17. DIAMOND, S., "Effects of Two Danish Flyashes on Alkali Contents of Pore Solutions of Cement-Flyash Pastes," Cem. Concr. Res., Vol 11, 1981, pp. 383-394.

18. LOPEX-FLORES, F., "Flyash and Effects of Partial Cement Replacement by Flyash," MS Thesis, Purdue University, 1982, 112 pp.

19. BAKKER, R. F. M., "About the Cause of the Resistance of Blastfurnace Cement Concrete to the Alkali Silica Reaction," Proc. 5th Int. Conf. on Alkali Aggregate Reactions, in Concrete, Cape Town, 1981.

20. DIAMOND, S., "Effects of Microsilica (Silica Fume) on Pore Solution Chemistry of Cement Pastes," Communications, J. Amer. Ceram. Soc. Vol 66, May 1983, pp. C-82 - C-84.

21. PAGE, C. L. and VENNESLAND, O., "Pore Solution Composition and Chloride Binding Capacity of Silica Fume - Cement Pastes," Materials and Structures, (RILEM), Vol 16, No. 91, 1983, pp. 19-25.

22. ASGEIRSSON, H., "Special Discussion", Proc. 5th Int. Conf. on Alkali Aggregate Reaction in Concrete, Cape Town, 1981, p. SD-1.

APPLICATION OF QUANTITATIVE EDXA ANALYSES AND MICROHARDNESS MEASUREMENTS TO THE STUDY OF ALKALI-SILICA REACTION MECHANISMS

Mitsunori Kawamura*, Kunio Takemoto** and Shigemasa Hasaba*

*Professor, **Research Assistant

Department of Civil Engineering,
Kanazawa University, Kanazawa, Japan

ABSTRACT

The combination of the chemical compositions at a spot in the reacting particle obtained by SEM-EDXA analysis and the microhardness measured at the same spot has a possibility of giving us some informations on the relationship between the progressive inward chemical reaction and the changes in rigidity within the reacting particle. Quantitative EDXA analyses were carried out by using the calibration curves prepared from a series of synthetic sodium-silica, potassium-silica and calcium-sodium-silica gels. The chemical and physico-chemical processes progressing within the reacting opal particles were correlated with the expansion of the corresponding mortar bars made with an opal aggregate. The reactive opal particles embedded in cement paste were found to soften in the vicinity of their periphery with a rapid increase of the alkalies concentration in the region at early ages. The changes in micro-hardness of the affected portions in the reacting particles brought about by drying also gave us some informations concerning the intrusion of water into the reacting opal particles with time. The EDXA analyses showed that a relatively great amount of calcium moved into the reacting opal particles. An indication that the movement of calcium into the opal particles was always behind the intrusion of the alkalies was also obtained. Explanations for the dependence of expansion on the particle size of the reactive aggregate and for the prevention of the expansion due to alakli-silica reactions by the addition of a fly ash were provided on the basis of the results obtained by the quantitative EDXA analyses. Key Words: EDXA analysis; Microhardness; Expansion; Fly Ash.

1. INTRODUCTION

In relation to the elucidation of alkali-silica reaction mechanisms, usefulness of the application of SEM and EDXA analysis to direct examinations of the progressive inward chemical reaction in a reacting aggregate in concrete has been pointed out by Diamond /1/. Thereafter, a few reports concerning the informations of local chemical compositions in reacting grains in concrete have been presented /2, 3, 4, 5/. On the other hand, there seems to be no research clarifying the local physical changes caused by the intrusion of Na^+, K^+, Ca^{++}, OH^- and water into reacting aggregate particles in concrete. A useful technique available for obtaining the informations regarding the mechanical changes of the reacting particles is microhardness test. A combination of the chemical compositions at a spot in the reacting particle obtained by SEM-EDXA analysis and the microhardness measured at the same spot has a possibility of giving us some informations on the relationship between the progressive inward chemical reactions and the changes in rigidity within the reacting particles. In this paper, some explanations for the dependence of expansion on particle size as well as for the mechanisms responsible for the reduction or prevention of deleterious alkali-silica expansion by the addition of fly ash are provided on the basis of the results obtained by the quantitative EDXA analyses being supplemented by the characteristics of microhardness within the particles.

