

THE PROCESS OF ALKALI-AGGREGATE REACTION, WATER ABSORPTION, REACTED AGGREGATE SWELLING, EXPANSION OF MORTAR AND CONCRETE AND POZZOLAN BEHAVIOUR

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SUMMARY

The reaction of alkalis and the reactive components of aggregate produces a reaction product which absorbs water and swells. The forces exerted by the water-absorbing reaction product are sufficiently great to expand and crack the confining mortar or concrete. The mechanisms of these processes are important since they explain the beneficial action of a pozzolan which inhibits or limits aggregate reaction and its consequent potentially disruptive expansion of mortar and concrete.

INTRODUCTION

Various discussions presented to the Conference on Alkali-Aggregate Reaction held in Cape Town, South Africa, 1981, expressed some concern about how the processes of aggregate reaction and concrete expansion occurred. It has become desirable to explain in some detail the mechanisms of aggregate reaction, water absorption, reaction product swelling and concrete expansion and disruption. Elucidation of these phenomena must be developed on two different levels, namely: (a) a molecular level on which aggregate reaction and water absorption proceed and (b) a relatively macroscopic level which deals with the swelling aggregate system as a unit, its interaction with the confining concrete and the cracking and expansion of the concrete.

It is necessary to recognize that the essential factors in the system are alkalis, reactive aggregate and free water and that reaction and expansion of reaction product are independent of the presence of concrete. When confined by being embedded in concrete, however, the swelling reacted aggregate exerts expansive forces which crack, expand and disrupt the concrete. It sometimes happens quite fortuitously that all the necessary requirements, notably aggregate containing some reactive material, cement containing a sufficiently large amount of alkalis ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) and some uncombined mixing water are present simultaneously and will inevitably cause the expansion and disruption of concrete.

It should be noted that both reactive and non-reactive aggregate particles are embedded in cement paste which consists of masses of gel and crystallites generally surrounding residual unhydrated clinker particles together with a random system of inter-connected spaces between the particle agglomerations. The interparticle spaces in the gel are very small and filled with water while those between the individual clinker-gel-crystallite clusters are relatively large and will generally be filled with both air and uncombined water. The uncombined water is therefore dispersed throughout the concrete and the major portion of it is not initially in contact with reacting particles and consequently is not immediately available for absorption or for the rapid dispersion of large amounts of reaction products. Both alkalis and free water must therefore diffuse from the surrounding concrete to reacting particles. Since these diffusion processes are relatively slow, reaction and water absorption processes proceed for long periods of time and the physical changes in reacting particles and the effects of the reaction product on concrete occur in an orderly sequence over a relatively long period of time.

The hydrated cement paste in which reacting particles are embedded, acts as a partial barrier which tends to confine the swelling reaction product to its site of formation but is not completely impervious to penetration by some of the readily deformable gel or sol products of reaction. The swelling of the reacting particle can force small amounts of these deformable products into spaces in the cement paste contiguous with the particle surface without causing expansion or disruption. While the hydrated cement paste therefore tends to confine the reaction product to its site of formation it does not act as a typical semipermeable membrane.

The inhibition of concrete expansion by pozzolanic material constitutes a special case of alkali-aggregate reaction and expansion and clearly illustrates the fact that semi-permeable membranes are not formed around reacting particles. Moreover, the beneficial action of pozzolans is possible only because the reacting and swelling particles are not contained within semi-permeable membranes or by an impervious hydrated cement paste.

#### REACTION OF ALKALIS AND SILICEOUS AGGREGATE AND ABSORPTION OF WATER BY THE REACTION PRODUCT

Potentially reactive aggregate together with non-reactive aggregate particles are completely embedded in cement paste which is undergoing hydration. The hydrating cement paste, which bonds onto the aggregate surfaces, consists of anhydrous and hydrated solids occupying approximately 50% of the paste volume and various interparticle spaces which together account for the remaining 50% of the paste volume. These interparticle spaces, which comprise large voids between the gel-coated clinker particles and small spaces within the gel and fine crystallite coatings, are filled with varying amounts of air and water or solution. The water or solution is the residual portion of the mixing water which has not combined with clinker compounds or been lost by evaporation. In aged concrete exposed to varying environmental conditions the uncombined water content can vary widely depending on ambient circumstances.

