

THE ROLE OF SOLVENT MIGRATION IN ALKALI-SILICATE

REACTIVITY

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ABSTRACT

Solvent migration is considered as an alternative to diffusion for the transport of material towards reactive silicate fragments. Cement paste is viewed as being composed of an inert phase and a mobile phase. The former includes the cement hydrates and sulphates and the latter consists of excess water and more soluble elements such as the alkalis though the precise location of particular ingredients is likely to vary from time to time in the evolution of the concrete. Migration of the mobile phase follows the release of hygroscopic silicon into the paste surrounding reactive aggregate fragments and the flow of the mobile phase effects a chromatographic transfer of ions in the direction of flow. The position of bands of high concentration of mobile ions depends upon the distribution coefficients of the species between the inert and mobile phases. Alkalies are concentrated into the mobile phase and are therefore transmitted with the solvent front. The position of this alkali front is dependent on the mass ratio of the mobile to the inert phases; the higher this ratio the closer is the peak concentration of the alkalis to the aqueous front. The height of this peak is directly proportional to the mass of alkali in the cement system. Formulae are given that describe the possible form of the distribution of concentration along the length of the flow in the most simple circumstances. These formulae are applied in approximation to the aggregate-cement reaction and it is shown that the estimated curves are of similar dimensions to those found experimentally. The process of solvent migration may also take place in other deleterious reactions such as alkali-carbonate reaction and reinforcement corrosion. It is suggested that simple tests may be developed permitting the detection of the propensity of aggregate for creating the solvent flow. Prevention of this flow is germinal to the prevention of reaction and if solvent migration is of significance then the single most important factor in reducing reactivity will be reduction of excess water.

Introduction

This paper puts forward a tentative model for alkali-aggregate reaction which may account for some of the complexities of the reaction zones. The model leads to suggestions for tests for reactivity and should itself be capable of test. The paper owes much to the symposium volume from last years meeting in Iceland and also rests in part on experiments carried out more recently by the author's colleagues A.B. Poole and A.Baker, who have examined the chemical variations found around opal and 'non-reactive' quartz in experimental concretes.

A basic problem presented by both this new data and that given for example by Thaulow and Knudsen (1) is the complexity of elemental distribution in the reaction zones. Even in simplified experimental concretes with regularly shaped aggregate pieces the distribution of alkalis, for example, may be discontinuous and in some parts of the gel zones there may be no alkali while nearby the concentration may be nearly two orders of magnitude greater than that found in the paste. It is common to appeal to some kind of diffusion process to account for this accumulation of ions in the vicinity of the aggregate and this is epitomised by statements made by Vivian (2) that for alkali-silicate reactivity to occur hydroxyl and metal ions have to diffuse to the silica surface and that the slow rate of accumulation of reaction products is attributable to the slow rate of ion diffusion. This diffusion process is selective in being able to pick out specific aggregate particles for reaction. Shells develop around certain reactive fragments even where these are but a small fraction of the aggregate. How then do the hydroxyl and metal ions choose the right fragment? What is the drive for this diffusive process?

In general the water and alkali concentrations in the gel zones may reach very high levels and the gels may locally become as high as 3 or 4M in alkalis. At these high spots the concentration is then several times that found in the pore fluid of the cement (3,4) and several times again that of the original cement. The diffusion of alkalis is thus creating a concentration gradient up which further ions must climb. This may perhaps suggest that the material being formed is energetically ~~more stable than the starting materials and that the gelatinous reaction product is analogous with a new crystalline phase appearing as the result of reaction between less stable solids or liquids.~~ It is obviously not

possible to argue that diffusion is directed by a concentration gradient for the levels achieved in the reaction zone are greater than those in the environment. Nor can a temperature gradient be postulated and paradoxically diffusion is occurring against a growing pressure. Moreover diffusion generated by chemical potential gradients cannot provide discontinuities or plateaux in the distributions of the chemical potentials and, unless there are temperature or pressure discontinuities the concentrations cannot be discontinuous either (5). Further, diffusion concentration profiles are usually of gaussian or high order binomial form and in general they will show different species migrating in different directions. The diffusion model cannot therefore readily account for the variability in composition of the reaction zones. Some of this variability may of course be analytical but there is sufficient evidence now available to justify the belief that the compositional variations are real.

