Pergamon

Cement and Concrete Research, Vol. 28, No. 1, pp. 25–31, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(97)00215-9

EFFECTS OF NaOH AND NaCl SOLUTIONS AND TEMPERATURE ON THE BEHAVIOR OF SPECIMENS SUBJECTED TO ACCELERATED AAR TESTS

A. Shayan
ARRB Transport Research, 500 Burwood Highway, Vermont South,
Victoria 3133, Australia

(Received August 6, 1997; in final form October 6, 1997)

ABSTRACT

Accelerated testing of aggregates for alkali-reactivity are performed largely through increasing the alkali level of the test specimens and elevating their storage temperature. Various researchers have used either or both of NaOH and NaCl solutions as storage media for specimens at different temperatures, and assessed the reactivity of the aggregates used in those specimens based on their measured expansion under the respective storage conditions. Authors have not always been able to explain their results for the different storage conditions. In this paper, explanations are offered for the different expansive behaviors of cement-aggregate combinations tested in the presence of 1M NaOH and NaCl solutions under storage temperatures of 38°C and 80°C. It has been found that the nature of the chemical reactions involved in these two solutions and temperatures, and the degree of alkali-reactivity of the aggregate, significantly influence the expansion of specimens of the same composition stored under the different chemical/temperature regimes. © *1998 Elsevier Science Ltd*

Introduction

Among factors used to accelerate the alkali-aggregate reaction (AAR) in order to identify the reactivity of aggregates in the laboratory in a relatively short time, elevated temperatures and enhanced alkali levels in concrete or mortar specimens have been the most common. Temperatures have ranged from 38°C, as in the mortar bar test (ASTM C227), to 127°C and even 150°C in some autoclave test methods. Enhanced alkali levels have usually been achieved by the addition of appropriate chemicals to the mortar or concrete mix, or storage of specimens in alkali-bearing solutions. NaOH and NaCl solutions appear to be the most commonly used solutions for this purpose. For instance, Chatterji (1) used saturated NaCl solutions at 50°C to accelerate AAR in mortar bars. Oberholster and Davies (2) introduced the use of 1 M NaOH solution at 80°C for testing mortar bars, whereas Swamy and Al-Asali (3) suggested that salt water was more appropriate for accelerating the reaction of concrete prisms in the laboratory. Kawamura et al. (4,5) studied the expansive behavior of opal-

---

Communicated by D.M. Roy.

bearing mortars immersed in 1 M NaCl solutions with respect to the pore solution composition and alkali content, but a clear explanation was not offered. Similarly, Berube and Frenette (6) could not explain some of their observations in relation to the contradictory behaviors of reactive aggregates in specimens stored at 38°C and 80°C in 1 M NaOH or 1 M NaCl solutions.

There is a need to understand, particularly, the chemical processes that are involved when important test parameters (largely temperature and chemical environment) are varied. This understanding will enable us to explain the results obtained in a particular test method, for example, Berube and Frenette (6). They tested concrete prisms in 1 M NaOH and 1 M NaCl solutions at 38°C and 80°C, using two very reactive Canadian aggregates, high and low alkali contents, and various storage conditions. They found that, with both aggregates, concrete prisms expanded much more in the 1 M NaCl than 1 M NaOH solution when they were stored at 38°C, and the alkali content of the concretes was high (3.9 kg Na_2O eq./m^3, achieved by adding NaOH in the mix water). However, when the alkali content of the concrete was low (1.7 kg Na_2O eq./m^3), expansion in 1 M NaOH was much larger than in 1 M NaCl, under the same storage temperature of 38°C. Berube and Frenette (6) were surprised at this result, and related it to permeability considerations. They were even more surprised that when the storage temperature was 80°C, expansion of concrete prisms stored in 1 M NaCl solution was far smaller than in 1 M NaOH solution for both high and low alkali contents.

Experimental work by the present author was aimed largely at resolving the sort of behavior observed by Berube and Frenette (6), and this paper offers explanations for their observations.

Developing the Explanations

Earlier work by the present author (7) has shown that storage of concrete prisms, made with some slowly reactive Australian aggregates, in saturated NaCl solutions at 50°C, i.e., under the conditions of the Danish test method (1), caused deleterious expansions only when alkali hydroxide had been added to the mix-water to increase the hydroxyl ion content of the concrete. This observation showed that, for the slowly reactive aggregates used, the NaCl solution did not have a primary role in the expansion. Similar results have been reported recently by Kawamura and Takeuchi (8).

More recent results obtained in the present study on the effects of temperature and some salts on the hydration of cement has shown that NaOH and NaCl behave differently and that temperature has an important effect on the hydration reactions. Figures 1–3 show x-ray diffraction (XRD) patterns of cement slurries made with water, 1 M NaOH, and 1 M NaCl, respectively, and stored for 14 days at temperatures of 23, 40, and 80°C.