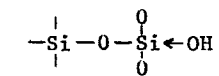
Alkalis which are derived from hydrating cement dissolve readily in mixing water to produce relatively high concentrations of alkali metal (Na + K) and hydroxyl (OH) ions together with smaller concentrations of calcium and sulphate ions. The chemical reaction of alkali hydroxides and reactive siliceous aggregate occurs in a heterogeneous system and may be affected by various interfacial phenomena which operate at phase boundaries, modify the reaction and the properties and behaviour of the solid. Apart from adsorption effects three reactions occur, namely:

- (i) Ions possessing sufficient energy approach and collide with the solid surface.
- (ii) In appropriate positions chemical reaction occurs, and
- (iii) Reaction products move from the solid-solution interface into the bulk of the solution.

All of these processes may affect the rate of reaction, the overall magnitude of which is determined by the slowest process. On account of the dispersed nature of the solution in concrete at atmospheric temperatures, the diffusion rate of ions will affect process (i), while the deficiency of water in contact with reacted solid will affect process (iii). Dissolved ions which collide with the solid surface but which do not produce chemical bonds may form intermediate complexes. In specific areas ions may attach tenaciously to the solid or may congregate in less strongly bonded associations and in larger concentrations than in the bulk of the solution. Ions are held in these latter positions by physical attraction forces rather than by chemical forces. The presence of adsorbed hydroxyl ions can assist in opening up the siliceous lattice, increasing its penetration by solution and thus promoting chemical reaction in depth within the aggregate particle.

The siliceous aggregate surface consists typically of oxygen atoms and has separate negatively and positively charged areas which result from the cleavage of silicon-oxygen covalent bonds. In addition the large number of silicon-oxygen bond defects in the lattices of opaline silica and siliceous glasses constitute sites where chemical reaction can readily occur. The relatively low densities and open lattice structures of cristobalite and tridymite are in marked contrast with the properties of non-reactive quartz and together with the large numbers of silicon-oxygen bond defects in opaline silica and siliceous glasses constitute the causes of siliceous aggregate reactivity. The latter factor, namely, the number of silicon-oxygen bond defects, however, has a major effect in determining the rate of aggregate reaction.

Hydroxyl ions in solution adsorb at positively charged surface sites, reduce the attraction forces acting between the surface oxygen atoms and by opening up the surface layers expose internal silicon-oxygen bond defects to reaction by the diffusing hydroxyl ions which form co-ordinate bonds with silicon atoms which have a deficiency in covalently bonded oxygen atoms as follows:



Such reactions also reduce attraction forces and open up the siliceous lattice so that with continuing solution penetration the reaction of the aggregate particle proceeds as more internal bond defects are exposed. Consequently, as reaction proceeds the number of O-Si-OH bonds increases and the siliceous aggregate particle breaks down into an increasingly large number of multi-negatively charged, hydroxylated silica micelles with associated diffuse layers of positively-charged alkali metal ions. Both negatively charged hydroxylated silica micelles and positively charged counter ions are associated with numbers of water molecules which are held either by co-ordinate bonds or by physical adsorption forces. Reductions in the free energies of these ions and water molecules ensure the continued diffusion of hydroxyl and alkali metal ions as well as water molecules from the cement paste solution to reacting aggregate particles.

It should be noted that the alkali-silica reaction product does not have a composition which is comparable with those of meta- and ortho-alkali silicates. Rather the alkali-silica reaction product consists of discrete aggregations of silica molecules forming partially reacted silica micelles which are deficient in alkalis, possess surface charges varying from one area to another and which are capable of acting as separate dispersed particles for a limited period of time when they have absorbed a critical amount of water. Although the initial water content of reacting aggregate particles is low, their water contents increase as reaction proceeds due to continued absorption by the micelles which are prevented from dispersing rapidly by diffusion and are therefore largely confined to their site of formation by the limited amount of solution in the cement paste in immediate contact with the particle surface. When the alkali-silica reaction product has absorbed approximately 20 times its weight of water the micelles can actually disperse, move independently and rotate. Under these conditions the alkali-silica complexes are unstable, the micelles orient to neutralize charges and flocculate to produce a coagulum which has a greatly reduced capacity for retaining its adsorbed water and no capacity for absorbing additional water. In order to re-disperse such a coagulum and to maintain a stable dispersion at a high water content, the alkali concentration must be increased significantly. This observation suggests that the residual reaction potential of partially reacted silica has a significant effect in maintaining the protective mechanism of pozzolans.