2. EXPERIMETAL

2.1 Materials

The cement was an ordinary Portland cement with the equivalent Na_2O of 0.78 percent. The reactive aggregate used was an opaline rock from the Akase opal mine in Ishikawa Prefecture. An X-ray pattern for this opal indicated the existence of α-cristobalite and quartz. Bulk specific gravity and absorption capacity of the reactive aggregate are 2.29 and 1.79 percent, respectively. The opaline rock was crushed by hand and sieved so as to obtain the aggregates with the size fractions (1) of 5 - 2.5 mm; (2) of 2.5 - 1.2 mm; (3) of 1.2 - 0.6 mm; (4) of 0.6 - 0.3 mm; (5) of 0.3 - 0.15 mm; (6) of 0.15 - 0.074 mm; (7) passing the 0.074 mm sieve. The amount of total, water soluble and available alkalies of the fly ash used were 1.04, 0.57 and 0.09 percent, respectively.

2.2 Procedures

2.2.1 Preparation of specimens

The mortar specimens for expansion test were prepared at the total aggregate cement ratio of 0.75. Toyoura Standard sand was used as the non-reactive aggregate. The amount of the total aggregate to be replaced by reactive aggregate was maintained at 10 percent by weight. The amount of fly ash to be added was 30 percent by weight of cement. The mortar specimens of 2.5 by 2.5 by 25 cm were stored in a fog box maintained at 38°C. The length changes of the mortar specimens were measured at intervals of two days according to ASTM C 227 test. In some specimens, 1.0 percent sodium hydroxide by weight of cement was added to raise the alkali concentration in mortar.

The proportions of the ingredients in the samples for microhardness test and EDXA analysis correspond to those in the mortars for expansion test except that Standard sand is excluded in the former. Thus, the water cement ratio of the cement paste matrix in which the opal particles were embedded was 40 percent. The opal aggregate cement ratio was held at 0.075.

2.2.2 Microhardness test

The microhardness tester with Vickers penetrater was used to measure the microhardness within a reacting particle. Measurements were made with the space of about 20 μm across the interface between cement paste and an opal particle in the polished surface of the specimens /6/.

2.2.3 Energy dispersive X-ray analysis

After completion of microhardness measurements, the specimens were fractured to yield blocks of about 10 mm on a side. The blocks were dried at a room temperature in a vacuum drying oven. EDXA analyses were made at the spots where microhardness measurements had been made and at some other spots using a ASM-SX scanning electron microscope (Shimadzu Co. Ltd.) equipped with an EDXA International energy-dispersive X-ray analyzer. The accelerating voltage, sample current and count rate were 15 kV, 0.5 - 0.8 nA and around 1200 cps, respectively. The spectrums for the Kα peaks of Na, K, Ca and Si were accumulated for a period of 100 seconds of counting. Homogeneous sodium-silica, potassium-silica and calcium-sodium-silica gels were synthesized after the procedure by Struble /7/ in order to obtain the calibration curves for determining the local chemical compositions in reacting opal particles in cement paste /8/.

3. EXPERIMENTAL RESULTS

3.1 Expansion test

The expansions at 30 days for the mortars made with the reactive aggregates of various size fractions are plotted in Fig.1 and 2. Mortar specimens

containing the first and second coarsest size fractions of opal of 5 - 2.5 mm and of 2.5 - 1.2 mm (Group I), and the finest one, < 0.074 mm, showed relatively low or no expansion, and those made with the intermediate-sized opal (Group II) greatly expanded. It may also be found that there is only a little difference in expansion between the mortar specimens containing the reactive aggregates of different size fractions ranging from 1.2 to 0.074 mm. The addition of fly ash of 30 percent by weight of cement to added NaOH-free mortars is found to completely eliminate expansion and to greatly reduce expansion even in the mortars with added NaOH of 1 percent, as shown in Fig.3, /9/.