Figure 1 shows that in the presence of water alone, significant amounts of ettringite form at 23°C and 40°C (peaks at about 9.61 Å, designated E), but no crystalline sulfoaluminate forms at 80°C. Also tobermorite, which produces the peaks at about 3.01 Å at the lower temperatures, is absent at 80°C.

When the mixing solution is 1 M NaOH (Fig. 2), ettringite does not form in the slurry, and the nature of the tobermorite phase (12.06 Å peak, at 23°C) is altered at higher temperatures (peaks at 13.7–15.9 Å, at 40°C and 80°C).

For the slurry made with 1 M NaCl solution (Fig. 3), ettringite forms at 23°C and 40°C,

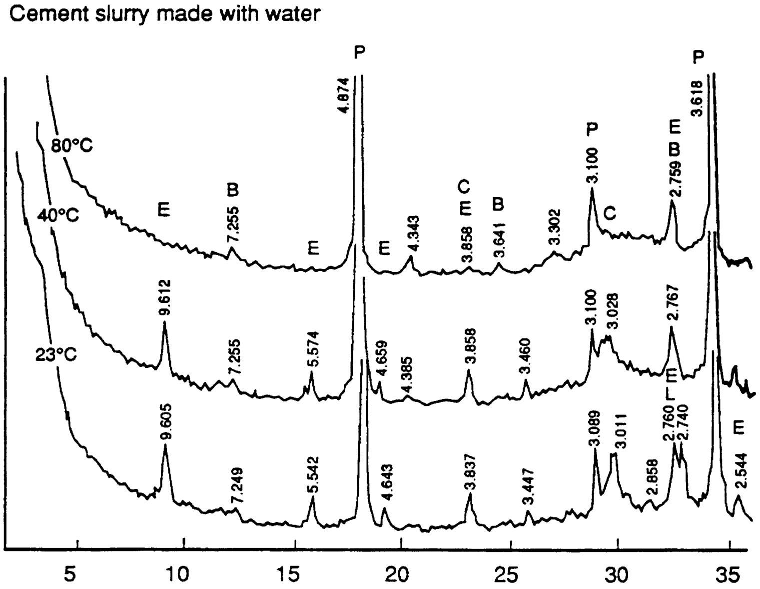

FIG. 1.

X-ray diffraction patterns of the solid phase of cement-water slurries treated at different temperatures for 14 days. The horizontal scale is in 2θ degrees, Cu Kα radiation. *E*, ettringite; *B*, brownmillerite; *C*, calcite; *P*, portlandite; *L*, larnite.

but not at 80°C (similar to the slurry made with water,but unlike that made with 1 M NaOH). In addition, calcium-chloroaluminate (Friedel's salt, $3CaO\ Al_2O_3CaCl_2{\cdot}0H_2O$) forms at 23°C and 40°C but not at 80°C.

Therefore, there are important mineralogical differences, firstly, between specimens subjected to 1 M NaOH and 1 M NaCl solutions, particularly at the lower temperatures, and secondly, between the higher and lower temperatures for each solution.

Based on these mineralogical changes, the present author can explain the differences in expansion observed by Berube and Frenette (6) of concrete prisms containing high- and low-alkali contents and subjected to the 1 M NaOH and 1 M NaCl solutions. The following explanations are offered in relation to the observations made by these authors. The explanations would also apply to the observations made by Kawamura et al. (4,5).

38°C Storage Conditions

Observation

The low-alkali concrete prisms expanded significantly in the presence of NaOH, but not NaCl.

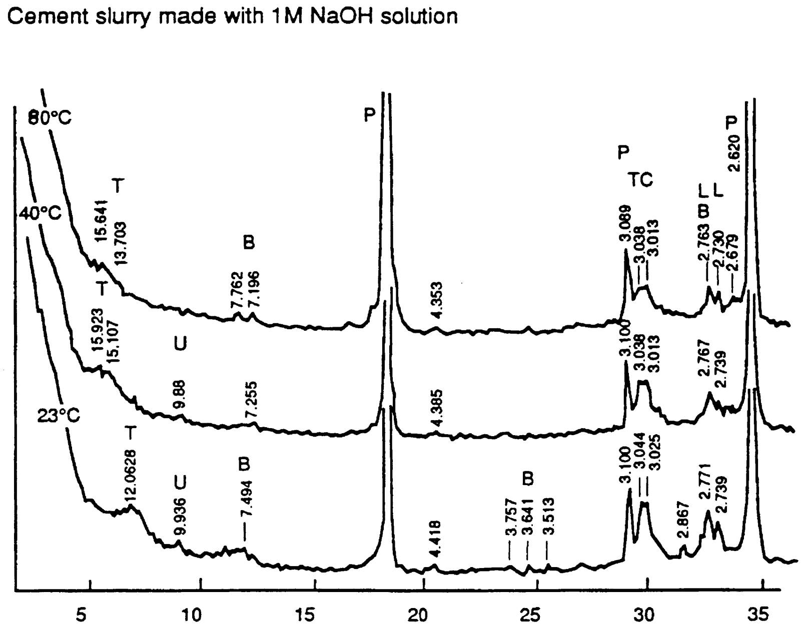
Cement slurry made with 1M NaOH solution

FIG. 2.

