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THE EFFECT OF SUPERPLASTICIZERS ON ALKALI-SILICA REACTIVITY

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ABSTRACT

Three types of superplasticizer were shown to increase the expansion of mortar bars caused by alkali silica reaction. When silica fume was incorporated into mortar bars as a partial replacement of cement the expansion decreased with increase in amount of silica fume up to 12%. Superplasticizers counteracted this effect and expansion could be doubled even when 12% silica fume was present in the mix. At the 24% fume replacement level, no expansion was registered either with or without superplasticizers.

1. INTRODUCTION

The development of concrete technology has been accompanied by extensive use of chemical admixtures such as accelerators, water reducers, superplasticizers, retarders, air-entraining agents, etc. The effect of those admixtures on alkali-aggregate reactions is often unknown. Perry and Gillott [1] reported that superplasticizer of naphthalene formaldehyde (SNF) type, in mortar bars containing 4% opal and 0 to 10% silica fume, increased expansion due to alkali-silica reaction, while lignosulphonate (LS) type superplasticizer decreased the expansion. A major objective of the present work is to clarify the influence of admixtures on alkali-aggregate reactions.

The effects are reported of three types of superplasticizers [sulphonated melamine formaldehyde (SMF), sulphonated naphthalene formaldehyde (SNF) and lignosulphonate (LS)] on the expansion of mortar bars containing the pessimum amount (2%) of highly reactive Nevada opal [2]. Results obtained by scanning electron microscopy, infrared spectroscopy, thermogravimetric analysis and x-ray diffraction are also reported.

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2. MATERIALS, METHODS AND RESULTS

2.1 Materials

The materials used in both the mortar bar dimensional change test (ASTM C-227) and in the osmotic cell test [3] were:

1. Type 10 low alkali cement;
2. Non-alkali expansive limestone from Exshaw, Alberta;
3. Opal, from Nevada, U.S.A, as an expansive component;
4. Silica fume slurry;
5. SMF, SNF and LS - type superplasticizers.

2.2 Methods

Dimensional change characteristics were determined by measurement of mortar bars and reactivity was assessed by an "osmotic cell" similar to that described by Verbeck and Gramlich [3].

The mortar bars were proportioned and cast according to ASTM C227 and dimensional change characteristics were recorded. The alkali content was boosted to 1.0% by addition of NaOH to the mixing water. In mortar bars with and without (control bars) superplasticizer, 2% opal was used as alkali-expansive component. The dosage of superplasticizer was according to the recommendation of the manufacturers. The osmotic cell was used to measure the change of flow rate between reservoir chamber and reaction chamber.

2.3 Results

2.3.1 Dimensional change Mortar bars made with SMF and LS superplasticizer and 0% silica fume showed larger expansions at all ages than control bars (zero superplasticizer) (Fig.1). Mortar bars made with 6% (and 12%) silica fume and superplasticizers expanded more than similar control bars made without superplasticizers (Fig.2). When 24% of cement was replaced by silica fume no expansions were registered at any age up to 16 months, regardless of whether superplasticizers were used or not.

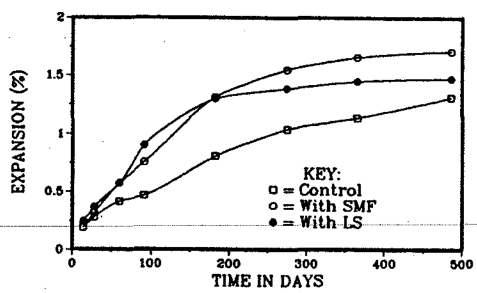

Fig.1. The Effect of Superplasticizers on Expansion (With 0% Silica Fume)

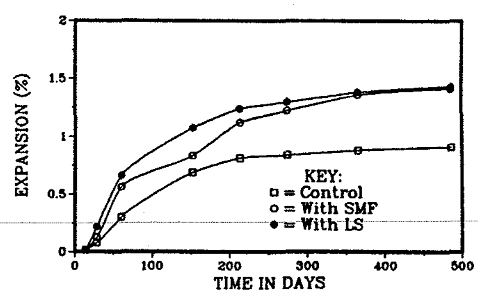

Fig.2. The Effect of Superplasticizers on Expansion (With 6% Silica Fume)

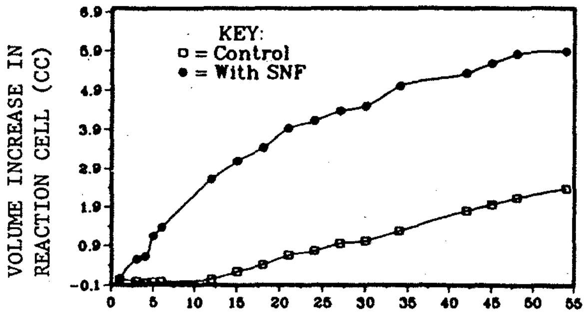

Fig.3. Osmotic Cell Results

2.3.2 Flow rate Fig.3 shows the large increase in rate of flow into the reaction chamber of the osmotic cell when the opal sample contained SNF superplasticizer in the same concentration as in the mortar bars.

