

**INFLUENCE OF NaOH ON MECHANICAL PROPERTIES OF CEMENT PASTE
AND MORTAR WITH AND WITHOUT REACTIVE AGGREGATE**

A. Shayan and I. Ivanusec

CSIRO Division of Building, Construction and Engineering
P.O. Box 56, Highett, Victoria 3190, Australia

ABSTRACT

The effects of added NaOH on the mechanical properties of cement pastes and mortars with and without reactive aggregate (5% opal in sand) were investigated by testing cubes (25 x 25 x 25 mm) and bars (13 x 13 x 100 mm), cured at 23°C in fog for 7, 28 and 90 days, for compressive strength and modulus of rupture respectively. Larger mortar bars (25 x 25 x 285 mm) were tested for expansion potential. A water/cement ratio of 0.4 and 0.6, sand/cement ratio of 2/1 and a range of cement alkali from 0.8 to 10.5% Na₂O equivalent were employed.

Only the mixes containing opal and added alkali showed excessive expansion. In all mixes, increasing amounts of NaOH decreased the strengths. However, the sharpest decrease in strength occurred at alkali contents below about 3% Na₂O content. The loss in strength of specimens containing the reactive aggregate was similar in trend to that for other specimens, indicating a significant interaction with cement of the added NaOH and the resulting effect on the strength loss. Alkali-aggregate reaction had little effect on compressive strength, whereas it significantly reduced the modulus of rupture in flexure. The loss in strength due to the addition of NaOH has been attributed to its influence on cement hydration and nature of the solid phases produced.

1. INTRODUCTION

It is well known that mortar and concrete suffer physical and mechanical damage in the presence of reactive aggregate and a sufficient amount of alkali, and this damage is usually attributed to alkali-aggregate reaction (AAR). However, the contribution to damage of the effect of the alkalies on the cement phase itself is not well understood, although the effect of alkalies on the hydration of cement has been investigated by several researchers. Jawed and Skalny [1] have provided a review on various aspects of alkalies in cement. According to this literature, high alkalies in clinker can (a) result in quick setting, (b) decrease the ultimate strength, and (c) increase expansion under water and shrinkage when drying. Vivian [2] showed that added NaOH reduced the tensile strength of mortars containing reactive aggregates due to microcracking, but it also reduced the tensile strength of those without reactive aggregate, although the causes for this observation were not identified. Alexander and Davies [3] found that although increasing the amounts of alkali decreased the compressive strength of cement pastes, intermediate additions increased the modulus of rupture whereas small and large additions decreased it.

Additions of alkali sulfate to cement [4] was found to cause early gain and later loss in compressive strength of concrete, and this was attributed to a higher water demand at constant slump. Odler and Wonnemann [5] found that alkali incorporated into the cement minerals did not affect the compressive strength, whereas they [6] showed that alkali sulfate added to the cement considerably reduced the compressive strength at all ages from one to 28 days. The added sulfates did not alter

the hydration of C_3S and C_3A phases, although the setting time was shortened particularly with added K_2SO_4 , due to the formation of syngenite $CaSO_4 \cdot K_2SO_4 \cdot H_2O$.

In experiments in which NaOH and/or KOH are added to the mix, to accelerate AAR, syngenite may not form but the hydration of C_3A and perhaps C_3S would probably be altered due to the increased alkalinity. It has been reported [7] that the incorporation of Na into CSH is much greater in NaOH solution than in neutral salt solution such as NaCl. Way and Shayan [8] investigated the effects of NaOH in mixing water on the nature of aqueous and solid phases during early hydration of a portland cement and found that at concentrations up to 1 M there were only kinetic effects, but at higher concentrations of 2 M and 4.5 M the nature of these phases were altered, and new phases formed. The CSH phase contained a significant amount of sodium which would affect its physical and mechanical properties. In this paper the effects of similar NaOH concentrations on the mechanical properties of cement pastes and mortars made with and without reactive aggregate are reported. The high concentrations are used to include situations that solid phase mineralogical changes have been observed. Moreover, because of salt migration and drying of concrete, localised zones of such high alkali concentrations may exist, particularly in concretes made with high alkali cements.

