ROLE OF METAKAOLIN IN SUPPRESSING ASR IN CONCRETE CONTAINING REACTIVE AGGREGATE AND EXPOSED TO SATURATED NaCl SOLUTION

T.R. Jones, G.V. Walters* & J.A. Kostuch
ECC International Ltd., Research & Development Department, St. Austell, Cornwall.
* ECC Quarries Ltd., Central Laboratory, Rockbeare Hill, Exeter, Devon.

We have studied the expansion of concrete prisms containing highly reactive aggregates and cured in concentrated salt solutions. This is a very severe test for ASR but by replacing part of the OPC with metakaolin it is possible to prevent expansion. From these and other measurements we propose a new model for ASR which explains gel formation and expansive behaviour in concrete over a wide range of conditions.

INTRODUCTION

The deterioration of concrete structures due to alkali-silica reaction, ASR, is a serious problem throughout the world. It is difficult and costly to repair damage caused by ASR; consequently there has been much research into its causes and many methods of prevention have been tested.

Three of the most common preventative measures are: (a) to avoid using potentially reactive aggregate (this is difficult in some regions), (b) to reduce the concentration of alkali metal ions (Na^+ and K^+) present in the concrete, and (c) to add pozzolanic material to the concrete mixture (Malquori (1)). Typical pozzolanic materials in current use are natural earths, fly ash, blast furnace slag, silica fume and calcined clays.

Previous work has indicated that, whether or not a concrete eventually shows expansion due to ASR depends on a multitude of factors. These include the mineralogy and particle size of aggregate, the source of Portland cement, and its content of soluble alkali metal cations. The porosity of the concrete and the environmental conditions to which it is subjected, are also important in determining the rate at which ASR proceeds, and hence the rate of deleterious expansion.

We have previously reported (Walters & Jones (2)) that expansion due to ASR was prevented if part of the ordinary Portland cement (OPC) in a concrete mixture was replaced by metakaolin. Only 10% replacement was sufficient to completely prevent expansion in concrete containing a known highly reactive aggregate when the test specimens were incubated for two years at 100% relative humidity (RH). We have now extended this work to more aggressive curing environments such as saturated NaCl solutions and M NaOH solutions (both at 38°C). Saturated NaCl was used because, in practice, concrete structures are often exposed to salt solutions and there is much evidence that damage due to ASR can be particularly severe in these cases.

METHOD

Concrete prisms were made by the method* described in (1) using flint/chert (unless otherwise stated), and other types of active aggregate from southern England. Inert limestone aggregate was used as required to produce a pessimum effect. Silica fume was obtained from Elkem Ltd. Samples of metakaolin were made from china clay and ball clay using a commercial calciner, and milled to <50 µm particle size.

In the ageing experiments, cast prisms were de-moulded after 24 hours and then incubated at 100% RH or immersed in saturated NaCl or M NaOH at 38°C. Some prisms were transferred to the salt solutions after they had been incubated at 100% RH for 20-30 months. Petrographic analyses were carried out (on prisms which had been incubated at 100% RH) by the Building Research Establishment, Watford, U.K.

Samples of exuded gel were taken from the outer surface of prisms, which had been incubated at 100% RH. They were dissolved after fusion with sodium carbonate, or in hydrofluoric acid/perchloric acid mixture, and elemental composition determined by atomic emission spectrometry. Part of the dried gel was placed on the stub of a scanning electron microscope, gold coated, and the X-ray fluorescence spectrum (EDXA) recorded.

Pozzolanic reactivity of the metakaolin was determined by the Chapelle test (Largent (3)).

To measure the $Ca(OH)_2$ content of concrete, a 6 kg cube was dried at 105°C, crushed to a fine powder and analysed thermogravimetrically.

---

* Draft British Standard Specification 812, Part 123.

RESULTS AND DISCUSSION

(a) Immersion of Prisms, Previously Incubated at 100% RH, in Saturated NaCl Solution

Figure 1 shows the effect of incubating the prisms at 100% RH, 38°C, followed by immersion in saturated NaCl. Results are shown for several aggregates known to be reactive with respect to ASR. In all cases there is a relatively large increase in expansion after transferring to salt solution. Chatterji et al (4) have reported that solutions of NaCl accelerate the alkali-silica reaction.