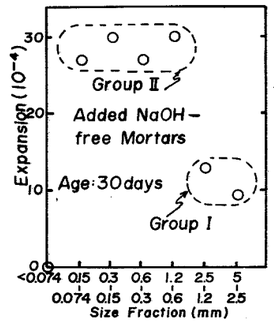

Fig.1 Expansions at 30 days for the mortars without added NaOH.

3.2 Changes in microhardness within reacting opal particles

Microhardness measured inside the opal particles of 5 - 2.5 mm range embedded in the cement paste with added NaOH of 1 percent indicated that the softened region progressing inward with time reached a depth of about a quarter the diameter of opal particles at the age of 28 days /6/. Enlargement of the softened region with time is clearly shown by the solid lines obtained by plotting the values of microhardness in wet samples in Fig.4 and 5. The microhardness of the softened region within about 300 μm from the interface in the cement paste with added NaOH of 1 percent decreases with time until 14 days. However, the rigidity of the region within about 50 μm from the interface at 28 days is higher than at 14 days. Comparing the distributions of microhardness for opal particles in the cement paste with added NaOH of 1 percent with those for the ones in the added NaOH-free cement paste indicates that addition of NaOH increases the thickness of the softened region in opal particles at all ages.

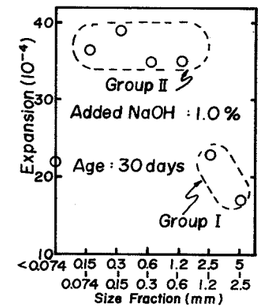

Fig.2 Expansions at 30 days for the mortars with added NaOH of 1 percent.

The plots connected with broken lines in Fig.4 and 5 show the microhardness obtained for the samples dried in vacuum at a room temperature. The microhardness of calcium-alkali-silica gels decreases as their water content increases. Therefore, differeces in microhardness between solid and broken lines are considered to be a measure representing the amount of water absorbed by the gels produced within the boundary of the opal particles. The region showing a great difference in microhardness between dry and wet samples reached a depth of about 75 μm at least by the age of 7 days in the opal particles embedded in the added NaOH-free cement paste. There occurred little enlargement of the region after 7 days, but the microhardness of the region drastically decreased with time, resulting in extremely low values at 28 days. These results indicate that the intrusion of water into the affected portion evidenced by a great reduction in microhardness with time after 7 days appears to relate to the increase in expansion after 7 days shown by the expansion curve in Fig.3.

3.3 EDXA spot analyses within reacting opal particles

$(Na_2O + K_2O)/SiO_2$ and CaO/SiO_2 mole ratios within the coarsest opal particles of 5 - 2.5 mm range embedded in the cement paste with added NaOH of 1 percent are plotted against the distance from the interface in Fig.6 and 7. Although a small amount of the alkalies reach a considerably great distance from the

interface even at 3 days, the intrusion of a great amount of the alkalies occurred after 7 days. While only a little or little calcium intruded into the opal particles at 3 and 7 days, the movement of calcium into the reacting particles after 7 days was so remarkable that calcium arrived at about 200 μm and 100 μm from the interface in the 14 days old samples with and without added NaOH, respectively. The intrusion of a great amount of the alkalies and calcium after 7 days coincides with the drastic reduction in microhardness in the peripheral regions after the age of 7 days. This fact indicates that the noticeable intrusion of the alkalies and calcium after 7 days simultaneously accompany the ingress of a considerably large amount of water. The solidification of the softened region within about 50 μm from the interface after 14 days in the added NaOH-bearing samples appears to relate to the movement of a relatively large amount of calcium into the reacting opal particles. As shown in Fig.6 and 7, CaO/SiO_2 and $(Na_2O + K_2O)/SiO_2$ ratios within the reacting opal particles in the 14 and 28 days old samples vary from spot to spot. Almost of the points with a high $(Na_2O + K_2O)/SiO_2$ ratio appear to have a high CaO/SiO_2 ratio.

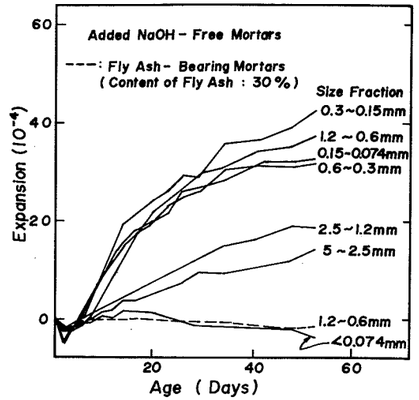

Fig.3 Expansion curves for the mortars made with the reactive aggregates of various size fractions.

