral admixtures to prevent the alkali-aggregate reactions depends upon an adequate dosage and their alkali content, these two parameters determining the increase or depletion of the alkalinity of the pore fluids. Because the kinetics of the hydration of these materials, and consequently the pozzolanic activity, are slow, accelerated methods can provide useful informations simulating their possible behaviour after long periods.

We developped a quick mortar bar test (hereafter designated by DMT, for Dual Micro Test) that takes into account the specific alkali solubilities of each component of the mortar and is performed at 150°C. The DMT method allows to characterize the pozzolanic properties of mineral additives with various cements and at various proportions in 3 days.

PRINCIPLE

Theoretical background

The method puts emphasis on the role of the aqueous phase trapped in pores of concrete in alkali-aggregate reaction. Experimental data reviewed by Nixon and Page (1) showed that the composition of these solutions in mortars and cement pastes can be either enriched or depleted in alkalis - with respect to those contained in the non blended mixes - when mineral additives are added. For blended cements, the knowledge of alkali solubilities is largely empirical so far. Practically, recommended reactive alkali levels are used (2, 3) in calculating the "alkali content in concrete". The proportions of "soluble" alkalis in OPCs, pfa, natural pozzolan, ggbfs and microsilica of csf are respectively taken as 100%, 17%, 50% and 100%.

Experimental background

The ASTM C441 standard method for testing the effectiveness of mineral admixtures has been found unsatisfactory by several authors (cf the discussion by Hobbs (2)). The NBRI test (4) seems promising (Duchesne (5)). In this method, the mortar bars are immersed in a NaOH solution for 12 days at 80°C.

In the DMT method, mortars are prepared with the cement, mineral additive at the desired proportion, and the actual aggregate to be used. The small mortar bars are cured in an alkaline medium that closely matches the composition in Na, K and OH^- of the related pore fluid after long term hydration. The concentrations of the solution in NaOH and KOH are calculated taking into account the water/cement ratio and the solubility of the alkalis of the clinker phase, the mineral additives and the aggregate(s) if necessary. The curing is completed at 150°C in order to accelerate the reactions. The procedure for preparating the mixes, casting the mortar bars and treating at 150°C is largely inspired from the work by Tang (6). It has benefitted from our previous experience with high temperature testing of mortars for detecting the reactivity of aggregates (Microbar method by Criaud (7, 8)). By comparison with the Microbar test, the vapour curing was found unnecessary because of the longer duration of the treatment (48 hours in the latter procedure instead of 6 in the former one).

MATERIALS AND METHOD

Procedure

The aggregate is crushed and ground to 630 µm and the 160-630 µm fraction is retained by sieving. For each desired association, three mortars are prepared, with constant water/binder (i.e. cement+mineral additive) equal to 0.35, and according to the following proportions : binder/aggregate(s) equal to 2, 5 and 8 (ratios by weight). This is to account for a possible pessimum effect due to the reactive aggregate. No alkalis are added.

Four small bars (1*1*4 cm) are casted for each mortar and demoulded at 24 hours. The initial lengths are measured. The bars are treated in an alkaline solution, the composition of which is close to that of the interstitial fluid within the mortar. The solubilities of the alkalis of each component is arbitrarily taken as 100%, 20%, 50%, 20% and 100% of their total content for OPC, pfa, ggbfs, natural pozzolan and microsilica of csf, respectively. These assumptions are in agreement with the literature and practical usage. Any suspected contribution of alkalis released by aggregates might be considered as well. Four specimens of each composition are soaked in 120 ml of the model solution for 48 hours at 150°C. After cooling and rincing, the bars are measured and the expansions are measured.

The equipment (sieves, mini-mixer, moulds, studs, stainless steel containers, measuring tool) is the same as the one for the Microbar test (7, 8).

Materials

Materials tested include various aggregates, combination of aggregates and OPCS. As to the blending agents, we carried out tests with condensed silica fume, microsilica, pulverized fly ash, natural pozzolan and blast furnace slag. Most of the aggregates used have an Na_2Oeq content less than 0.5%. The Lessines aggregate is an exception (Na_2Oeq = 5.18%). The detailed experiments dealing with the duration of the cure and the evolution of the solution were achieved using the Spratt limestone, a non-reactive limestone, an OPC and the materials given in the table 1.