Figure 2 shows the effect of varying the proportion of flint/chert active aggregate in the mixture. The flint chert is known to give maximum prism expansion when it constitutes approximately 25% of the aggregate (the pessimum value) (2). It is seen from Figure 2 that when flint/chert constitutes more than 60% of the aggregate, expansion proceeds at a slower rate, even in NaCl solution.

(b) Immersion of Prisms, Previously Incubated at 100% RH, in M NaOH Solution

Figure 3 compares the effect on expansion of immersion in M NaOH and in saturated NaCl. It is seen that M NaOH increases expansion, but is less effective in this respect than saturated NaCl. This is discussed later.

(c) Effect of Silica Fume on Expansion

Prisms in which silica fume partly replaced OPC were aged, either by incubating at 100% RH, or by immersing in saturated NaCl immediately after demoulding. Figure 4 shows that 10% silica fume protected the concrete against expansion for more than 48 months, *provided that the environment was salt free*. However, when immersed in saturated NaCl, 10% silica fume protected against expansion for only 18 months. Thereafter expansion was extremely rapid.

Thus we see that immersion in saturated NaCl is a severe test for expansion due to ASR. Concrete formulations containing a range of aggregate types, or silica fume, showed increased expansion in NaCl. Indeed some samples showing negligible expansion when incubated at 100% RH for up to 4.5 years, nevertheless suffered rapid expansion when immersed in saturated NaCl or M NaOH.

(d) The Effect of Metakaolin on Expansion

Figures 5 and 6 show the effect of replacing 15% of the OPC by metakaolin. In Figure 5 the specimens were incubated at 100% RH for at least 24 months prior to immersion in saturated NaCl. In Figure 6 the specimens were demoulded after 24 hours, and immediately immersed in saturated NaCl. In both cases, metakaolin has prevented any expansion of the concrete for the duration of the tests to-date (21 months immersion in NaCl solution). Longer term trials are in progress and will be reported later.

(e) Petrographic Examination

The petrographic examination showed that prisms not containing metakaolin contained high concentrations of portlandite (calcium hydroxide) in the cement matrix, together with unhydrated Portland cement clinker grains, and cracks filled with silica gel. Prisms containing 25% substitution of cement by metakaolin showed no cracking due to ASR, and portlandite was not detected in the matrix. The cement paste was virtually isotropic in plane and polarised light. Remnants of the excess metakaolin were identified.

(f) Pozzolanic Reactivity Tests

Chapelle tests showed that metakaolins from china clay and ball clay reacted with 1.13 kg and 1.26 kg $Ca(OH)_2$ per kg metakaolin, respectively. The main products of reaction are calcium silicate hydrate (CSH), gehlenite hydrate (C_2ASH) and other calcium aluminium silicate hydrates, (de Silva and Glasser (5)). Assuming that 20% of OPC is converted to $Ca(OH)_2$ during curing, and taking metakaolin to react with 1.2 times its mass of $Ca(OH)_2$, we calculate that metakaolin reacts with all the $Ca(OH)_2$ in concrete if it replaces 14.3% of the OPC.

The reactivity of the silica fume was found to be 0.4 kg $Ca(OH)_2$ per kg silica fume.

Thermogravimetric analysis (TGA) of mortar pastes containing metakaolin were carried out over a range of curing times. Results are shown in Figure 7. It is concluded that metakaolin reacts rapidly and continuously with calcium hydroxide formed while the OPC cures.

From the ratio of TGA peak areas at 28 days with and without metakaolin (27.5 and 100 units respectively), the thermogravimetric analysis indicates that 1 kg metakaolin reacts with 1.25 kg $Ca(OH)_2$. Thus the Chapelle test, which refers to a metakaolin/lime mixture, and the TGA analysis, which refers to "real" concrete, are in good agreement.

(g) Analysis of ASR Gel

Analysis of dried exuded gel gave the results in Table 1. The EDAX spectrum is shown in Figure 8.