Since the volume of a reacting aggregate particle is defined and constrained by hydrating cement, its increasing water absorption increases the particle volume which in turn induces swelling forces and their transmission to the confining cement paste. It should be noted that a semi-permeable membrane is not formed around the reacting particle and that, although hydrated cement paste prevents the rapid dispersion of the swelling reaction product, it does not act as a semi-permeable membrane. Although the amount of alkali-silica reaction product which can diffuse away from the particle is largely restricted by the limited quantity of uncombined solution in cement paste, small amounts of deformable reaction product can be dispersed into spaces in the cement paste contiguous with the particle surface. When the cement paste is cracked by the swelling particle, the reaction product is unconfined and can escape without hindrance. The swelling particle however will continue to widen the crack and expand the concrete because it behaves as a rigid solid during its initial volume increase. As the absorbed water content increases, the properties of the reacting particle change progressively from a rigid gel to a deformable gel and finally to a fluid sol.

The vapour pressures of free water and solutions in cement paste are greater than that of reaction product in which water molecules are either co-ordinated with ions or combined with or adsorbed on solid surfaces. Consequently, water vapour diffuses from the cement paste to the reacting aggregate particle and despite some transient vapour pressure changes and minor volume adjustments in the swelling gel, the accumulation of water significantly increases the reacting particle volume. Resultant swelling pressures and concrete disruption follow inevitably from this change in distribution of water from the cement paste to the reacting particles.

The volume increase and therefore the potential swelling force exerted by a reacting particle are reduced by three different factors, namely: (i) Sorption compression of adsorbed water, (ii) Deformation and displacement of hydrated cement paste elements in contact with the swelling particle, and (iii) Dissipation of some reaction product into spaces in the cement paste. Sorption compression represents the small decrease in the volume of absorbed water since the separate volumes of free water and anhydrous solid can be shown experimentally to exceed that of swelling gel.

Cement paste consists of intimately associated structural elements comprising hydrous gel and crystallites which form coatings on the surfaces of residual clinker particles, relatively small water-filled spaces within the coatings and much larger inter-particle spaces between the individual gel-crystallite-clinker agglomerations. These latter spaces may contain air and water but do not contain hydrated cement compounds. The swelling particle exerts forces on the cement paste elements which are in contact with their surfaces, initially causing minute amounts of deformation and radial displacements without causing expansion and disruption. Ultimately, as resistance to further radial displacement increases, circumferential displacement commences, microscopic cracks are initiated in the cement paste and as these propagate, expansion and disintegration of mortar and concrete occur. The voids and inter-particle spaces in the hydrated cement paste adjacent to the reacting particle surface, can accommodate any surface reaction product which absorbs water rapidly and changes from a rigid gel to a deformable gel or to a sol. These readily deformable reaction products do not contribute directly to mortar or concrete expansion and the later developing cracks provide an increasingly large free space into which deformable reaction product can be forced without causing undue stresses or significant mortar and concrete expansions.