In relatively fine opal particles, the influences of the reactivity, size and shape of opal particles selected for examination exceeded the progressive reaction with time, resulting in the irregularity of distributions of the alkalies and calcium within opal particles among ages /6/. Fig.8 and 9 show that the opal particles less than 1.2 - 0.6 mm range had changed into calcium-bearing alkali-silica gels throughout the whole region within the boundary of opal particles at least by the age of 14 days.

Fig.10 and 11 show the distributions of the alkalies from the interface to the center of the cross section of opal particles in the samples with and without fly ash, respectively. It is apparent from Fig.10 and 11 that the penetration of the alkalies into opal particles at early ages and subsequent progress of active reactions within them occurred in the fly ash-bearing samples. The amount of alkalies mobilized inward in the samples with fly ash appear to be even larger than that in the fly ash-free samples. Furthermore, it should be noted that the addition of fly ash brought about a great increase in calcium concentration rather than in alkali concentration in the gels formed. The fact that a large amount of calcium moved into opal particles in the samples containing fly ash is more clearly indicated by plotting the results of EDXA analyses as $CaO/(Na_2O + K_2O)$ mole ratio, as shown in Fig.12.

4. DISCUSSION

4.1 Dependence of expansion on the size of reactive aggregate particles

As described previously, mortar specimens made with the opal aggregates of various sizes are divided into two groups and the finest one, < 0.074 mm, with respect to their expansions at 30 days. Fig.8 and 9 show that $(Na_2O + K_2O)/SiO_2$ ratios in the gels formed at 14 days range from 0.01 to 0.1 and CaO/SiO_2 ratios from 0.01 to 0.07 with the exception of high values at the

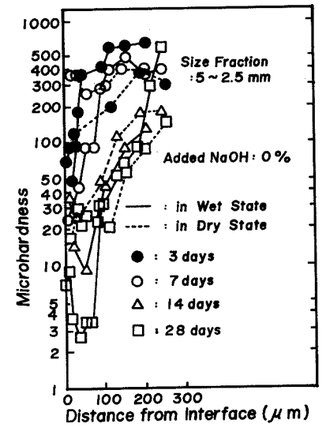

Fig.4 Microhardness within opal particles embedded in the added NaOH-free cement paste.

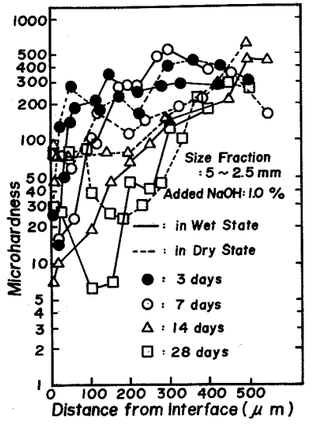

Fig.5 Microhardness within opal particles embedded in the cement paste with added NaOH of 1 percent.

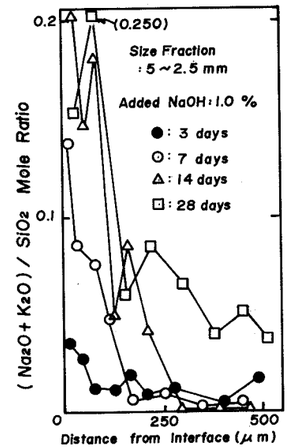

Fig.6 Distributions of alkalies concentration within opal particles of the 5 - 2.5 mm range.

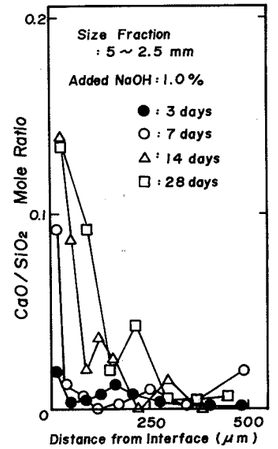

Fig.7 Distributions of calcium concentration within opal particles.