3. DETAILED INVESTIGATION AND INTERPRETATION

3.1 Microstructure Studies

Special samples were prepared for study on the scanning electron microscope (SEM). Cement paste bars were cast in the same proportions as used in the mortar bars and particles of opal, about 5 mm in diameter, were embedded in the paste. After allowing time for reaction to take place, the opal was exposed by gently striking the bars. The intact opal was carefully oven-dried in a CO_2-free atmosphere, and mounted on an SEM sample stub. The SEM and EDAX results showed that there were differences in both morphology and composition of opal-paste interface products when samples made with and without superplasticizers were compared. Samples without superplasticizer developed "mud-like" alkali-silica gel (Fig.4a) which contained relatively little calcium. The samples with SNF, SMF and LS superplasticizer developed a relatively "rigid" product which contained more calcium (Fig.4b).

Opal samples were treated for about 20 days in dilute solutions of the three superplasticizers and compared on the scanning electron microscope with untreated samples of the same material. At relatively low magnification untreated opal had a dense, glassy appearance whereas the surface of opal treated with superplasticizers was found to be porous showing evidence of chemical attack (Fig.4c). The dilute solutions of the three superplasticizers had a similar concentration to that used in the mortar bars. Chemical analyses indicated that the concentration of Na_2O was 0.499, 0.714 and 2.224 g/l in the solution of SNF, SMF and LS superplasticizer respectively. The opal was also treated with solutions of NaOH which had the same concentrations with respect to Na_2O as the solutions of superplasticizers. Comparison on the SEM showed that after the etch in alkali the opal was even more porous than after the superplasticizer treatment (Fig.4d).

3.2 Infrared spectroscopy

The infrared spectrum of untreated opal was compared with the spectra of

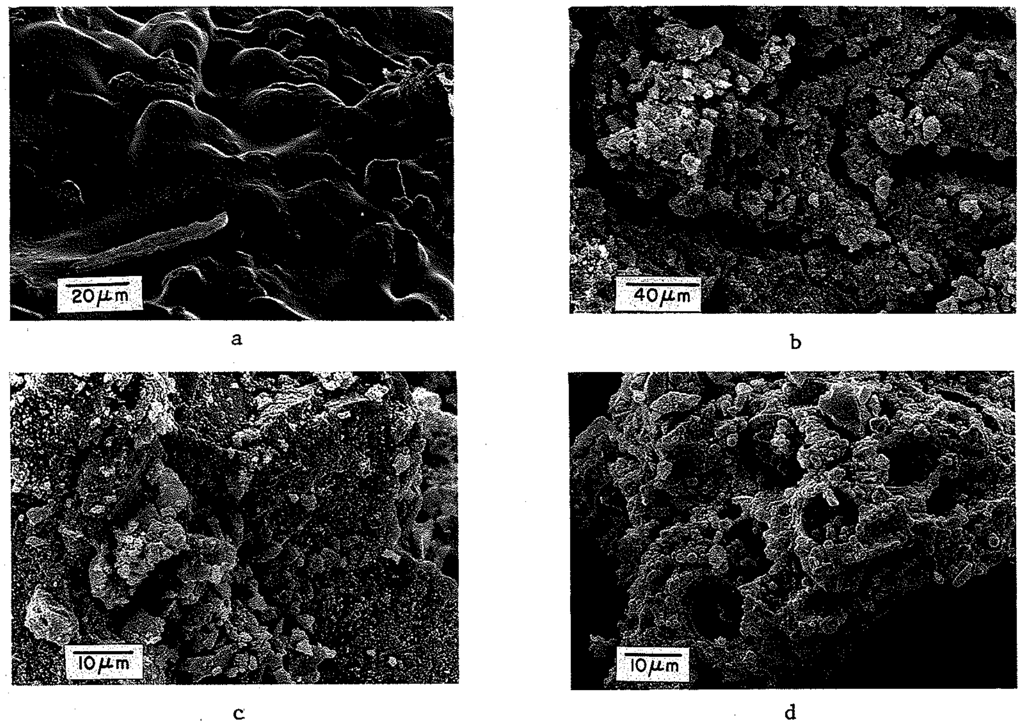

Fig.4. SEM's of Reacted Opal.
a: 3 months in cement with no superplasticizer.
b: 3 months in cement with SMF superplasticizer.
c: 20 days in SMF superplasticizer solution.
d: 20 days in NaOH solution.

similar samples which had been treated with the dilute solutions of the three superplasticizers. In each case a comparison was made of the "disorder coefficient" calculated by the method of Bachiorrini[4]. The disorder coefficient of the SiO_4 group is defined as the ratio of the breadth at 1/3 peak height, of the absorption band at about 830-700 cm^{-1} to the "relative optical density". The disorder coefficient is an indication of the combined effect of rotational, translational and positional disorder, substitution of foreign ions, clustering of foreign ions and incipient phase separation and introduction of point defects [5, p.87].