#### CHANGES WHICH OCCUR IN REACTED PARTICLES AND WHICH AFFECT THEIR CAPACITY TO EXPAND MORTAR AND CONCRETE

On account of the nature of the reaction between alkalis and reactive silica particles and the concomitant absorption of water, the surface zone of the reacting particle is first attacked by alkalis and absorbs water before the internal zone of the particle is reacted and begins to absorb water. Consequently, the surface zone changes from a rigid unreacted solid to a reacted swelling solid which becomes increasingly deformable as it absorbs water and transforms finally to a deformable gel or even to a fluid sol before the internal zone of the particle undergoes these changes. Some swelling deformable gel and fluid reaction product (sol) derived from the surface zone of the reacting particle is forced into spaces in the hydrated cement paste adjacent to the particle surface as the somewhat delayed swelling of the internal zone of the particle commences. Although such dissipation of portion of the outer zone reaction product temporarily delays and reduces concrete expansion, its filling of spaces adjacent to the particle surface ensures that the delayed swelling of the internal zone of the causes a circumferential displacement of hydrated cement elements and induces incipient crack formation which is the precursor of concrete expansion and disintegration.

While relatively small reacting particles situated close to external concrete surfaces may produce damp or even wet patches of cement paste which contrast clearly with unaffected cement paste, very large reactive particles will often produce "pop-outs". The surface layer of hydrated cement paste or mortar which directly overlies the swelling particle is displaced as a hinged lid and exposes the swelling particle. In this latter instance the total volume of swelling reaction product greatly exceeds the volume that can be dissipated in voids, interparticle spaces and cracks and the cohesive strength of the overlying mass of cement paste or mortar is not sufficient to prevent rapid failure and extensive displacement. The development of "pop-outs" creates new space into which swelling gel or sol can expand and therefore illustrates how the development of cracks limits the magnitude of concrete expansion.

As additional water is absorbed by the reacting internal zone of the particle after the concrete commences cracking, reaction product swelling proceeds and forces more and more of the outer zone deformable reaction product (either deformable gel or sol) into cracks and voids. Generally the rate of widening of cracks increases rapidly to a maximum and then declines slowly and continuously. When the rate of crack widening is declining, an increasing proportion of each increment in reaction product volume is being dissipated as deformable gel or sol forced into cracks and voids without increasing crack widths or concrete expansion. Eventually the stage is reached when the incremental volume increase in reaction product displaces deformable gel or sol into cracks and voids without exerting any increase in expansive force on the concrete and thereby ceases to widen cracks and increase overall concrete expansion. This latter condition assumes adequate amounts of alkalis and free water are available and that reactive aggregate is the limiting factor in the system. If either alkalis or water becomes limiting, the expanding system reaches an arrested condition which persists until additional alkalis or water are supplied to it.

At a relatively late stage in the reaction and expansion processes clear sol or readily deformable gel may be observed within affected concrete or exuding from cracks onto the concrete surface. In some instances the clear sol or gel is converted to a white, opaque non-swelling product formed either by reaction of clear alkali-silica complex with calcium hydroxide derived from hydrating cement which produces an insoluble calcium-alkali-silica complex or by the flocculation of the unstable alkali-silica complex sol when it attains a critical water content.

Two distinctly different surface crack patterns may be observed on expanding concrete. The fine, closely-spaced random crack pattern is produced by expanding particles near the concrete surface where restraint on expansion movements is relatively low. Less numerous wide open cracks which are often widely spaced are produced by expansions and displacements of masses of concrete deep within the concrete mass. The orientation of these cracks is always determined by the restraints imposed on expansion movements. The number of cracks observed in any affected concrete mass is generally fewer than expected for two reasons, namely: (i) Cracks which do not intersect the exposed surface at an obtuse angle are very difficult to observe, and (ii) Numbers of swelling particles tend to act in concert to produce a single, common crack rather than a number of separate cracks.

On account of the diffuse arrangement of the essential reaction components in concrete, the nature of the chemical reaction and water absorption processes and the involvement of surface phenomena, the significant changes in state of the reaction product entailing conversion from a rigid solid to a deformable gel and eventually to a fluid sol are time dependent and do not occur simultaneously or instantaneously throughout the entire reactive particle. These induced differential effects, which are modified by the size of the reactive particles, concentration of alkalis and amount of free water in the cement paste and acting in concert with several other important factors, affect the performance of pozzolan particles and promote their non-disruptive, protective action in potentially expansive concrete.