Table 1 - Analysis of Exuded Gel

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Wt.%	29.6	0.89	0.09	38.4	0.12	1.79	0.88

The presence of Al_2O_3 may be due to particulate impurities, as Al was not detected in the EDAX spectrum. Ignoring Al, Fe and Mg, the chemical formula for the gel is:

$$(SiO_2)\ (CaO)_{1.39}\ (K_2O)_{0.039}(Na_2O)_{0.029}.nH_2O$$

The EDAX spectrum is very similar to that observed by Durand and Berard (6) for gel found in the pores of concrete containing reactive aggregate. It is suggested that this gel is a relatively well defined phase which is formed in the pores of the concrete, and can exude. It probably corresponds to the "high calcium gel" described by Wang and Gillot (7), and by Davies and Oberholster (8,9).

From the observed composition we conclude that it is formed by the reaction of one part of active silica with 1.71 parts of calcium hydroxide plus 0.07 parts of sodium oxide equivalent (by mass), i.e.

$$\underset{1}{SiO_2} + \underset{1.71}{Ca(OH)_2} + \underset{0.07}{Na_2O} \rightarrow (SiO_2)(CaO)_{1.39}(Na_2O)_{0.068} \qquad (1)$$

GENERAL DISCUSSION

We propose a simple model that accounts for the results described above, and is compatible with earlier observations by other authors:

(1) Particles of active silica react with Na^+ (or K^+), OH^- and Ca^{++} ions (the latter two from $Ca(OH)_2$) to give a "high Ca^{++} gel" with empirical formula $(SiO_2)(CaO)_{1.4}(Na_2O)_{0.07}$.

(2) The formation of "high Ca^{++} gel" causes expansion, and the degree of expansion is proportional to the amount of "high Ca^{++} gel" that accumulates in the concrete matrix.

(3) The rate of formation of "high Ca^{++} gel" depends mainly on the rate of diffusion of Na^+ and Ca^{++}, i.e. on the concentration of these ions in the pore water.

(4) The final amount of "high Ca^{++} gel" formed depends (for a given level of active silica) (a) on the ratio of available calcium hydroxide to active silica and (b) on the ratio of available sodium ions to active silica. To convert all the active silica to "high calcium gel", according to the stoichiometry of equation (1) the $Ca(OH)_2$:active SiO_2 ratio should be 1.7 or greater and the Na_2O:active SiO_2 ratio should be 0.07 or greater.

In our experiments, the concentrations of OPC, aggregate and Na_2O (equivalent) in the concrete were 700 kg m^{-3}, 1625 kg m^{-3} and 7.0 kg m^{-3} respectively. If we assume that OPC generates 20% by mass of $Ca(OH)_2$ as a result of hydration, it follows that the cured concrete contains 140 kg m^{-3} of available $Ca(OH)_2$ which, according to our model, can react with a maximum of 82 kg active silica to give "high Ca^{++} gel". This value, 82 kg, is 5% of the total aggregate, which is typical for the pessimum concentration of highly reactive silicas such as opal (Hobbs (10)). Since our aggregate contained 35% flint/chert, compared with the pessimum value of approximately 25%, we calculate that our concrete specimens contained 115 kg m^{-3} of active silica.

"High Ca^{++} gel" cannot form in significant quantities, and hence expansion is inhibited, if the $Ca(OH)_2$:active SiO_2 ratio is significantly less than 1.7. For example, by increasing the concentration of active aggregate to 100% (Figure 2) the $Ca(OH)_2$:active SiO_2 ratio is decreased to 0.43. Similarly, by replacing 20% of the OPC by silica fume the ratio would decrease to 0.44. Replacement of 10% of the OPC by silica fume only reduced the $Ca(OH)_2$:active SiO_2 ratio to 0.68. Figure 4 shows that, at this ratio, expansion is negligible at 100% RH, but relatively rapid in saturated NaCl.

Another way to achieve this reduction of the $Ca(OH)_2$:active SiO_2 ratio is to add PFA or slag, both of which contain active silica. However, certain grades of PFA and slag contain high levels of CaO (up to 30%) and these are known to be less effective in preventing expansion due to ASR. Indeed, the extra soluble Ca^{++} added with such pozzolans can actually <u>increase</u> expansion by increasing the quantity of "high Ca^{++} gel" formed. Thomas et al (11) have recently discussed the role of PFA in altering the Ca content of gel formed by ASR. They suggested that Ca^{++} fixes the fluid gel and leads to expansion.