An alternative to the diffusion model is that of solvent migration. This is directly analogous with chromatography in that what is required is an inert phase through which a solvent can migrate; a mobile phase able to reach local equilibrium with the inert phase; and a mechanism for causing the mobile phase to migrate through the inert. For the present reaction the stable cement hydrates and sulphates constitute the inert phase and the aqueous fluid of the interstices of the cement paste is the mobile phase. This aqueous fluid then largely corresponds with the water in excess of that required by stoichiometry for the cement hydrates and is largely held within pores, attached loosely to the surfaces of the solid materials or dispersed through paste gels. The composition of this hydrous phase is likely to vary considerably throughout the development of the concrete but will evidently hold much of the alkali content of the paste.

Undoubtedly in alkali-silicate reaction water and alkalis migrate to the aggregate but the cause of the migration is less readily identified. The migration of ions to specific aggregate fragments (and not to others) shows that it is the aggregate itself which controls or causes the motion of ions. The alkalis and water must of course be present but the initiation and probably the rate of the reaction must be governed by specific properties of the aggregate. Experiments with opal have shown that the gel is produced almost wholly within the aggregate and that as well as the water and alkalis, magnesium and calcium may also penetrate into the opal.

It is also well known that the aggregates have relatively high solubility in alkaline fluids compared with more stable material (6), and it could be argued that it is this solubility that controls the reactivity. The solubility will be influenced by many factors but for each aggregate the result will be that silicon atoms are released into the surrounding paste and into pores within the aggregate. It is therefore possible that the slow release of hygroscopic silicon atoms creates the necessary attraction for the hydrous mobile phase of the paste. Other ions are then released into the reaction zone as a consequence of this flow, and it is important that this mechanism collects the transported ionic species into sharply defined bands which may achieve very high concentration. The precise form of the distribution of concentration will depend on the adsorption isotherm of the system but it is shown below that it is possible to estimate the expected forms of the zones for simple 'ideal' systems. In general, the profile of these solute-rich bands is roughly gaussian with the flow mechanism tending to concentrate the solute into a very narrow band while the developing concentration contrast induces diffusion away from the position of maximum concentration.

Hence the essence of the present proposal is that reactive aggregate slowly produces by diffusion a high concentration of silicon atoms in its environment. This creates an attraction for the water of the paste and causes this pore fluid to migrate slowly towards the aggregate. Soluble ions are carried in the flowing fluid to produce sharply defined zones of high concentration near the aggregate fragments or within their decay products. The formation of first silica gel and then alkali-silicate gel continues to promote the influx of water and hence additional alkalis. This process goes on until the gel becomes mobile and in fact leaves the site of generation. The formation of the alkali-silicate gel does not itself inhibit reaction because, as experiments made by the author and A. Baker have shown, aggregates such as opal are appreciably soluble in sodium silicate gel. Movement of the gel away from the source of silicon may then permit reverse migrations, for, the high concentrations of alkalis and water reached in the gels may induce solvent flow into the paste. New alkali fronts may therefore be expected in the inert phase surrounding the moved gel.