#### THE BEHAVIOUR OF POZZOLAN PARTICLES

Soluble alkalis react simultaneously with both reactive aggregate and pozzolan in amounts that are directly proportional to their surface areas. Consequently comparing the behaviour of equal weights of relatively coarse aggregate and very fine pozzolan particles the major proportion of the soluble alkalis reacts with the latter. In practice the proportion of alkalis which reacts with aggregate particles can be further reduced by replacing cement with pozzolan (thereby reducing the total available alkalis) and in quantities which greatly exceed the amount of reactive material in the aggregate. Under these conditions the extent of aggregate reaction resembles that typically developed when the cement has a very low alkali content (i.e. the aggregate reaction does not proceed rapidly and is quite superficial). Both reacted aggregate and reacted pozzolan particles absorb water and the available water is partitioned according to the total amounts of particles. Consequently the major proportion of the available water is absorbed by reacting pozzolan particles.

Some pertinent aspects of the dynamic particle reaction - water absorption system in relation to its enveloping cement paste - should also be considered. The rate of transformation of the initially-formed, low water content rigid gel to a higher water content deformable gel and finally to a fluid sol depends on the alkali concentration which determines the rate of silica reaction and indirectly affects the availability of free water in the cement paste and the rate of water absorption by the reaction product. Although the initial rates of reaction of alkalis and aggregate and of alkalis and pozzolan particles are equal, the rate of reaction will diminish rapidly for aggregate compared with that for pozzolan because the distances through which alkalis must diffuse to react with aggregate are relatively long compared with those for pozzolan particles. Consequently, the pozzolan particles undergo a more rapid reaction than reactive aggregate particles and on account of their very small size the pozzolan reaction is essentially a surface zone reaction. Since water absorption depends on the degree of prior silica reaction, reacted pozzolan particles absorb water at a more rapid rate than reacted aggregate particles. As a result of their rapid absorption of water, reacted pozzolan particles and especially their surface zones, transform very rapidly from a rigid gel condition to a

deformable gel and finally to a fluid sol. The almost simultaneous swelling and transformation of the pozzolanic particles into deformable products, which are forced into voids and spaces in the cement paste adjoining pozzolan particle surfaces, ensures that the increased volume of the swelling particle is dissipated without exerting undue expansive forces on the cement paste and without cracking the concrete. It is therefore most important to ensure that the mean volume of pozzolan particles is small (ideally all particles should be 45 micron diameter) so that, as reaction proceeds, differentiation between surface and internal zones of these small particles is negligible. Thus virtually the whole pozzolan particle reacts, absorbs water, swells and transforms into deformable products very rapidly and all these different processes proceed almost simultaneously. The maximum size of pozzolan particles must be limited to ensure that coarse, oversize particles do not add to the reactive component in the aggregate.

Examination of mortar and concrete containing an addition of pozzolan will reveal that as reaction proceeds the cement paste surrounding pozzolan particles becomes saturated with fluid sol which occupies the available free spaces. Estimates made from measurements of these sol-filled zones have indicated that the volume of free space in the hydrated cement paste within these zones exceeds the space needed to accommodate the estimated volume increase of the pozzolan particle. In contrast to pozzolan particles the amount of deformable surface zone alkali-silica complex produced by reacting aggregate particles is very small compared with the total potential volume increase of the particle. The large size of aggregate particles ensures that the entire mass of each one is not affected instantaneously and that the reaction, water absorption and swelling processes do not occur simultaneously and are staggered in occurrence both within the mass of the particle as well as in time.

In concrete containing pozzolan particles, reactive aggregate particles remain in a relatively unreacted and unexpanded state and will continue to remain in this state unless additional alkalis and water are supplied to promote their further reaction and expansion. It is considered that excess pozzolan is desirable in concrete to ensure that: (i) The major proportion of the total available alkalis reacts preferentially with pozzolan rather than with reactive aggregate, (ii) Some pozzolan remains to react with slow diffusing and slow dissolving alkalis and (iii) Such residual pozzolan is also available to react with any alkali that may be released when the alkali-silica complex reacts with calcium hydroxide to form the white, opaque non-swelling calcium-alkali-silica complex.