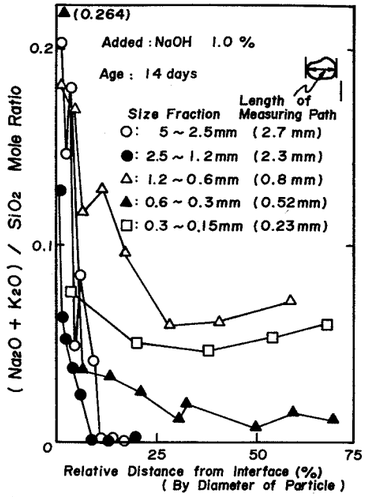

Fig.8 Distributions of alkalies concentration within opal particles of various size ranges.

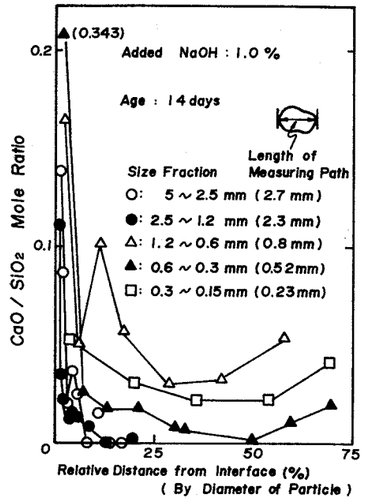

Fig.9 Distributions of calcium concentration within opal particles of various size ranges.

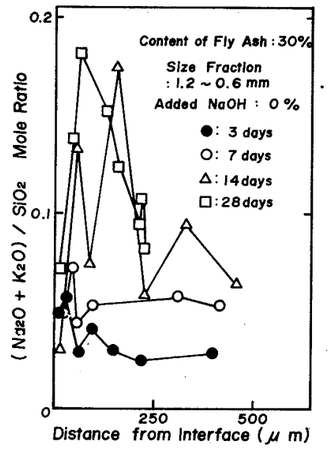

Fig.10 Distributions of alkalies concentration within opal particles embedded in the fly ash-bearing cement paste.

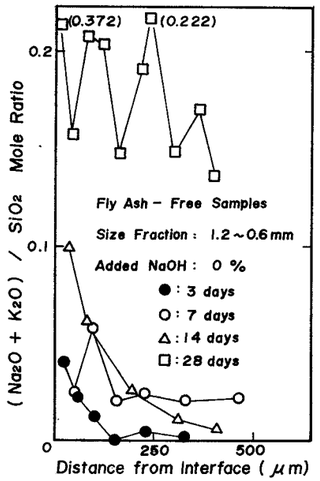

Fig.11 Distributions of alkalies concentration within opal particles embedded in the fly ash-free cement paste.

points close to the interface and at several other points. There seem no definite differences in $(Na_2O + K_2O)/SiO_2$ and CaO/SiO_2 ratios of the gels formed by alkali-silica reactions among the size fractions of the reactive aggregate. A great gap in expansion between Group I and Group II may be explained by the fact that the transformation of opal particles to gels throughout the whole region within the boundary of opal particles less than 0.6 - 1.2 mm range is contrasted with the formation of gels in the limited region near the periphery of particles in the first and second coarsest size fractions. Since the formation of gels progresses throughout within particles in the specimens of Group II, there may be little differences in the amount of the gels formed among size fractions leading to little differences in expansion among them. These results suggest that the expansion of the mortar specimens at least until the age of about one month depend upon the amount of gels rather than upon their chemical compositions.

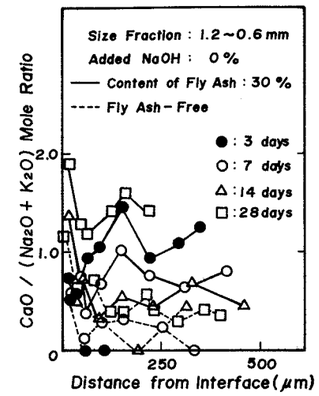

Fig.12 $CaO/(Na_2O + K_2O)$ ratios within opal particles embedded in the cement pastes with and without fly ash.