In our model, Na^+ ions partake in the initial dissolution of the active silica, and are also incorporated into the "high Ca^{++} gel". As discussed above, the concrete used in our tests contained 140 kg m^{-3} of $Ca(OH)_2$ which according to the stoichiometry of Equation 1, requires 5.7 kg of Na_2O to be incorporated into "high Ca^{++} gel". Concentrations of Na_2O higher than 5.7 kg m^{-3} would enhance the reaction rate: concentrations lower than 5.7 kg m^{-3} would progressively reduce the amount of "high Ca^{++} gel" formed. This is consistent with our observation that immersion in M NaOH is less effective than immersion in saturated NaCl (Figure 3). The generally accepted view that ASR can be prevented by maintaining Na_2O levels below, say, 3 kg m^{-3} is also consistent with the proposed model.

Kawamura and Ichise (12) have reported that the addition of small quantities of NaCl and $CaCl_2$ to mortar containing Beltane opal increases both the rate and extent of expansion, by factors of between 1.5 and 3. In their mortar, the $Ca(OH)_2$:opal and Na_2O:opal ratios were 1.5 and 0.07 respectively, which are slightly less than required stoichiometrically for "high Ca^{++} gel". Therefore, according to our model, it is not surprising that extra Na^+ increases the rate of dissolution of opal, while extra Na^+ and Ca^{++} increase the quantity of "high Ca^{++} gel" formed.

Wang and Gillott (7) have studied the effect of adding $Ca(OH)_2$ and fume silica (separately and together) to mortar containing opal. Adding $Ca(OH)_2$ increased expansion slightly, even though the $Ca(OH)_2$:opal ratio in their untreated mortar was high at 4.9. However, by replacing 20% of the OPC by silica fume, they reduced the $Ca(OH)_2$:active silica ratio to 0.65, and observed that expansion was negligible over a period of 560 days. By adding both $Ca(OH)_2$ and silica fume, they obtained a $Ca(OH)_2$:active SiO_2 ratio of 1.0 and expansion occurred, albeit delayed. This is consistent with our results when the concrete was immersed in saturated NaCl (Figure 4) where silica fume was used to reduce the $Ca(OH)_2$:active SiO_2 ratio to 0.88 or 0.68).

Pettersson (13) recently observed that granulated silica fume caused expansions in mortar bars immersed in $NaCl/Ca(OH)_2$solutions for 2 months, whereas the same quantity of fully dispersed silica fume caused no expansion. (The $Ca(OH)_2$:fume silica ratio in their experiments was 1.8, i.e. near to the stoichiometry required for "high Ca^{++} gel".) A simple explanation for their results is that high concentrations of soluble silicates are generated around granules of silica fume. These are converted into localised high concentrations of "high Ca^{++} gel", which enter cracks and instigate expansion. With fully dispersed silica fume, the gel is distributed evenly throughout the matrix. Cracking only begins when sufficient gel has diffused into large pores, or to sites of weakness - i.e. expansion is delayed. It has been observed by other authors that fume silica can delay, but not necessarily eliminate, expansion due to ASR.

This is supported by studies by Vivian (14), and by Hobbs and Gutteridge (15) who showed that the rate of expansion depends on the size of opal particles. They found that particles less than 50 µm in diameter cause no expansion over 200 days (for reasons outlined in the previous paragraph). Particles in the size range 50-150 µm cause delayed expansion, particles in the size range 150-850 µm cause maximum expansion, and particles larger than 1 mm give reduced expansion.

The Role of Metakaolin

We have shown that metakaolin reacts with $Ca(OH)_2$ almost as rapidly as it is formed while the cement cures. About 15% replacement of OPC by metakaolin is sufficient to remove all the $Ca(OH)_2$. This gives a concrete which is highly resistant to expansion, even in such aggressive environments as immersion in saturated NaCl. It should be noted that we do not yet know the minimum replacement required to prevent expansion although we do know (2) that 10% replacement, to give a $Ca(OH)_2$:active SiO_2 ratio of 0.37, is sufficient to prevent expansion when incubated at 100% RH.