X-ray diffraction patterns of the solid phase of cement-(1 M NaOH) slurries treated at different temperatures for 14 days. The horizontal scale is in 2θ degrees, Cu Kα radiatin. *T*, tobermorite; *U*, U-phase, a Na-substituted, calcium-monosulfoaluminate; *B*, brownmillerite; *P*, portlandite; *C*, calcite; *L*, larnite.

Explanation

This is simply because the very reactive aggregates require sufficiently high concentrations of OH^- ions for the reaction and expansion to occur. Obviously, this condition is lacking in the low-alkali concrete prisms stored in the 1 M NaCl solution. Therefore, this behaviour is to be expected, and was later noted by Duchesne and Berube (9). However, if the C_3A content of the concrete is high (e.g., 12%), then its interaction with NaCl could perhaps generate enough additional OH^- to cause expansion with very reactive aggregates.

Observation

The high-alkali concrete prisms expanded much more in 1 M NaCl than 1 M NaOH solution.

Explanation

Close examination of Figure 1 of Berube and Frenette (6) shows that, for the high-alkali concrete prisms, the initial expansion up to the age of about 6 to 7 months was in fact higher in the 1 M NaOH than 1 M NaCl solution. High-alkali concrete prisms produced high expansions even when stored at 100% relative humidity, and about 0.25% expansion had

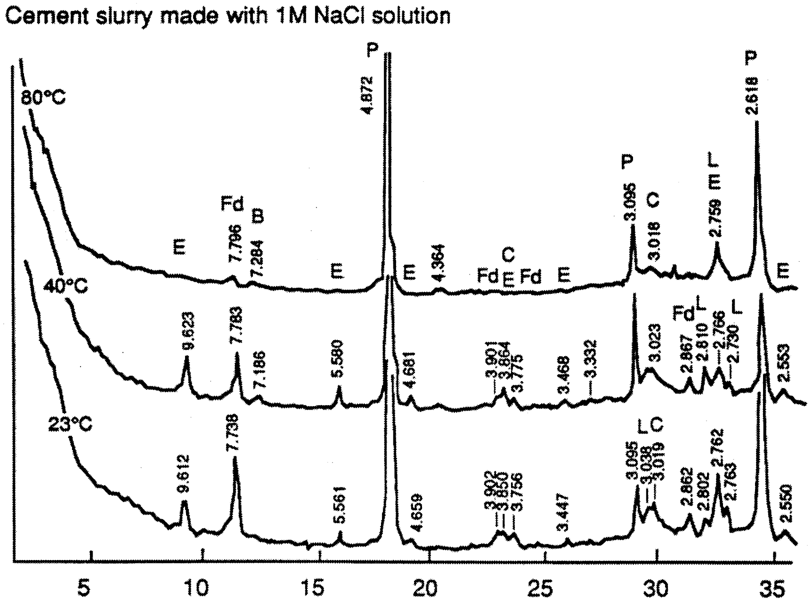

FIG. 3.

X-ray diffraction patterns of the solid phase of cement-(1 M NaCl) slurries treated at different temperatures for 14 days. The horizontal scale is in 2θ degrees, Cu Kα radiation. *E*, ettringite; *Fd*, Friedel's salt; *B*, brownmillerite; *P*, portlandite; *C*, calcite. *L*, larnite.

occurred at this age under all these three conditions. It is only after this stage that expansion in NaCl exceeds that in the NaOH solution or at 100% R.H. It is suggested that the 0.25% expansion in the concrete prisms at the earlier stage must have been associated with significant internal microcracking, and storage in 1 M NaCl resulted in the formation of both ettringite and Ca-chloroaluminate in the microcracks and enhanced the expansion. Shayan and Ivanusec (10) showed that in the presence of reactive aggregate, and the consequent microcracking, ettringite can behave similarly by precipitating in microcracks and causing additional expansion. This effect is indicated in Figure 4, taken from the above reference, showing expansion curves for mortar bars that incorporated either of the following ingredients: opal to cause AAR, added gypsum to enhance the formation of ettringite, or opal plus added gypsum to combine the two effects.

Figure 4 shows that without the opal, no significant expansion was noted for the specimens that contained additional gypsum and that had the potential to form considerable ettringite. Only in the presence of opal and the resulting AAR-microcracking was this potential for additional ettringite precipitation (and additional expansion) realised. The above also explain the results obtained by Kawamura et al. (11).