TABLE 1 - Characteristics of a few blending agents used in this study. The proportion always refers as the percentage of additive with respect to the total amount of binder.

Type	Na_2O %	K_2O	Proportion %
OPC	0.23	1.22	40 to 100 %
ggbfs	1.00	0.62	60
fly ash	0.07	0.61	20
pozzolan	0.29	0.79	20

RESULTS

Duration of the cure

Expansion measurements were carried out after 6, 12, 24 and 48 hours of alkaline treatment at 150°C for several compositions of mortars using the Spratt aggregate in order to determine the optimal length of curing. A plateau is reached after 24 hours for the mortars containing OPCs and reactive or non reactive aggregates (figure 1). Yet, as expansions containing pfas and natural pozzolans were not stabilized before 48 hours, this duration was retained for all subsequent testings.

Effect of the treatment on the mortars

In the absence of mineral admixtures, the mortars made out of an OPC and a reactive aggregate lead to expansions which depend both on the alkali content of the cement and on the actual reactivity (ie silica-silicate, slow or rapid) of the aggregate. As expected also, the sound aggregates and alkali-rich OPCs, or reactive aggregates combined with low alkali OPCs yield little or moderate expansion. Examples are given in table 2.

The expansions of mortars containing mineral additives and reactive aggregates decrease with increasing content in blending. But both the specific pozzolanic activity and the alkali content (or rather soluble alkalis) of the mineral admixture have also a noticeable effect on the level of expansion.

TABLE 2 - Selection of results for mortars containing reactive and sound aggregates, OPCs with various Na$_2$Oeq content, and mineral additives.

PR = potentially reactive   S = Non reactive

Nº	Aggregate	Binder		Na$_2$Oeq % OPC	Na$_2$Oeq % Pozzolan	Expansion % at b/a = 2, 5 and 8			Expansion % 38°C
1	Spratt		OPC	1.50		0.202	0.618	0.308	
2	Spratt		OPC	0.93		0.235	0.096	0.090	0.178
3	Spratt	20%	pfa	0.93	1.65	0.108	0.075	0.060	
4	Spratt	40%	pfa	0.93	1.65	0.040	0.032	0.018	
5	Spratt		OPC	1.05		0.184	0.039	0.006	
6	Spratt	20%	pfa	1.05	0.47	0.139			
7	Spratt	20%	poz	1.05	0.81	0.169			
8	Spratt	60%	ggbfs	1.05	1.41	0.135			
9	Chert 1		OPC	0.50		0.031	0.015	-0.001	
10	Chert 1		OPC	0.78		0.131	0.104	0.067	
11	Chert 1		OPC	1.05		0.212	0.406	0.384	
12	Chert 1	10%	csf	1.05	0.20	0.053	0.092	0.113	
13	Chert 1	20%	poz	1.05	0.81	0.017	0.013	0.025	
14	Chert 1	20%	pfa	1.05	0.47	-0.021	-0.032	-0.003	
15	Nelson Limestone		OPC	0.93		0.054	0.032	0.030	0.038
16	Ottawa		OPC	1.05		-0.015	-0.012	0.018	
17	Nelson 10, Spratt 90 %		OPC	0.93		0.188	0.076	0.059	0.175
18	Nelson 40, Spratt 60 %		OPC	0.93		0.125	0.091	0.056	0.131
19	Lessines		OPC	0.50		-0.007	-0.034	-0.044	
20	Lessines		OPC	0.50		0.047			
21	Lessines		OPC	1.05		0.384	0.193	0.082	
22	PR1 Limestone + Chert		OPC	0.89		0.653	0.495	0.274	0.196
23	S2 Dolomite		OPC	0.89		0.096	0.085	0.077	0.052
24	PR1 40, S2 60 %		OPC	0.89		0.561	0.153	0.144	0.248
25	PR1	20%	pfa	0.89	1.65	0.223	0.176	0.133	
26	PR1	40%	pfa	0.89	1.65	0.060	0.055	0.067	
27	PR3 Chert 2		OPC	0.71		0.225	0.177	0.146	0.033
28	S4 Limestone 2		OPC	0.71		0.125	0.106	0.099	0.045
29	PR3 60, S4 40 %			0.71		0.187	0.151	0.123	0.038
30	PR3 90, S4 10 %			0.71		0.230	0.171	0.140	0.031
31	PR5 Limestone 3		OPC	1.15		0.318	0.156	0.101	0.164
32	S6 Limestone 4		OPC	1.15		-0.028	-0.008	-0.018	0.020
33	PR5 10, S6 90 %			1.15		0.020	0.016	0.009	0.021
34	PR5 40, S6 60 %			1.15		0.142	0.043	0.024	0.024
35	PR7 Limestone 5		OPC	1.15		0.135	0.017	0.013	0.200
36	PR7 10, S6 90 %			1.15		0.022	0.023	0.015	0.024
37	PR7 40, S6 60 %			1.15		0.042		0.025	0.036
38	PR7	20%	poz	1.15	6.41	0.064	0.032	0.026	0.142
39	PR7	40%	poz	1.15	6.41	0.060	0.020	0.032	0.065
40	PR7	20%	poz	1.15	1.73	0.182	0.164	0.174	0.271
41	PR7	40%	poz	1.15	1.73	0.171	0.179	0.220	0.033
42	PR7	20%	poz	1.15	7.88	0.133	0.034	0.022	0.090
43	PR7	40%	poz	1.15	7.88	0.072	0.038	0.013	0.029
44	PR8 Polyphase		OPC	0.68		0.175	0.100	0.059	
45	PR8	20%	poz	0.68	3.69	0.183	0.103	0.074	
46	PR8	40%	poz	0.68	3.69	0.018	0.024	0.037	