#### CONCLUDING REMARKS

Although alkali-silica reactions and water absorptions by the reaction products are similar for both aggregate and pozzolan particles, the behaviour of these reaction products and their effects on concrete are very different. These differences clearly illustrate the importance of the size of the reactive particles and the significance of kinetic factors on reaction product behaviour.

The extent of surface reaction, the rate of water absorption and the transformation of the reaction product from a rigid solid to a deformable gel or sol occur at different rates and affect the performances of pozzolan and aggregate particles in vastly different ways. These differences produce all the subsequent divergent effects which pozzolan and aggregate particles have on concrete expansion. The arcana in pozzolan behaviour involves virtually instantaneous reaction of the whole particle and its high, rapidly attained alkali-silica ratio which result from the very large surface/volume ratios of very small particles. In contrast to the long reaction time and slow water absorption by reacting aggregate particles, individual pozzolan particles produce very small quantities of reaction product which absorbs water so rapidly that it converts readily to a deformable gel or sol. While the proportion of deformable reaction

product produced from a reacting aggregate particle at an early stage of reaction is very small, virtually all of the swelling pozzolan particle becomes deformable at an early stage and can be dissipated into spaces in the surrounding hydrated cement paste without unduly stressing or expanding the concrete.

The alkali-silica complexes are potentially unstable and are capable of reacting with additional alkalis. Their capacity to react with additional amounts of alkalis ensures that pozzolans and pozzolan reaction products will continue to protect reactive aggregate particles from undue reaction. Reactive aggregate therefore in the presence of pozzolan remains in an arrested reaction condition. It is most unlikely that alkalis in sufficiently large amounts could penetrate into concrete and cause a deleterious aggregate reaction.

Penetration of water or water vapour into concrete can occur but will tend to transform reaction product on the surfaces of reacted particles into deformable gel or sol which can dissipate, without causing undue concrete distress, into spaces in the surrounding cement paste. While large amounts of absorbed water increase the swelling of reacted aggregate and in turn increase concrete expansion, the presence of excess water promotes reaction product dispersion and sol formation. Dissipation of sol into spaces in the cement paste brings the alkali-silica complex into contact with calcium hydroxide and may promote the formation of calcium hydroxide-alkali hydroxide-silica reaction products which do not absorb water and cause concrete expansion but may improve strength and cement paste permeability. Such pozzolanic reaction processes could therefore assist in explaining the beneficial effects of pozzolans on the performance of blended cements.

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#### ABSTRACT

The moisture binding capacity of concrete with alkali-silica reactive aggregate is discussed. The discussion includes practical measurements in a swimming pool wall. It is concluded that it is reasonable to suggest that the creation of alkali-silica-gel contributes to the selfdesiccation of the concrete.

Keywords: Moisture, relative humidity, measurements, alkali-silica-gel.

#### 1. INTRODUCTION

Moisture analysis is an important tool to use in making a diagnosis of the damages in a structure, as water is necessary in most deterioration processes, including the alkali-silica reaction (a.s.r) /1/. In such an analysis it is necessary to know, which moisture level can be expected in a sound undamaged structure. This problem is treated below.

The principal idea in the treatment is that concrete curing without exchange of water with the surroundings dries due to the chemical reactions to a certain degree. This selfdesiccation is well known in connection with the cement hydration. But the chemical reactions also include a.s.gel, which has two effects. Firstly the amount of evaporable water is reduced as the gel contains some non-evaporable water /3/. Secondly the gel will contribute to the hygroscopic binding capacity of the concrete, so that the sorption curves will lie higher than those for a concrete without a.s.gel.

Concerning the concepts shortly: The sorption diagram shows the equilibrium water content by weight as a function of the relative humidity in surroundings. The material is able to contain more water, when it has dried out to the equilibrium state (desorption), than when it has taken up water to the same relative humidity (adsorption). It is only the desorption curves which are treated here. (The adsorption isotherms are previously treated in /2/).

In the following the calculation of the desorption curve of a concrete is discussed and the selfdesiccation effect of a concrete with a.s.gel is shown by an example.

\*) From 1983-09-01: Building Materials Laboratory, Technical University, Lyngby, Denmark.