2. EXPERIMENTAL

The composition of the type A portland cement batch used in this study had a total Na_2O equivalent of 0.8%. A non-reactive sand was used for making mortar specimens, and 5% of the sand fraction was replaced by Opal V17 (the same as used by Vivian [2]) to produce the reactive aggregate. A known low calcium, low alkali fly ash was used in some mortars to replace 20 or 30% by weight of the cement.

Mortar bars (25 x 25 x 285 mm) with or without the reactive aggregate or flyash were made at a cement/sand ratio of 1/2 and a water/cement ratio of 0.4, demoulded after 24 hours, stored in a fog room at 23°C, and their expansion measured weekly. Specimens for measuring compressive strength were cement paste or mortar cubes (25 x 25 x 25 mm) made at the same cement/sand ratio with water/cement ratios of 0.4 and 0.6, and those for measuring modulus of rupture (three point loading) were bars (13 x 13 x 100 mm) of the same composition. The solutions used for making the specimens had NaOH concentrations of 0, 0.5, 1.0, 2.0 and 4.5 M, giving a wide range of alkali content. The specimens were cured at 23°C in fog for 7, 28, and 90 days before testing.

A portion of cement paste specimens was pulverised ($<75\mu m$) for X-ray diffraction (XRD) analysis, and a limited number of paste specimens were subjected to scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Expansion of mortar bars

The expansion curves for duplicate 25 x 25 x 285 mm mortar bars of different mixes and at the various alkali levels are shown in Fig. 1. The control sand shows an increased expansion at 3.8% alkali level, but the rate of expansion indicates that even at one year it would not be expected to exceed 0.05%. When 5% of the sand was replaced by 5% of the opal the expansion increased very sharply, although this was less evident at the lowest alkali level (0.84%) at 12 weeks. Replacement of 30% of the cement by the low calcium, low alkali fly ash was effective in reducing the expansion of the mortar bars, containing opal and added alkali, but neither eliminated the expansion nor brought it down to a safe level. This arose because of the strong reactivity of the opal and the high

levels of alkali employed. Figure 1 shows that the mixes provide a wide range of expansion potential at the various alkali levels. Although the samples made for strength testing were much smaller than those used for expansion measurements, their expansion potential is expected to follow those shown in Fig. 1.