Variation of the binder/aggregate ratio

Similarly to the Microbar method (8), this variation was introduced to account for a possible pessimum effect. In most cases, for any particular mortar, expansions decrease when the b/a ratio is raised. But the maximum of DMT expansion is rather encountered at b/a equal to 5 or 8 when the mix involve an aggregate of chert type, as given in table 2. The presence of natural pozzolans were also found to influence the trend of the expansions versus b/a. Hence the conditions for preventing possible AAR are better assessed if these three tests are carried out in parralel, the maximum of expansion being retained for decision making.

Influence of the alkalis of the aggregate

This effect was tentatively studied through the case of the Lessines porphyry (Na_2Oeq = 5.18%). Because the experimental determination of the soluble alkalis as such an aggregate is debatable, an arbitrarily high proportion of 10% was supposed to be possibly active. This yielded a very moderate expansion, though slowly increasing with the duration of the cure, but further experiments would be needed to confirm the role of the alkalis from the aggregates.

Evolution of the alkaline solution during the cure and chemistry of the reaction

The model solutions were analyzed for Na and K after completion of the abovementionned experiments. The variation of their compositions are illustrated for potassium on the figure 2. Generally, the concentration in K (and Na) decreases early, and the hydroxyl ion concentration decreases too. Then it reaches a steady state, but more rapidly than the corresponding expansion does. Yet, the situation corresponds to the uptake of K (and Na) by the mortar. The comparison of the figures 1 and 2 indicates that the uptake of alkalis is not responsible for the expansion of the mortars. Swelling of the bars is actually delayed with respect to the former phenomenon. Thus Na and K unlikely enter the composition of a reaction product.They might be incorporated in the CSH formed under these conditions, though this hypothesis could not be evidenced by analytical means. No gel is observed, as expected, because such a compound would likely pass into the solution. The silica concentration may reach several tens of mmol per liter of solution.

It is worth mentionning that previous treatments of the same specimens (ie those compositions given in table 1) at 150°C in water proved that Na and K are released into solution. This is in agreement with the work of by Wiekers et al (9). They obtained analytical results regarding the composition of the squeezed pore fluids of cement pastes treated at high temperatures under autoclave conditions. The Na and K contents were found to increase in the solution. By contrast to the former results, the silica content of the solution was always very low (0.3 mmol/l) in this set of our experiments. The expansions measured in such conditions, ie treatment in water for 48 hours, were always lower than 0.05% for all combinations, but correlate surprinsingly well with those obtained in solution.