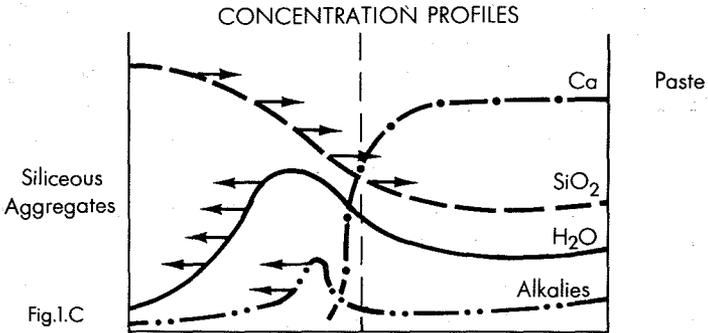
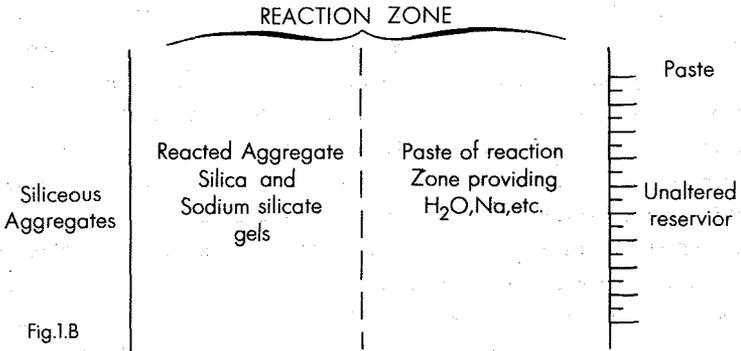
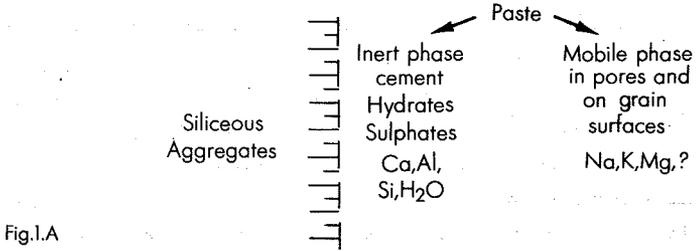


Figure 1. Schematic representation of alkali-silicate reaction in terms of solvent migration. Concentration profiles are given with concentration increasing upwards.

Qualitative Aspects of Solvent Migration in Concrete

Discussion of the application of solvent migration to concretes is facilitated by figure 1. Before reaction commences a simple boundary surface exists between the paste and the aggregate (fig. 1A). The aggregate boundary is represented as a plane and the paste is considered to have the two phases mentioned above. The inert phase includes the growing calcium silicate hydrates and soon acquires all the sulphate and available calcium (7). Considerable space exists between the growing hydrate phases and in this accumulates the residual water. Much of this water is presumably adsorbed onto the surfaces of solids and is dispersed through gels. It is evident that the alkalis are concentrated into this phase (7) though much of the alkali content may itself be adsorbed with the water on the surfaces of the crystallites. For this reason it may be quite difficult to determine the position of these elements even with the electron-microprobe. It is also likely that much of the movement of these soluble ions occurs in this surface layer. All elements must be distributed between the two phases of the paste and distribution coefficients should be definable for each ion and for each in the presence of the others. The data available at present does not allow these coefficients to be calculated but it is evident that Si, Al and Ca are overwhelmingly concentrated into the inert phase for much of the time during which the alkali-silicate reaction takes place. Conversely, Na, K, Li and perhaps Mg are dominantly in the mobile phase. The situation of Fe may vary considerably according to the pH and the oxidation potential of the system and in relatively reducing conditions it is likely that the Fe will enter the mobile phase. Inter-elemental effects may change the equilibria of even the alkalis and calcium and it is likely for example that high chloride concentrations may influence cation distribution coefficients.