There are two major differences between metakaolin and silica fume. Firstly, metakaolin reacts with three times as much $Ca(OH)_2$ as does silica fume. Secondly, there are no soluble silicates or swelling silicates formed: all the products of reaction are strongly cementitious crystals of CSH and calcium aluminium silicate hydrates. These are resistant to leaching, so it is expected that concrete containing metakaolin may be resistant to salt and acidic solutions.

Where the $Ca(OH)_2$:active silica ratio in concrete has been reduced, for example by adding metakaolin or silica fume, or by incorporating excess reactive aggregate, it would be interesting to examine the effect of immersion in $Ca(OH)_2$ slurry. Could this treatment restore the $Ca(OH)_2$:active SiO_2 ratio, and cause expansion?

CONCLUSIONS

Our model does not describe the detailed chemical reactions which lead to dissolution of active silica or the mechanism by which the gel swells. However, we do propose that swelling is due to the formation of a calcium sodium silicate of formula $(CaO)_{1.39}(Na_2O)_{0.068}(SiO_2)nH_2O$ ("high Ca^{++} gel"): the amount of "high Ca^{++} gel" formed depends on the ratios of soluble Ca^{++} to active silica, of OH^- ions to active silica, and of soluble Na^+ to active silica. The Ca^{++} and OH^- ions are supplied by the $Ca(OH)_2$.

If the $Ca(OH)_2$:active SiO_2 ratio is greater than 1.7, maximum expansion is observed. If the ratio is in the approximate range 0.6-1.7, there is less expansion, and it may be delayed. If the ratio is less than about 0.6 then little, if any, "high Ca^{++} gel" is formed and expansion may be negligible.

Similarly, the Na_2O:active SiO_2 ratio must be greater than 0.07 for expansion to be relatively rapid. As the ratio decreases, so does the rate and extent of expansion.

We believe our model is consistent with many of the ideas of Hobbs (10,15), Chatterji (4), Davies and Oberholster (8), Thomas et all (11), and other authors, but there are differences in detail. From the measured stoichiometry of the "high Ca^{++} gel" we derive semi-quantitative explanations for pessimum curves and the effects of adding fume silica, fly ash, $Ca(OH)_2$ or metakaolin. Other phenomena are also consistent with this model, e.g. the effects of immersion in NaCl and NaOH solutions, the effect of calcium-rich fly ash and blast furnace slag on ASR expansion, and the importance of active silica particle size.

Metakaolin reacts rapidly with 1.1-1.3 times its mass of $Ca(OH)_2$, which is formed as the concrete cures. If 10% of the OPC is replaced by metakaolin expansion due to ASR is prevented when concrete is incubated at 100% RH.

If 15% of the OPC is replaced by metakaolin, virtually all the $Ca(OH)_2$ is replaced by cementitious forms of CSH and calcium aluminium silica hydrates. The resulting concrete is highly resistant to expansion, even when immersed in saturated sodium chloride solution.

REFERENCES

1. Malquori, G., 1960, "Portland-Pozzolan Cements", 4th International Symposium, on the Chemistry of Cement, Washington, D.C., 983.

2. Walters, G.V. and Jones, T.R., 1991, "Effect of Metakaolin on Alkali-Silica Reactions", Durability of Concrete: 2nd International Conference, Montreal 1991, Vol II, p.941. American Concrete Institute.

3. Largent, R., 1978, Bull. Liaisons Lab. Ponto Chausées 93, 63.

4. Chatterji, S., Thaulow, N., Jensen, A.D., and Christensen, P., "Mechanism of Accelerating Effects of NaCl and $Ca(OH)_2$ on ASR", 7th International Conference on Concrete AAR, 115. Noyes Publications, N.J., 1987.

5. de Silva, P.S., and Glasser, F.P., 1990, Adv. in Cement Res. 3, 167.

6. Durand, B., and Berard, J., 1987, Materials and Structures 20, 39.

7. Wang, H., and Gillott, J.E., Cement and Concrete Res. 21, 647.

8. Davies, G., and Oberholster, R.E., "Chemical and Swell Properties of the ASR Product", 8th International Conference on Chemistry of Cement, Rio de Janeiro, 1986, p.249.