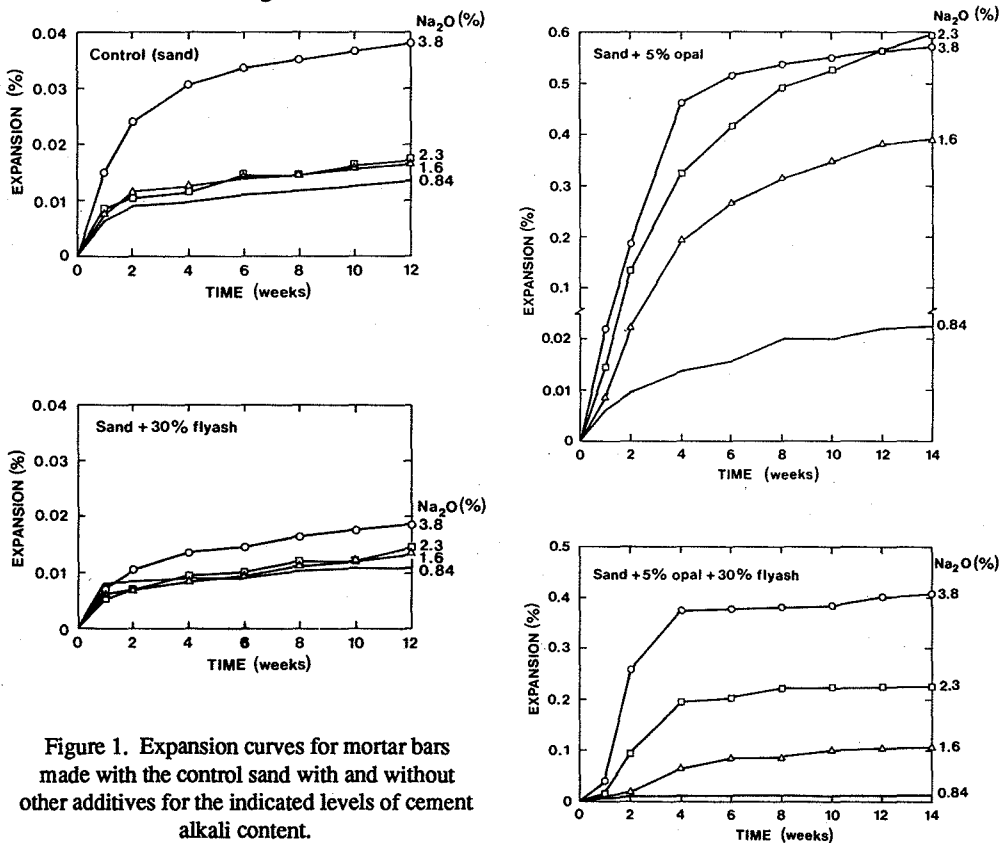


Figure 1. Expansion curves for mortar bars made with the control sand with and without other additives for the indicated levels of cement alkali content.

3.2 Compressive strength

Figure 2 shows the compressive strength as a function of alkali content of the cement paste and mortar cubes for the different mixes at the two water/cement ratios and at the three different ages. Each data point represents the mean of four determinations. The effect of alkali content on strength loss follows a similar pattern for different mixes at each water/cement ratio and age. Comparing the expansion levels of the different mixes at 7, 28 and 90 days (Fig. 1) with the strength losses shown in Fig. 2 shows that the level of expansion and compressive strength loss are not proportional. For example, mortar bars containing sand plus 5% opal have expansion potentials of at least an order of magnitude greater than those containing sand alone, but the compressive strengths of these mixes, especially at 90 days, are very similar. Other researchers [9,10,11] have also reported that compressive strength is not a good indicator of AAR and does not reflect its occurrence. However, Fig. 2 shows that the compressive strengths of all mixes, including the cement paste, drop sharply with increasing additions of alkali, i.e., irrespective of AAR, indicating that the interaction between alkali and cement itself was responsible for the drop, which is sharpest at alkali levels below about 3% Na₂O. It appears that the compressive strength of these mixes reaches its lowest limit at about 5% Na₂O particularly in the case of W/C = 0.6. The causes of strength loss will be discussed in the following sections.

3.3 Modulus of rupture (in flexure)

The moduli of rupture of the 12 x 12 x 100 mm bars in flexure, made from the various mixes, are shown in Fig. 3 as a function of cement alkali content. Despite its highest compressive strength, the cement paste had a lower modulus of rupture than the control mortar at all ages and at both the 0.4 and 0.6 W/C ratios.

At seven days, when expansion had not occurred in the mortar bars containing opal, they show some gain in modulus of rupture relative to the control mortar bars, but a sharp loss with additions of alkali. Moreover, the paste and the control mortars also show a continuous drop in modulus of rupture with increasing alkali level. These findings indicate that the drop in modulus of rupture at early age occurs as a result of the interaction between the cement and the alkali. At 28 days when considerable expansion has occurred in mortar bars containing 5% opal, the largest difference between the moduli of rupture of these and the control mortar bars is observed. Modulus of rupture and tensile strength have been found to be more sensitive indicators of AAR than is compressive strength [9,10,11]. At 90 days there seems to be a slight recovery probably due to further hydration and a possible healing effect. Nevertheless, both the control mortar and the cement paste show significant drops in their moduli of rupture at increased levels of alkali, once again indicating the adverse