After a period measureable in days, months or even years, the planar initial boundary between the aggregate and paste is replaced by a zone of reaction which includes some of the aggregate and that part of the paste that has contributed material to the reaction. The latter may not be noticeably changed except close to the aggregate, for water and ions that have moved into the aggregate may be made up by transfer from the much larger reservoir of paste surrounding the reaction zone (fig. 1B). The concentration gradients to be expected in a simple model involving solvent migration are illustrated in fig. 1C. The direction of motion

of the atomic and molecular species are indicated by arrows. Silica diffuses from the aggregate against the aqueous flow and may be expected to show a gaussian concentration profile slightly modified by the influence of the flowing aqueous phase. If Si were to be released from the inert into the fluid phase in abundance at any stage during the reaction it is likely that a silicon-rich band would be produced farther from the aggregate surface. The movement of the silicon away from the aggregate is here presumed to cause the aqueous flow and water will therefore show a concentration profile with a maximum within the zone of reaction. Solutes such as Na and K are concentrated into narrow bands of gaussian form at some position along the path through which flow has taken place. The precise position and form of these bands depends on the relevant distribution coefficients, the forms of the adsorption isotherms and the total amount of each element and uncombined water available. The curves given in fig. 1C are similar to those found in experimental concretes but it is to be expected that gel mobility, particularly in real concretes will distort the concentration gradients considerably. A further complication is that there is little information available concerning the rates of flow of the aqueous fluid. It is to be expected that this must be very slow indeed, a condition that will lead to the formation of sharp concentration bands and hence very high localised concentrations. However, if the rate of motion changes with time or the flow rate varies with direction, the form and position of the migrating fronts will be complicated and lead to lateral discontinuities in concentration.

Quantification of Solvent Migration

If it can be assumed that the adsorption isotherm for the inert and mobile phases of the paste is linear then relatively simple formulae describe the form of the distribution of ions in the flowing fluid. Thus if the distribution coefficient for component 'i' between the two phases is K_i , then

$$K_i = C_i^B / C_i^A$$

where C^B and C^A are the concentrations of component 'i' in the mobile and inert phases respectively. If the mass of 'i' in the mobile and inert phases initially are m_i^m and V_i^s and V^m and V^s are the volumes of the mobile and inert phases then

$$K_i = \frac{(m_i^m/V^m)}{(m_i^s/V^s)} \quad \text{and} \quad K_i V^m/V^s = \frac{m_i^m}{m_i^s}$$

If the ratio of the volumes of inert and mobile phases are fixed then $\frac{m_i^m}{m_i^s}$ is a constant which is here termed 'r'. If the mobile phase is allowed to flow through a distance of N units of length then, the (n+1)th unit of length will contain the fraction

$$(N!r^n)/(n!(N-n)!(1+r)^N) \quad \dots 1$$

of the total mass of a given mobile element (8). If this mass in the (n+1)th unit is 'w' then

$$\log w = \log N! - \log (N-n)! - \log n! + n \log r - N \log (1+r) \dots 2$$

This expression can be differentiated for constant total mass of component 'i' and constant N and r to give the number of units of length from the origin for which the concentration is a maximum. If this maximum is the (R+1)th unit of length then

$$R = Nr/(1+r) \quad \dots 3$$

The ratio of the distance moved by the solute to the distance moved by the solvent is then 'R_f' where,

$$R_f = r/(1+r) = n/N = n.h.a/V^m \quad \dots 4$$

where h is the unit of length and V^m is the total volume of fluid to have passed through an area of cross section a. The whole form of the distribution of an element can be obtained from these expressions but the width of the concentration band can be more simply found from the empirical formula

