

CHEMICAL TREATMENTS AND ADDITIVES TO MINIMIZE ALKALI REACTIVITY

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1. ABSTRACT

Deterioration of alkali reactive concrete has been attributed to the expansion of the silica gel in the presence of water. Silica gel's affinity for water is due to its large, active surface which attracts ions and polar water molecules. Chemical treatment to reduce the activity of the surface has proven successful in reducing the expansion due to alkali reaction.

Phosphate ion was found to be one of the more effective agents in reducing expansivity in the lab tests. Hardened concrete specimens made with reactive aggregate were treated with phosphate solution prior to rapid AR testing, and expansion reduced to acceptable levels. Phosphate in various forms and concentrations was introduced into the mix containing reactive aggregate. Depending on the particular combination, AR was either reduced or unaffected.

The treatment offers promise of reducing AR when using susceptible aggregate in new concrete, and may arrest AR in old concrete.

2. INTRODUCTION

As one working theory, alkali reactivity can be considered as a surface reaction. It is the minerals with high surface areas and/or highly active surfaces that participate in the alkali silica or silicate reactions. The active surfaces result from some internal disorder of the crystal lattice - straining, substitution, or incomplete crystallization. The active surfaces usually possess a net negative charge which attracts positively charged cations such as Na and K usually present in the pore water. The cations, in turn, attract the hydroxyl ion. Thus a 'sandwich' of the pore surface, cations and anion is formed, extending, in that order, from the surface into the pore. The ions can be considered as surface sorbed. The surface sorption probably grades by degrees into, and becomes chemisorption, and ultimately the alkali reaction.

Using this as a scenario, it was postulated that if the sandwich can be changed or destroyed, alkali reactivity can be reduced or eliminated. A search for an ion that would readily disrupt the sandwich was initiated. One of the prime candidates was the phosphate ion - it is inorganic, large, and possesses a strong negative charge. It was thought that the phosphate ion

would bind to the Na or K cation and displace the OH anion. Sodium and potassium phosphates are most soluble, and occur as a variety of compounds, from acidic to basic. Calcium phosphate is insoluble in water, but slightly soluble in a strong alkaline solution. Addition of more Na and K to the system was thought counterproductive, so Ca phosphate was chosen as the chemical most likely to succeed in reducing AR. The test chemical was monocalcium phosphate monohydrate.

3. EXPERIMENTAL PROCEDURE

3.1 Sample Preparation and Treatment

The aggregate from Ontario as described in **RAPID METHODS OF PREDICTING ALKALI REACTIVITY** article in this volume[1] and in [2] was used for this test. The six reactive aggregate types were: 2 silica-, 1 silicate-, and 3 carbonate reactive. One non-reactive carbonate aggregate was used as control. The gradations, component ratios, and curing method were as described in the above-mentioned article[1].

In one set of experiments, the aggregate was treated before the concrete was cast. In the second, the aggregate was left untreated, but the concrete was treated after curing. The treatment solution was monocalcium phosphate monohydrate, acidified to bring it into solution. In one case, insoluble calcium phosphate (IP) was used in the mix with untreated aggregate, and the concrete was also untreated.

Concrete blocks containing the aggregate were cast and cured in water for 28 days. The blocks were cored to produce 19mm diameter, 70mm long cores. The ends of cores were squared and dimpled (the LVDT rods were seated in the dimples).

3.2 Method of Measurement

The Double LVDT rapid AR test method described in [1] was used to test for the alkali reactivity of the cores by measuring their length at 2 day intervals for a total of 22 days. The method is similar to that of the NBRI test [3] in that it uses 80°C 1N NaOH solution as the means of accelerating AR. The differences between the NBRI and this method are the sample size, use of concrete rather than mortar, and the measurement of length after the sample cools to room temperature rather than at 80°C.