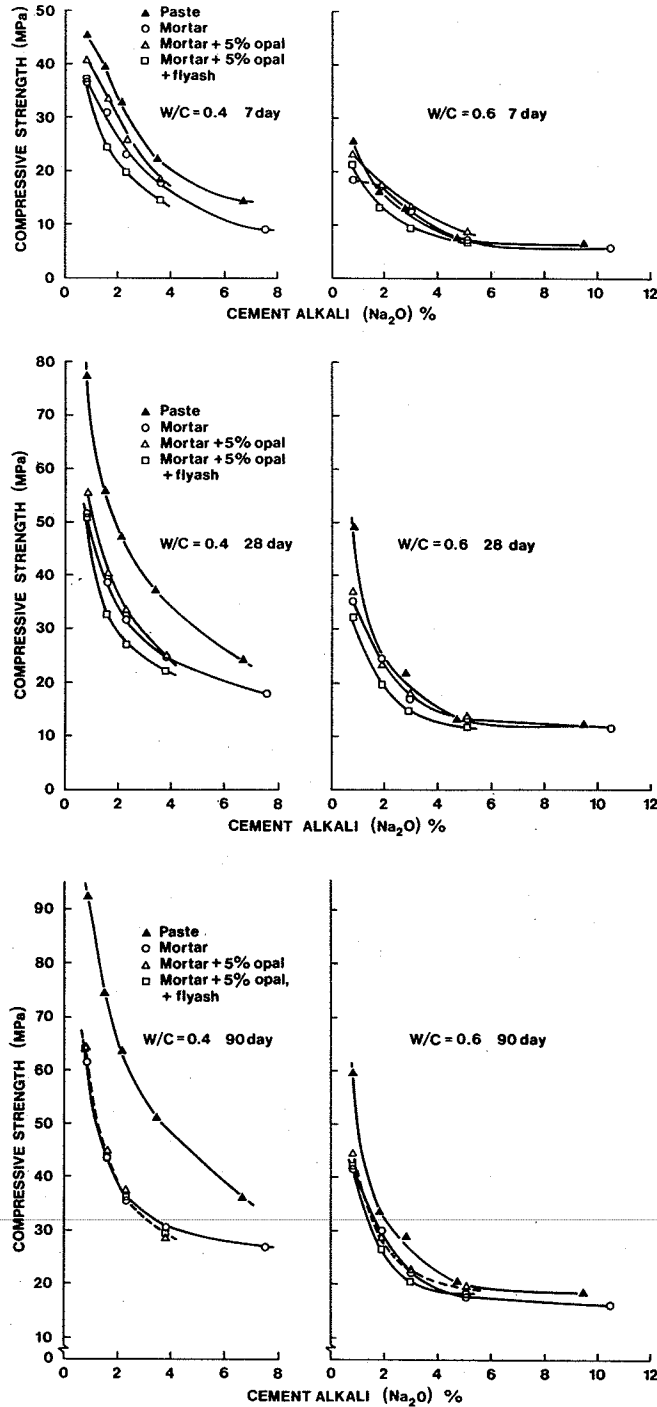


Figure 2. Compressive strength of cement paste and mortar cube specimens of various mixes at the indicated water/cement ratios and ages, as a function of cement alkali content.

effect of the added alkali on the cement hydration and strength development. These data indicate that, in the presence of reactive aggregate, high levels of alkali not only reduce the modulus of rupture of the mortar (or concrete) due to AAR, but also due to the interaction of alkali with the cement. As with the compressive strength, the drop in the modulus of rupture is also sharpest at the lower levels of alkali addition. The modulus of rupture of fly ash mixes drop at seven days but recovers with further curing. It must be noted that high levels of native alkali in cement minerals may not have such severe effects as those caused by the added alkali [5,6].