$$N = 16n^2/w^2 \quad \dots 5$$

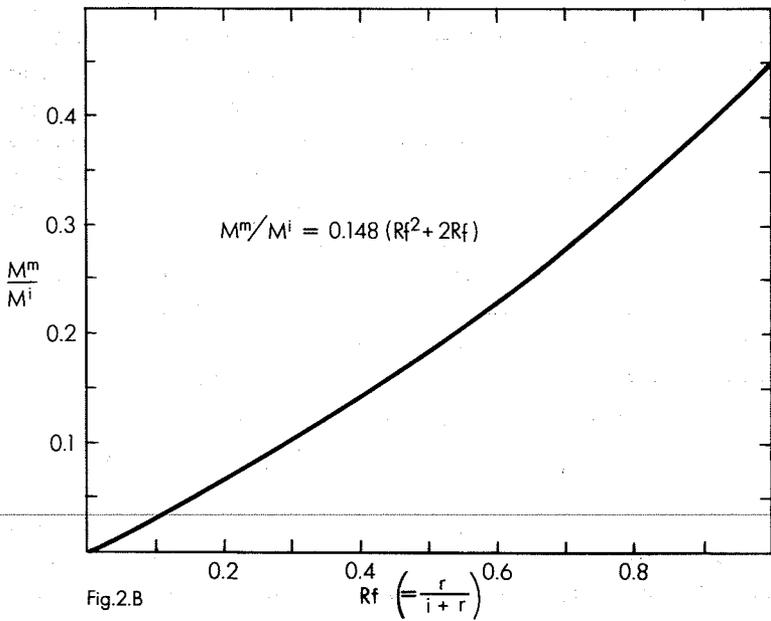
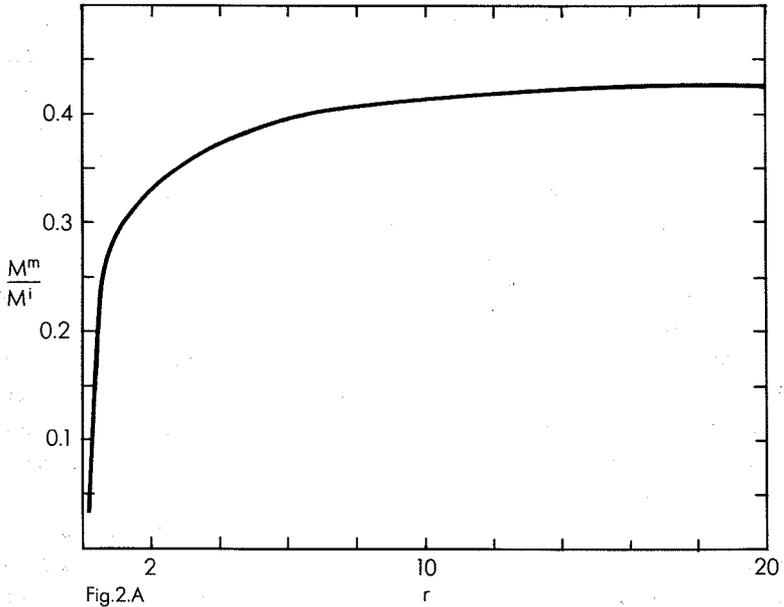
where w is the width of the band and n the number of length units at which maximum concentration occurs.

If the form of the adsorption isotherm is not linear the form of the solute-rich band may be changed considerably (5). Also since the R_f value is dependent on K_i then the position of maximum concentration will change if K_i changes. However, from 4 it is evident that a very considerable change in K_i is required to cause substantial difference in the position of this maximum.

Application to an Alkali-Silicate Reaction System

The data required to calculate the form of the solvent migration fronts are not yet available for the concrete system. There is information on the concentration of alkalis in the aqueous paste of the set paste (7) but the amount of water in mobile phase is not known and hence the distribution coefficient for the alkalis cannot be found. However if arbitrary values are assumed for the ratio of masses of mobile to inert phases and a fixed value of 0.7M is assumed (10) for the concentration of alkalis in the mobile phase and 0.1M for the whole cement system then K_1 can be found for various mass ratios m^m/m^i . Possible values of 'r' can then be plotted against the mass ratio if estimations are made of the densities of the mobile and inert phases (fig. 2A). This graph shows the way in which r approaches infinity as the mass ratio of the two phases increases; reflecting the condition that all the alkali is then in the mobile phase. Values of R_f are then plotted against m^m/m^i in fig. 2B which shows that $m^m/m^i = k(R_f^2 + 2R_f)$ where k is a constant. It is evident that as the fraction of the mobile phase increases so the solute front approaches the solvent front, and the position at which high alkali concentration is attained in the area of reaction is dependent on the proportion of excess water in the mix. With high levels of excess water the alkalis will become concentrated close to the aqueous front while with low levels of surplus water, and hence R_f , the alkali front will be more likely to remain in the paste and outside the area of potential gel formation. With little or no excess water there will be no flow and the alkalis will remain stationary. The assumptions made for the densities of inert and mobile phases are 2 and 1 respectively but the selection of different values for these densities will not change the form of the curves though the constant for the curve in fig. 2B will change. No attempt has been made to refine these relationships further since it is intended to illustrate only the kind of relationship that might be found in concretes pending the acquisition of more satisfactory data.