9. Davies, G., and Oberholster, R.E., "The ASR Product - a Mineralogical and Electron Microscopic Study". 8th International Conference on Cement Microscopy, Orlando, Florida, 1986, p.303.

10. Hobbs, D.W., 1981, Mag. of Concrete Res. 33 (117), 208.

11. Thomas, M.D.A., Nixon, P.J. and Pettifer, K., Durability of Concrete: 2nd International Conference, Montreal 1991, Vol. II, p.919, American Concrete Institute.

12. Kawamura, M., and Ichise, M., 1990, Cement and Concrete Res. 20, 757.

13. Pettersson, K., 1992, Cement and Concrete Res. 22, 15.

14. ~~Vivian, H.E. (1951), Austral. J. Appl. Sci. 2, 349.~~

15. Hobbs, D.W., and Gutteridge, W.A., 1979, Mag. of Concrete Res. 31 (109), 235.

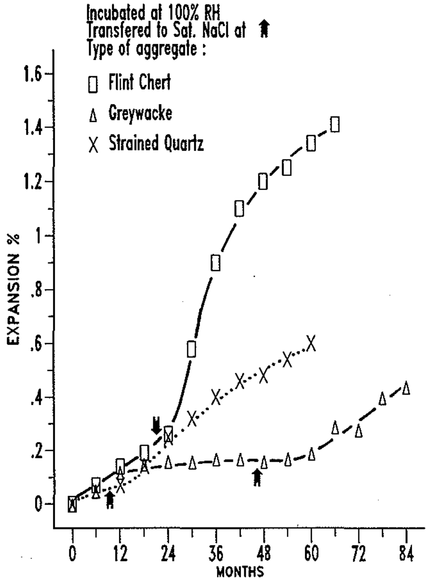

Figure 1 Expansion in sat. NaCl- effect of aggregate type.

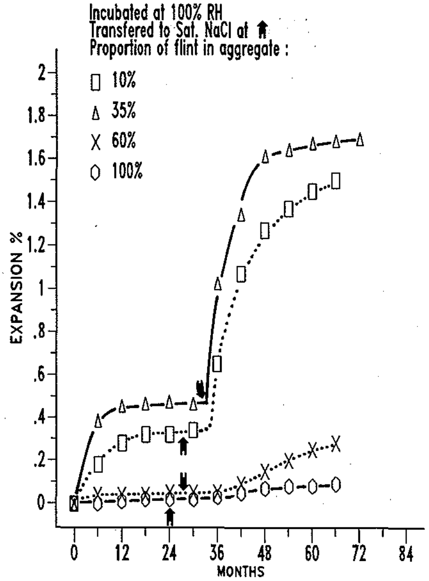

Figure 2 Expansion in sat. NaCl effect of % flint in aggregate.

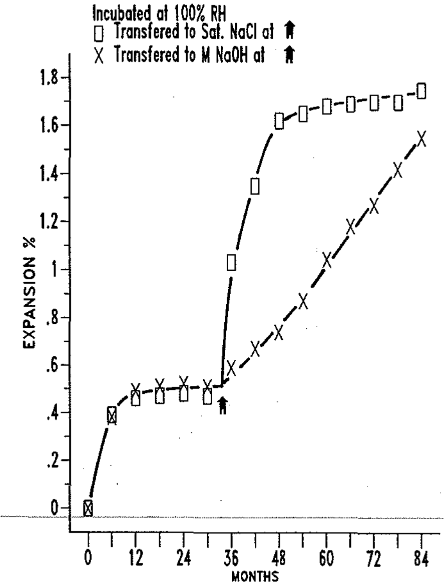

Figure 3 Expansion in sat. NaCl and M NaOH.