The intrusion of calcium into reacting silica grains embedded in cement paste has been reported by several authors /3, 4, 5/. It was also shown in this study that a relatively great amount of calcium was mobilized into reacting opal particles in almost cases. The changes in the distribution curves of calcium and alkalies within reacting opal particles with time, as shown in Fig.6 and 7, manifest that the movement of calcium into reacting particles was preceded by a relatively rapid intrusion of the alkalies. This result is not inconsistent with the concept by Powers and Steinouer that "surface diffusion of adsorbed lime through the already reacted part of a silica particle can enable the lime to react the site in adequate amount" /9/.

4.2 Mechanisms of the prevention of the expansion due to alkali-silica reactions by the addition of fly ash

According to the results of EDXA analyses given in Fig.10 and 11, active alkali-silica reactions undoubtly occurred within opal particles embedded in the fly ash-bearing cement pastes. A finding that the amount of calcium in the gel formed in the specimens containing fly ash was considerably greater than that in the ones without fly ash is particularly interesting as an evidence supporting the concept by Verbeck and Gramlich /10/. According to their concept, it is not primarily a matter of the quantity of calcium hydroxide throughout cement paste matrix, but rather a matter of its location or availability to silica surface that has a significant effect on the course of alkali-silica reactions. Hence, the concept suggests that the fly ash functions so as to bring about an increase in the amount of calcium hydroxide adjacent to silica surface, e.g. by distributing calcium hydroxide more uniformly throughout the fly ash-Portland cement system, resulting in the production of the gels with high calcium concentrations. In fact, it had been confirmed that fly ash accelerated the early hydration of cement and the calcium hydroxide formed was adsorbed on the surface of negatively charged grains of fly ash /11, 12/. Ogawa et al. also found that the lime rich zone existed near pozzolan particles in the hardened pozzolan-bearing C_3S paste /11/. Taking account of these findings as well as the concept by Verbeck and Gramlich, it may be possible that the fly ash plays an important role in raising calcium concentration in the gels produced within the reactive

aggregate particles. As far as the results obtained in this study were concerned, the fly ash did not inhibit alkali-silica reactions at all, but facilitated the mobilization of calcium into reactive aggregate particles leading to the formation of the gels with high calcium concentrations. Therefore, the reduction or elimination of expansion brought about by the addition of the fly ash appears to be attributable to the formation of gels with high calcium concentrations and/or to the reduction in the mobility of water through the fly ash-bearing cement paste matrix. However, an indication that the addition of calcined kaolin to the mortars containing the reactive aggregate almost completely inhibited alkali-silica reactions was also obtained in another series of experiments /13/. This result can be explained by the reduction in hydroxyl ion concentration of the pore solution resulting from surface reaction of the siliceous pozzolan /1/. It may be likely that the mechanisms responsible for reduction or elimination of the expansion caused by alkali-silica reactions are different for different types of pozzolans.

5. CONCLUSIONS

The application of the combined technique of quantitative EDXA analysis and microhardness measurements to direct examinations of the progressive inward chemical reaction and physicochemical absorption of pore solution in reacting aggregate particles in mortars provides the following several informations regarding alkali-silica reaction mechanisms.

(1) The intrusion of water into the affected portion inside reacting opal particles after 7 days is evidenced by a great reduction in microhardness.

(2) The solidification of the softened region within about 50 μm from the interface after 14 days found in a coarse opal grain embedded in cement paste appears to relate to the intrusion of a relatively large amount of calcium.

(3) The expansion of the mortars at least until about one month depend upon the amount of gels formed rather than upon their chemical compositions.

(4) The fly ash used in this study did not inhibit alkali-silica reactions at all, but facilitated the mobilization of calcium into reactive aggregate particles.