Further illustrations of the properties of solvent migration in concretes can be made by treating experimental data, such as the analytical data given by Thaulow and Knudsen (1), to show the possible form of concentration gradients to be expected. From this data the experimental concentration-distance curves have been drawn (fig. 3A). In fig. 3B are given the curves expected from the solvent migration model for the



width of gel observed experimentally and the quantity of water found to be transferred into the reaction zone. It is reasonable to assume that all the water now in the gel has been transferred from the paste and hence, given an estimate of the volume percentage of mobile phase in the paste, the width of the paste zone required to provide the necessary water can be estimated. Here, the volume fraction of the mobile phase can be estimated at about 0.33 and the total volume fraction of water in the gel zone is about 0.3. This means that since the gel width is about $150\mu\text{m}$ then the width of paste required to supply the water was about $135\mu\text{m}$ and the total width of the reaction zone was about $285\mu\text{m}$. The effective

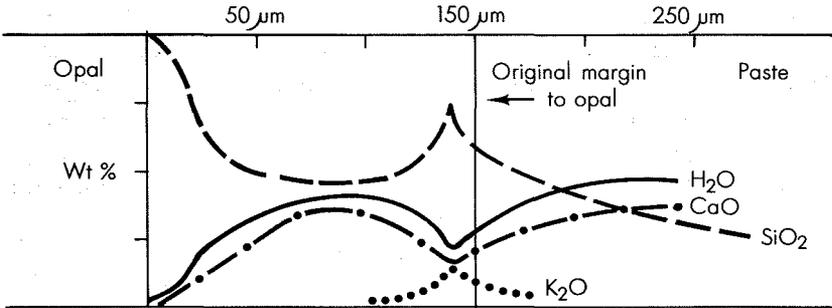


Fig.3.A

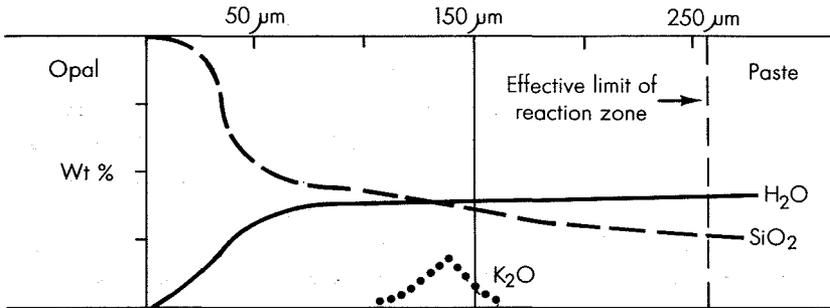


Fig.3.B

Figure 2 (left). Illustrative plots of the variation of 'r' and 'R_f' with the ratio of the mass of the mobile phase to the inert.
 Figure 3 (above). Comparison between experimental and calculated (B) concentration gradients in alkali-silicate reaction.

distance travelled by the water front is however best set by considering the maximum in the water concentration-distance curve. This is expected to be about midway through the gel zone. Hence the total effective length of flow may have been about $210\mu\text{m}$. With an assumed value of $\frac{m}{m^i}$ of about 0.26, corresponding with the estimated volume percentage of the mobile phase, the R_f value would have been about 0.7 and the distance of the alkali concentration maximum from the effective starting surface in the paste would be about $145\mu\text{m}$ and from equation 5 the width of the band would have been about $40\mu\text{m}$.