Also, the microcracking implies further penetration of the NaCl into the concrete matrix and reaction with the aluminate phases that could probably cause greater expansions than the formation of these phases in the microcracks. This also explains the observations of Sibbick and Page (12) in relation to the effects of NaCl solution on the expansion of concrete prisms containing high alkali levels, for which they did not offer an explanation. The mechanism

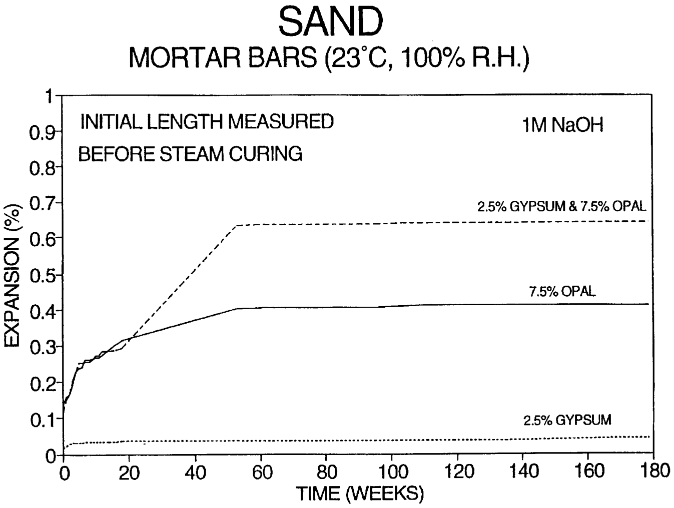

FIG. 4.
Expansion curves for mortar bars made with a sand and with or without 2.5% of added gypsum (by mass of cement) or 7.5% opal (by mass of sand), having 1 M NaOH as the mixing solution. The mortar bars were demoulded 5 h after casting for initial length measurement, and then steam cured at 75°C for 8 h before storage at 23°C, 100% RH for monitoring their length changes.

involved is, in fact, a salt attack that has resulted after the concrete had been damaged by AAR.

Storage Condition of 80°C

Figures 1 through 3 show that neither ettringite nor Friedel's salt form under this curing condition. Therefore, the observed expansion is related to AAR alone, which is evident in Berube and Frenette's results when the storage solution is 1 M NaOH. Storage in 1 M NaCl and water cause far less expansion than that caused by 1 M NaOH. (Note: Figs. 2 and 3 in Berube and Frenette (6) are misnumbered, i.e., Fig. 3 should read Fig. 2, and Fig. 2 should read Fig. 3). This is due to a lack of adequate OH^- concentration in 1 M NaCl and water. The fact that the high-alkali concrete prisms did not expand in water or the NaCl solution is very likely related to the leaching of the alkali hydroxide (7) from the concrete into these solutions, and also to the short period of storage.

Conclusions

All the observations made by Berube and Frenette (6) and those by Kawamura et al. (4,5) can be explained based on the effects of temperature and chemical environment on the mineralogy of phases formed in the cementitious phase (which in turn influences the chemistry of the pore solution). The above information reinforces the present author's previous statements that secondary ettringite formation, (and it seems Freidel's salt as well) can cause some additional expansion in the concrete, if microcracking has already been caused by other mechanisms such as AAR.

References

1. S. Chatterji, Cem. Concr. Res. 8, 647 (1978).
2. R.E. Oberholster and G. Davies, Cem. Concr. Res. 16, 181 (1986).
3. R.N. Swamy and M.M. Al-Asali, Proc. 7th Int. AAR Conf., Ottawa, Canada 324 (1986).
4. M. Kawamura, K. Takemoto, and N. Terashima, Mag. Concr. Res. 40, 143 (1988).
5. M. Kawamura, M. Igarashi, and K. Takeuchi, Proc. 9th Int. AAR Conf., London 527 (1992).
6. M.A. Berube and J. Frenette, J. Cem. Concr. Composites 16, 189 (1994).
7. A. Shayan, Proc. 2nd Australia/Japan Workshop on Durability of Reinforced Concrete Structures, DBCE, Highett, Victoria, Australia, Paper 2.47, 1988.
8. M. Kawamura and K. Takeuchi, Cem. Concr. Res. 26, 1809 (1996).
9. J. Duchesne and M.A. Berube, Proc. 10th Int. AAR Conf., Melbourne, Australia 830 (1996).
10. A. Shayan and I. Ivanusec, Cem. Concr. Composites 18, 161 (1996).
11. M. Kawamura, K. Takeuchi, and A. Sugiyama, Mag. Concr. Res. 48, 237 (1996).
12. R.G. Sibbick and C.L. Page, Proc. 10th Int. AAR Conf., Melbourne, Australia 822 (1996).