4. RESULTS OF EXPERIMENT

Only the results of treatment of the silica-reactive aggregates and concretes are discussed in the following, since ASR reaction is the most common of the alkali reactions. The reactive aggregates are the Putnam chert and Sudbury. In all of the experiments below, a non-reactive aggregate was used for comparison.

4.1 Treated Aggregate:

In this series of experiments, three sets aggregates were dried and each set immersed in a 10% solution of the phosphate for 15 seconds and 1 minute respectively. After immersion, the two sets of aggregates were bench-dried for 24h, and immersed again, for a total of 5 treatments. The short duration, repeated treatment were intended to simulate possible method of treating aggregates in a plan setting. After the last bench drying, the aggregate was cast into concrete blocks.

Cores were prepared as described above. The initial length measurements of the cores were taken in dry and saturated states, and all subsequent changes in length during exposure to hot, 1N NaOH solution were compared to the initial dry length.

The results of the test are shown in Figs. 1 and 2. The expansivity of treated aggregate is compared to that of untreated aggregate. As can be seen, the aggregate treatment prevents the expansion of the concrete.

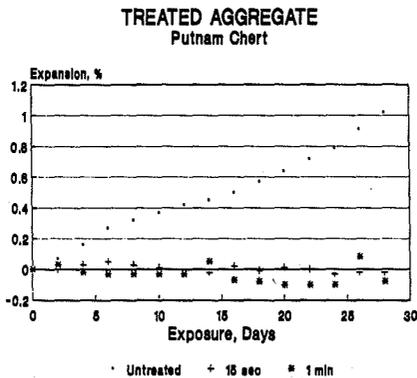


Fig. 1. AR expansion of treated Sudbury aggregate

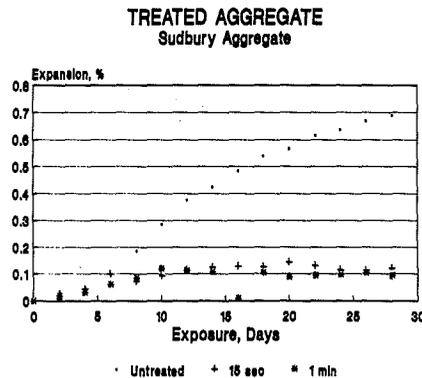


Fig. 2. AR expansion of treated Putnam chert aggregate

4.2 Treated Concrete:

Cores were obtained from concrete blocks containing untreated aggregate. One set of cores was untreated, and three sets treated. The treatment consisted of immersing each set of the cores in the solution for 15 seconds, 1 minute, and 1 hour, respectively, and allowing them to bench dry for 24h. The treatment was repeated five times. During the treatment, the concrete surface reacted with the solution and precipitated an insoluble calcium phosphate layer within the 1 to 2 mm surface layer of the core. An SEM examination of the surface revealed a discontinuous coating of crystals. Although the phosphate precipitate partially blocked the pores, the concrete still remained permeable.

The cores were exposed to hot NaOH solution, and their length measured every two days for 28 days. The results are shown in Figures 3 and 4. Again, it is seen that the treatment effectively prevented the expansion of concrete.

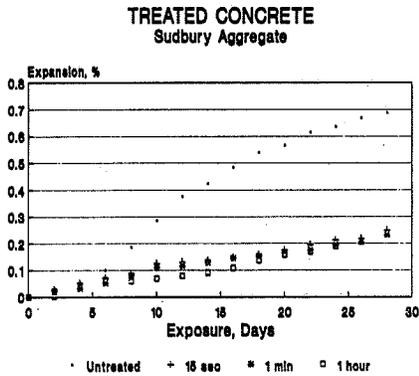


Fig. 3. AR expansion of treated concrete (Sudbury aggr.)