3.4 XRD and SEM of cement paste

Solid phases formed when the cement was reacted with various concentrations of NaOH solutions have been reported earlier [8]. Generally, formation of ettringite was delayed and formation of $\text{Ca}(\text{OH})_2$ enhanced with increasing NaOH concentration, but in addition, at a concentration of 2 M and 4.5 M ettringite or monosulfate did not form, and a sodium substituted monosulfate called the 'U-phase' $4\text{CaO}\cdot 0.9\text{Al}_2\text{O}_3\cdot 1.1\text{SO}_3\cdot 0.5\text{Na}_2\text{O}\cdot x\text{H}_2\text{O}$ with an enlarged lattice spacing (from 9.6 to 10.0 Å) formed. At these concentrations, in addition to calcium silicate hydrate gel a crystalline form, i.e., CSH(I) also formed, and very finely crystalline $\text{Ca}(\text{OH})_2$ and a form of anhydrous $\text{Na}_2\text{SO}_4(\text{III})$ were also detected in precipitates formed in solutions filtered from cement paste. In the cement paste bars, used for determining modulus of rupture the U-phase was detected by XRD, but other new phases were not obvious because bulk samples were crushed and the concentration of these phases was probably low. The cracking of cement paste made with high NaOH concentrations during fog curing indicated the adverse effects of the new phases and these probably caused some loss in strength. Moreover, the calcium silicate hydrate contained sodium ($\text{Na}_2\text{O}/\text{SiO}_2 = 0.17$) which would have affected its physical and mechanical properties. The value of 0.17 seems to be the limit of Na substitution into CSH under the conditions of the present experiments. This is probably the reason

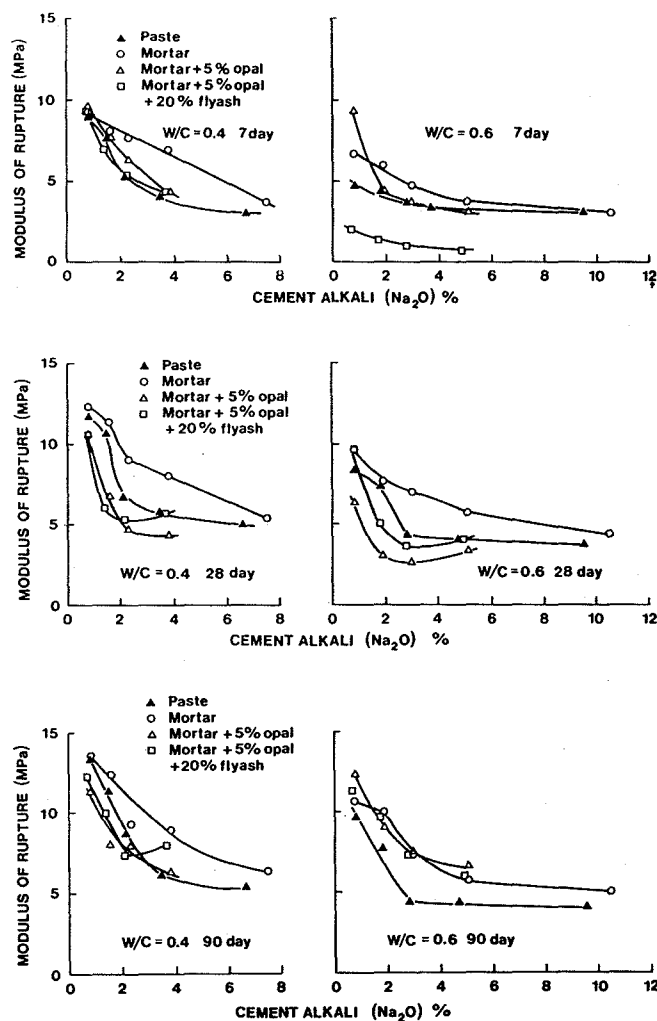


Figure 3. Modulus of rupture of cement paste and mortar bar specimens of various mixes at the indicated water/cement ratios and ages, as a function of cement alkali content.