The exploration of approximations can be taken further by applying the full expression given above (equation 2) to find the concentration levels of the alkalis to be expected in the gel zone. The mobile fluid will have initially about 2% weight of alkalis (as Na-equivalent), and this will be extracted to a maximum concentration of about 2.7% Na_2O -equivalent by weight in the zone of enrichment in the gel. This compares with the experimental value of 1.8% Na_2O -equivalent and is obviously of the correct order; especially when allowance is made for the considerable kurtosis which the experimental water concentration profile shows in comparison with the estimated. This flattening of the water distribution curve would also be expected to apply to the alkali distribution. The assumptions and approximations used in this analysis are not too unreal for the present experimental system and the resemblance between the estimated and observed alkali concentration curves suggests that the model may deserve further exploration in the light of further data.

Conclusions

It is concluded that since experimental observations indicate that water migrates to the site of alkali-silicate reaction and that the distribution of alkalis is discontinuous, then solvent migration may be considered as a possible mechanism for the transfer of material. Estimations based on the formulae normally taken to describe the effects of solvent migration show sufficiently good agreement with the experimental curves to suggest that the search for further data relating to the distribution of ions between the inert and mobile phases would be justified. It is to be expected that if the process applies to alkali-silicate reactivity it may play a part in other processes. Alkali-carbonate reactivity, for example, may be initiated by flow towards

hygroscopic aggregate fragments where the active ingredient may be an expansive clay or a highly porous but slowly permeable carbonate. Perhaps also the transfer of material in iron reinforcement corrosion problems, where iron is deposited on surfaces or in porous aggregate fragments, may also involve solvent migration.

The detailed distribution of elements around alkali-silicate fragments will depend on the shapes of the fragments. Sharp edges and corners will show the most rapid accumulation of gel and the highest concentration of alkalis while concave surfaces would be expected to have narrower reaction rims. The increase in alkali in the reaction zone would enhance the solubility of the silicate aggregate and release of silicon into the reaction zone and thence the quantity of water to migrate towards the reaction zone. A chain reaction can therefore be established which is inhibited only by the growing pressure and the availability of water. The total width of the reaction zone should therefore depend on the quantity of water available and the concentration of alkalis in that aqueous phase.

The motion of the aqueous phase towards the aggregate would be expected to change the equilibria that exist between the mobile and inert phases. The production of a zone in the paste which is rich in alkalis, for example, might well modify the solubility of Ca, Si, Al and Mg in the aqueous phase. The possibility exists that while Mg, say, becomes less soluble with the progress of reaction, Ca, Si and Al may become more soluble. These elements may therefore become mobile and move with the alkali front to enter the zone of reaction. It seems not impossible therefore that the silica of the reaction zone is derived from both the paste and the aggregate. Some of the results obtained by A.B. Poole (personal communication) strongly suggests that this is so and that both Al and Ca can form bands of high concentration near the paste gel interface.

If the process of solvent migration is of importance it should lead to the construction of tests for reactivity. A strong dye for example that is highly soluble in the aqueous phase would be expected to ~~migrate with the water and should show up the movement and allow the rate of flow to be measured.~~ In addition it is apparent that if water flow does control the extent to which reaction takes place then the single most important factor in limiting potential reactivity will be

the reduction of excess water to the lowest possible levels. Failing that, it may be possible to prevent migration by the use of additives. Either a highly soluble additive may be used that passivates the aggregate surface or a hygroscopic material may be dispersed throughout the paste. The latter would be equivalent to the addition of a pozzolana and perhaps a suitable additive might be dried sodium silicate.

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Val de la Mare Dam