REFERENCES

1. DIAMOND, S., Mechanisms of alkali-silica reaction and expansion- a review and reassesment, pp.71, Unpublished, 1974.
2. KNUDSEN, T. and THAULOW, N., Cem. Concr. Res., 5, 443 - 454, 1975.
3. THAWLOW, N. and KNUDSEN, T., Sym. on Alkali-Aggregate Reactions, Preventive Measures, Reykjavik, 189 - 203, 1975.
4. POOLE, A.B., in "The Effect of Alkalis on the Properties of Concrete" Cement and Concrete Assn, London, 163 - 175, 1976.
5. DIAMOND, S., BARNEYBACK, R.S. AND STRUBLE, L.J., Proc. the 5th Int. Conf. on Alkali-Aggregate Reaction in Concrete, D252/22, pp.10, 1981.
6. KAWAMURA, M., TAKEMOTO, K. and HASABA S., Trans. of JCI, 4, 1 - 8, 1982.
7. STRUBLE L.J., MS Thesis, School of Civil Engineering, Purdue Univ., 1979.
8. DIAMOND, S., Cem. Concr. Res., 2, 617 - 632, 1972.
9. POWERS, T.C. and STEINOUER, H.H., ACI Journal, 51, 785 - 811, 1955.
10. VERBECK, G. and GRAMLICH, C., Proc. ASTM, 55, 110 - 1131, 1955.
11. OGAWA, K., UCHIKAWA, H. and TAKEMOTO, K., Cem. Concr. Res., 10, 683 -696, 1980.
12. DIAMOND, S. AND KINTER, E.B., H.R.R., 92, 83 - 92, 1966.
13. KAWAMURA, M., TAKEMOTO, K. and S. HASABA, in the course of preparation.

REACTIVE AGGREGATES AND THE PRODUCTS OF ALKALI-SILICA REACTION IN CONCRETES

Poole, A. B. and Al-Dabbagh, I.

Queen Mary College, University of London, London E1 4NS. U.K.

ABSTRACT

Potentially alkali-reactive flint particles from U.K. aggregates have been examined and compared to similar non-reactive particles using electron probe micro-analysis and scanning electron microscopy. It is found that reactivity of particles correlate with their impurity contents and with their colour. There is an indication that the micro-textures in flint also relate to reactivity.

A.S.R., Flint, Micro-analysis

1. INTRODUCTION

Although alkali-aggregate reaction in concrete has been recognised in the U.S.A. since the late 1930's is was only in 1976 that it was positively identified in some concrete transformer bases on the U.K. mainland. A number of concrete structures in South West England have now been shown to have deteriorated as a result of alkali-silica reaction between flint particles in the fine aggregate and alkalis from the cement paste.

A number of tests to identify potentially reactive aggregates have been devised with perhaps the best known being the A.S.T.M. Chemical Method, C289,and the Mortar Bar Method, C227, for alkali-silica reactivity and the Rock Cylinder Method, A.S.T.M.,C586,for alkali-carbonate reactivity. Among other methods which have been used as a screening test for checking aggregate for potential reactivity is the Gel Pat Test devised by Jones and Tarleton in 1958 /1/. This test involves the embedding of a suspect aggregate in an O.P.C. tablet which is ground to expose the aggregate and stored in a $\frac{1}{2}$N solution of KOH and NaOH.

As part of a programme of testing of alkaki reactive aggregates in the U.K. organised by Dr. Nixon of the Building Research Establishment /2/ small amounts of some 15 samples of potentially reactive and non-reactive fine aggregates from British sources were provided in order to test the validity of the pat test procedure as a screening test for potential reactivity. Several series of cement pats were prepared using these aggregates and stored in alkalis at 20°C, 30°C, 40°C and 50°C for periods up to 56 days. The results of these tests will be reported elsewhere but in general terms it was observed that very few aggregate particles reacted to produce gel under the 20°C storage condition but all 15 samples contained particles which showed reaction after storage at 50°C. The cement/aggregate pats used in this study were then used to provide examples of potentially reactive and non-reactive material for further study.

2. EXPERIMENTAL CONSIDERATIONS

2.1 The Petrography of the Samples

Examples of reacted and non-reacted particles of aggregate were broken from the face of the cement tablets using a dental drill and other methods. These methods set a practical size limit on particles extracted of about 1 mm. Thus the petrographic descriptions summarised in Table 1 below concentrate on the mineralogical composition of the fraction of the sample with particle sizes in excess of 1 mm.