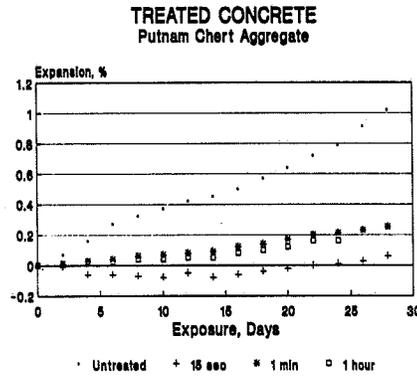


Fig. 4 AR Expansion of treated concrete (Putnam chert)

4.3 Phosphate Additive:

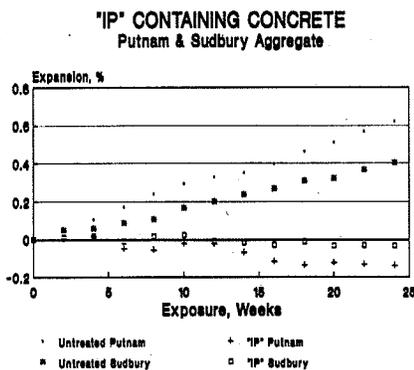


Fig. 5. AR of concrete with phosphate additive.

The next project was designed to test the effect of insoluble calcium phosphate as an additive to the mix. The phosphate was crushed and +50 to -100 size fraction and substituted for the equivalent sand fraction of the mix. The concrete was made with the same coarse aggregate as above. The concrete was cast and cured as before, and cores cut from the concrete blocks. The cores were not treated further.

Figure 5 shows the results. The additive succeeded in preventing expansion; the highly reactive Putnam aggregate even showed some minor net contraction.

5. DISCUSSION OF RESULTS

While it is clear that the phosphate treatment resulted in the reduction of the expansion, the operating mechanism is far from certain. Phosphate treatment was also shown to reduce the freeze-thaw damage of aggregate and concrete in tests done in this lab. The effectiveness of the phosphate treatment in reducing damage due to two apparently diverse mechanisms must be explained.

One explanation is that the phosphate ion interferes with the surface sorption and chemisorption of cations and anions. In the case of alkali reactivity, the phosphate probably prevents the formation of the alkali silica gel. No gel formation was noted on treated concrete specimens, whereas the untreated ones revealed cracking and gel presence. Calcium phosphate is relatively insoluble in water, but has limited solubility in a strong alkaline environment. Up to 2500 ug/ml of phosphate can be dissolved in 1 N NaOH solution.

The proposed scenario is as follows: AR reaction is essentially a surface-dominated reaction. Only the active or very large surfaces of the siliceous minerals participate in the reaction. Normally, the alkali metals of sodium and potassium are strongly attracted (adsorbed) to the active mineral surface, and in turn attract the hydroxyl anion to themselves. The concentration and proximity of hydroxyl anions cause silica to go into solution and form silica gel. (Silica is soluble in a high pH environment).

If present, the phosphate anions preferentially bond with the alkali cations at the mineral surface at the expense of the hydroxyl anions. Solubility of silica is decreased, and no gel forms.

An alternative hypothesis is that even if silica gel forms, its expansivity is reduced. Phosphate ions are attracted to the alkali sites within the gel, satisfying the charge, and reducing the number of water molecules normally clustered at the sites. The osmotic pressure difference is reduced, and no expansion takes place.

Whether the above ideas are correct needs to be tested by further research. It should be noted that just as AR depends on number of factors that affect the concrete mix, so does the effectiveness of treatment. Less spectacular results were obtained with some other mixes and different phosphate treatment methods. These variables are being investigated, as is the effectiveness of other chemicals and treatments in reducing AR.

5. CONCLUSIONS

When the chemistry of AR is better understood, better methods of prevention can be found. The phosphate treatment appears to be effective in reducing AR in silicate aggregates. It is somewhat less effective in carbonate AR. Phosphate is thought to interfere with the dissolution of silica and in the formation of gel. Alternatively, it reduces the osmotic potential and the swelling pressure in the gel that does form.

6. ACKNOWLEDGMENTS

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7. REFERENCES

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