The infrared spectra showed broadening of the absorption bands of the treated samples with a corresponding increase in values of the disorder coefficients. The results therefore indicate increased structural disorder in the opal treated with the superplasticizers.

3.3 Thermogravimetric Analysis

Lange [6] showed that two types of water exist on the silica surface - physically adsorbed and hydrogen bonded water. In addition hydroxyl is attached to the outermost Si atoms. Differences in bond strengths result in water being lost over three temperature ranges: 105°C; 105° ∿ 180°C and 180° ∿ 500°C. The weight loss at 105°C is associated with desorption of

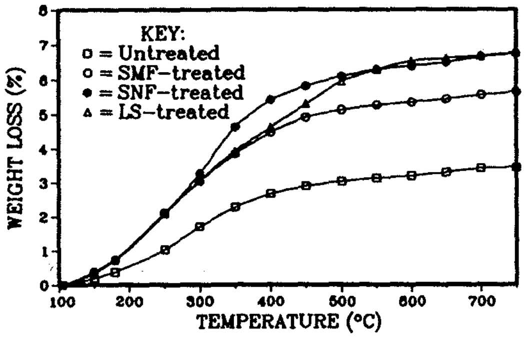

Fig.5. Thermogravimetric Analysis of Nevada Opal- Untreated and Treated with Superplasticizers.

physically bound water, the water lost between 105° ∿ 180°C is attributed to loss of water held by hydrogen bonds and the weight loss in the 180° ∿ 500°C temperature range is associated with dehydroxylation.

Fig.5 shows the weight losses of untreated and superplasticizer-treated opal. The superplasticizer-treated samples showed by far the largest weight losses. This suggests that superplasticizer-treatment breaks down some internal Si-O bonds creating more silanol surface to which water is attached by hydrogen bonds. If this suggestion is correct and water-loss is responsible for the weight-loss in untreated-and treated-samples the ratio of the weight-loss at 500°C to that at 180°C would be expected to be about the same. Comparison of the data shows that this is indeed so. The weight loss for untreated opal was 0.38% at a temperature 180°C, and 3.08% at 500°C. The weight losses for SNF-, SMF- and LS-treated opal were 0.71%, 0.75% and 0.75% respectively at 180°C, and 6.01%, 5.13% and 5.95% at 500°C. Hence the ratio of the weight loss at the two temperatures is about 8 for untreated and for superplasticizer-treated samples supporting the above suggestion.

3.4 X-ray Diffraction

X-ray diffractograms of opal treated with the dilute solutions of the three superplasticizers were compared with the diffractogram of untreated opal. A peak at about 2.02A, attributed to tridymite, showed some weakening on diffractograms of samples treated with superplasticizer but no other changes in crystallinity were detected.

4. DISCUSSION

Mortar bars made with opal, 0%, 6% and 12% silica fume and any of the three superplasticizers showed greater early age rates and ultimate magnitudes of expansion than corresponding control bars containing no superplasticizer. In bars made with no silica fume the control bars showed a gradual increase in amount of expansion to an age of 400 days. The bars made with SMF and LS type of superplasticizer showed high expansion rates at ages up to 150 days followed by decreases in expansion rates at greater ages; total magnitudes of expansion remained greater than in the control bars.

In bars made with 6% silica fume replacement of cement the ultimate magnitude of expansion of bars made with and without superplasticizers was lower than in bars made without silica fume. The bars made with SMF and LS type superplasticizers however still showed much higher expansions than the control bars (Fig.2). In bars made with 12% silica fume the expansion of all bars was delayed for about 2 months. At later ages the expansion of bars made with superplasticizers was greater than that of the control bars (no superplasticizers) though the magnitude of expansion at 400 days was smaller than in bars made with 6% silica fume.

Microstructural analysis indicated that superplasticizers in the mortar changed physico-chemical properties of gel products such as ability to flow, solubility and moisture absorption capacity. Treatment of opal in dilute solutions of superplasticizers led to an increase in the disorder coefficient and development of a corroded appearance on surfaces. Thermogravimetric analysis also suggested break-down of internal Si-O bonds with increase in exposed silanol groups. Analysis by x-ray diffraction indicated very little or no change in the crystalline mineralogy of the opal. Further investigations are continuing.

5. CONCLUSION

1. A superplasticizer in mortar bars containing 2% opal as an alkali-reactive component increases the expansion due to alkali-silica reaction.
2. Attention should be paid to the use of silica fume if alkali-silica reaction is possible. If the amount of silica fume is equal to or less than 12%, the presence of superplasticizers will dramatically increase the expansion caused by alkali-silica reaction.
3. Increase in expansion due to the presence of superplasticizers is probably linked to changes in the opal itself and in physico-chemical properties of the gel products such as viscosity and surface tension.

6. REFERENCES

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