This may raise the question of matching the composition of our model solution more precisely, that is, more closely to what it is at a higher temperature (150°C) than the one (ambient) for which the literature provides sufficient experimental data.

The cause of expansion is thus not identified, but the formation of an alkali-rich CSH, well distributed within the mortar, is favoured. Further investigations are under achievment regarding this point.

VALIDATION OF THE METHOD

The reduction of the expansion

The general action of the pozzolanic materials is indeed to reduce the expansion caused by AAR. The results given above show that the DMT expansion obtained for a mortar made out of an unblended cement and a reactive aggregate is decreased when the test is then performed with a blending agent in addition to the former mix, provided that it is used at sufficient amount. The proportions which are effective, according to our test, are found to be those classically recommended for prevention of AAR in concrete (BCA, LCPC,...). These results are indirect proofs that the DMT test does reveal effectively and selectively the beneficial action of various mineral admixtures.

Correlation with other testing methods

We performed systematically for 25 compositions on the one hand the DMT test at 150°C and, on the other hand, a more conventionnal testing method at 38°C. These compositions include combinations of reactive and unreactive aggregates in the absence of mineral additive, as given in table 2. A series of mortar bars (dimension 2.5*2.5*28 cm) were casted according to the ASTM C227 procedure but part of the cement was replaced by the mineral additive when necessary. No alkalis were added. The bars were stored at 38°C and 100% RH. After one year, all expansions were stabilized. The correlations are presented in figure 3.

The potentially reactive combinations of cement-aggregate(s)-additive yield both high maximum DMT expansion and expansions at 38°C above 0,10%. Similarly, for non reactive mixes, the low DMT expansions correlate well with the expansions at 38°C.

Several points found in the lower right corner of the figure could be reasonably explained either by the slowly reactive nature of the aggregate (not evidenced at 38°C) or by the alkali-rich pozzolan used (Nos 41, 42), the release of which takes place too slowly at 38°C for a significant expansion be observed within the elapsed time. Conversely, one combination (No 38) yields an higher expansion at 38°C than at 150°C, but this has not been explained. The figure 3 also comprises combinations of several potentially reactive aggregates, with no pouzzolanic material, the DMT of which expansions correlate well with the relevant expan- sion at 38°C. Nevertheless, this method does not attempt to evaluate the potential reactivity of aggregates or their combination. The main features of the figure lead to suggest that the conditions for preventing damages due to AAR are met when the studied composition yields a DMT expansion lower than 0.12%.

A second set of experiments was undertaken involving 2 different reactive aggregates and a non reactive limestone, and 3 OPCs (Na_2Oeq content = 0.50, 1.05 and 1.50%) combined with microsilica devoid of alkalis, at 5 and 10%. 1x1x4 cm mortar bars were casted and half of them were placed in an container at 60°C and 100% HR for 3 months. This procedure is presently under study for measuring expansion due to AAR on actual compositions of concrete prisms (10). The other half of the mortar bars was submitted to the DMT test. The maximum DMT expansion agrees well with the expansion at 60°C, as it is shown on the figure 4. This result also allows confidence in the acceleration of the reaction kinetics of the pozzolanic material by temperature.

CONCLUSIONS

The effectiveness of any mineral additive for preventing AAR can be reliably assessed by using the DMT mortar bar method described here. The intrinsic properties of the blending agent (nature, soluble alkali content) and the percentage of replacement within the cement are taken into account through the calculated solution composition. Expansions of 0.12% or higher are obtained after 48 hours fo treatment at 150°C for potentially reactive compositions.

During the treatment, an uptake of Na and K by the mortar bar is observed, together with a decrease of the hydroxyl ion concentration in the solution. Steady state concentrations of Na, K and OH are obtained from 6 hours on. Considering the small size of the bars and the diffusion rates at 150°C, it is likely that the external solution and the pore fluids within the mortar are very close in composition. The chemistry of the pozzolanic reactions at 150°C are not well elucidated, nor are the causes of the expansion, as no gel is observed.

The DMT results correlate well with other expansion tests performed at 38 and 60°C. The proportions of pozzolanic materials necessary to actually reduce the risks of AAR are found to be those commonly used in practice and to depend on their nature.