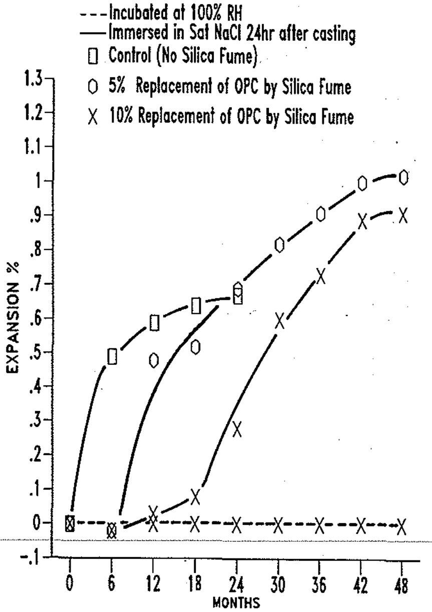

Figure 4 Expansion in sat. NaCl - effect of silica fume.

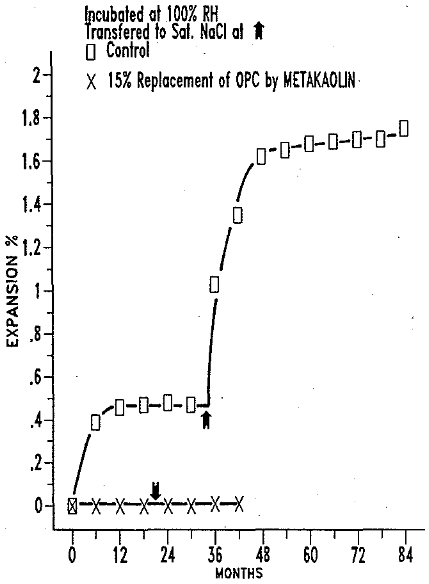

Figure 5 Expansion in sat NaCl – effect of metakaolin.

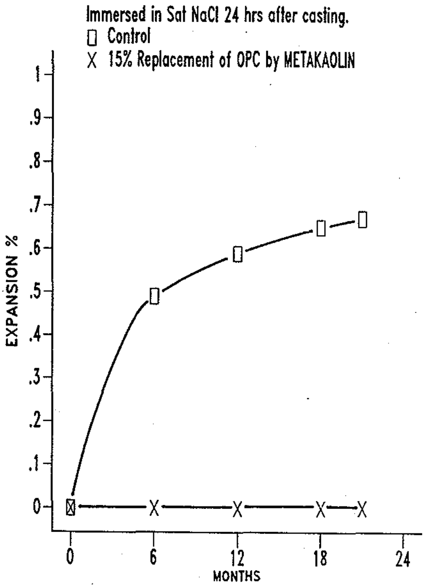

Figure 6 Expansion in NaCl – effect of metakaolin.

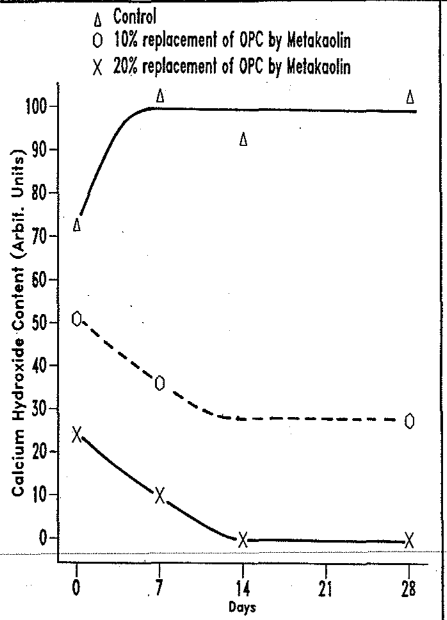

Figure 7 $Ca(OH)_2$ content of concrete – effect of metakaolin.

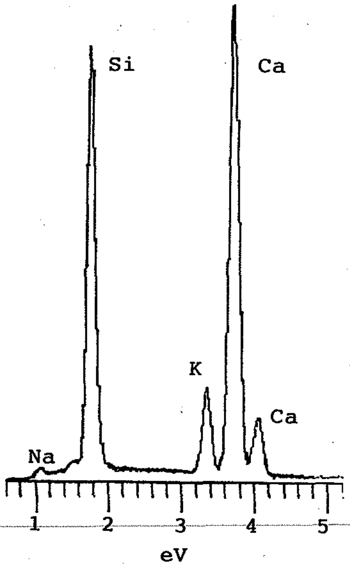

Figure 8 EDAX spectrum of gel from surface of prism.