why the curves in Figs 2 and 3 tend to level off at higher alkali levels particularly at W/C = 0.6, where all the cement minerals were found by XRD to be completely hydrated. At W/C = 0.4, a considerable amount of unhydrated cement was present, even at 90 days, and strength would probably drop further with increased addition of NaOH. It is of interest that the sharpest drop in compressive strength and modulus of rupture occurred at low levels of alkali addition, i.e., before new phases were produced in the cement. It appears that the substitution of Na in CSH, which probably occurs at these lower alkali levels has a more significant effect on the mechanical properties of the cement phase than the formation of the new phases.

SEM of a limited number of specimens containing low and high alkali indicated morphological differences, and a less dense structure for those containing high alkali contents. These features will be reported elsewhere.

4. CONCLUSIONS

This work has shown that addition of increasing amounts of sodium hydroxide not only enhances AAR and its resulting expansion, but also weakens the cement paste matrix as a result of interaction with the cement hydration. The compressive strength of the small mortar cubes used here was not affected greatly by AAR, but was considerably reduced due to the addition of NaOH. The moduli of rupture of the small mortar bars used in this work were reduced considerably as a result of AAR, and also due to the effect on cement hydration of the enhanced NaOH levels.

5. REFERENCES

- [1] Jawed, I. and Skalny, J., Alkalies in Cement: A Review. II – Effects of Alkalies on Hydration and Performance of Portland Cement, Cement and Concrete Research, **8**, 37-52, 1978.
- [2] Vivian, H.E., Studies in Cement Aggregate Reaction. Part XIII – The Effect of Added Sodium Hydroxide on the Tensile Strength of Mortar, Bulletin No. 256, CSIRO, Melbourne, 48-52, 1950.
- [3] Alexander, K.M. and Davis, C.E.S., Effect of Alkali on the Strength of Portland Cement Paste, Australian J. Applied Science, **11**, 146-156, 1960.
- [4] Osbaeck, B. and Smidth, F.L., Alkalies and Cement Strengths, Proc. 6th Int. Conf. on Alkalies in Concrete, Copenhagen, 93-100, 1983.
- [5] Odler, I. and Wonnemann, R., Effect of Alkalies on Portland Cement Hydration. I – Alkali Oxides Incorporated into the Crystal Lattice of Clinker Minerals, Cement and Concrete Research, **13**, 477-482, 1983.
- [6] Odler, I. and Wonnemann, R., Effect of Alkalies on Portland Cement Hydration. II – Alkalies Present in Form of Sulfates, Cement and Concrete Research, **13**, 771-777, 1983.
- [7] Suzuki, K., Nishikawa, T., Ikenaga, H. and Ito, S., Effect of NaCl or NaOH on the Formation of C-S-H, Cement and Concrete Research, **16**, 333-340, 1986.
- [8] Way, S.J. and Shayan, A., Early Hydration of a Portland Cement in Water and Sodium Hydroxide Solutions: Composition of Solutions and Nature of Solid Phases, Cement and Concrete Research, 1988.
- [9] Nixon, P.J. and Bollinghaus, R., The Effect of Alkali Aggregate Reaction on Tensile and Compressive Strength of Concrete, Durability of Building Materials, **2**, 243-248, 1985.
- [10] Swamy, R.N. and Al-Asali, M.M., Engineering Properties of Concrete Affected by Alkali Silica Reaction, ACI Materials Journal, Sept.-Oct., 367-374, 1988.
- [11] Hobbs, D.W., Some Tests on Fourteen Year Old Concrete Affected by Alkali Silica Reaction, In: Concrete Alkali-aggregate Reaction, E.G. Grattan-Bellew, editor, Noyes Publications, N.J., 342-346, 1987.