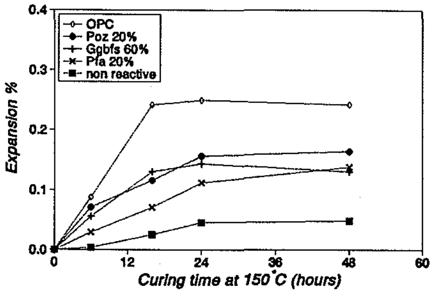
The DMT test represents a very quick approach allowing to prescreen a large number of preventative cement / admixtures / aggregate combinations. Those retained can subsequently be evaluated through a performance test on the actual concrete composition. We are presently developping such an accelerated test at 150°C. Preliminary results are promising.

REFERENCES

1. Nixon, P., and Page, C., 1987, Proceedings of the K. and B. Mather Int. Conference on Concrete Durability, Atlanta, American Concrete Institute (2), SP 100-94, 1833-1862.
2. Hobbs, D.W., 1988, Alkali-silica in concrete, ed. by Thomas Telford, London, 183 pp.
3. Laboratoire Central des Ponts et Chaussées, 1991, Recommandations Provisoires pour la prévention des désordres dus à l'alcali-réaction, 45 pp.
4. Oberholster, R.E., and Davies, G., 1987, *in* Concrete Alkali-Aggregate Reactions, Noyes Publication, ed. by P. Grattan-Bellew, 60-65.
5. Duchesne, J., 1989, Caractérisation d'ajouts minéraux face aux réactions alcalis-granulat dans le béton, thèse de maîtrise, Université Laval.
6. Tang, M.S., Han, S.F., and Zhen, S.I., 1983, Cement and Concrete Research 13, 417-422.
7. Criaud, A., Vernet, C., and Defossé, C., 1990, Workshop on Canadian Developments in testing for Alkali-Aggregate reactivity, Toronto.
8. Criaud, A., Vernet, C., and Defossé, C., 1992, Proceedings of the 9th ICAAR, London (this volume).
9. Wieker, W., Bade, T., Winkler, A, and Herr, R., 1991, 1st International workshop on hydration and setting, Dijon.
10. Bollotte, B., 1992, Proceedings of the 9th ICAAR, London, (this volume).

Acknowledgments

The authors gratefully acknowledge J.P. Barruet, A. Denoyelle and P. Haffray for their assistance in casting and measuring. Messrs Curcio and Cussino (Unicem), and Mr J. Bayles (Coplay Cement) carried out testing at 38°C and are thanked for their contribution. B. Bouquet typed the manuscript.



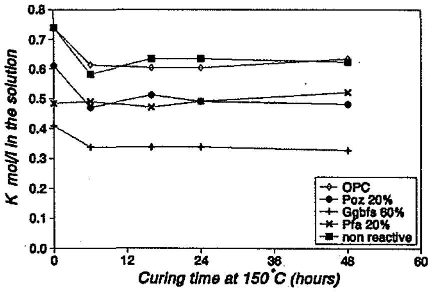
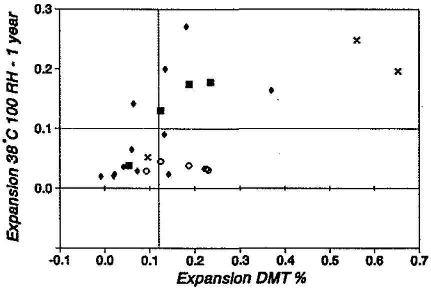


Figure 1. DMT expansion versus the duration of the cure (Spratt Agg.; b/a=2)

Figure 2. Variation fo the K concentration during the treatment.



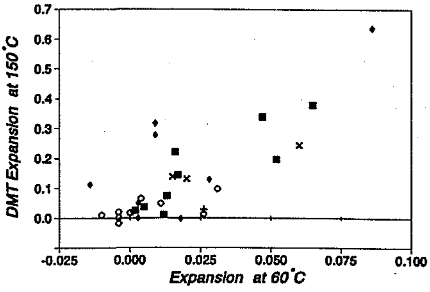


Figure 3. DMT expansions % versus mortar bar expansions % at 38°C

Figure 4. DMT expansions % versus expansions % at 60°C.