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Chemistry of alkali–silica reaction and testing of aggregates

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> "*I will show you fear in a handful of dust.*"
> *T.S. Eliot*

Abstract

Engineers and real state owners are demanding that concrete aggregates should be tested for their alkali–silica reactivity, before their use, by some accelerated test method. An analysis of the consumer's requirements shows that actually two, contradictory, demands are made on the test methods. These are: (a) to ascertain alkali–silica reactivity of an aggregate in a reasonably short time and (b) to evaluate and set an acceptance limit of long-term expansion of a reactive aggregate–cement combination. This contradiction is often ignored in national standards and only one test method is specified. However, it is known that concrete expansion, due to alkali–silica reaction, could be suppressed by using sufficient quantity of a pozzolan even when the concrete is exposed to a strong alkaline solution.

Most of the available test methods for the evaluation of alkali–silica reactivity of aggregates are empirical. In this paper, I propose to examine different test methods in the light of recent fundamental understanding of the mechanism of alkali–silica reaction and expansion. The emphasis is on the alkali–silica reactivity of aggregates themselves and not on the acceptance limit. The mechanism of alkali–silica reaction and expansive pressure generation suggest that the most appropriate condition of testing is to expose the test specimens to a solution of moderate hydroxyl ion concentration, preferably $Ca(OH)_2$ solution, and high ionic strength. The high ionic strength should be achieved by adding sufficient quantities of an "indifferent" electrolyte like a neutral alkali salt to the alkaline solution.

The fundamental understanding of the mechanism of alkali–silica reaction suggests a simple chemical test method for the evaluation of aggregates themselves. This method has been tested with Danish aggregates and an acceptance criterion has been suggested. Preliminary experiments show that the reactivity of samples of Japanese andesite, British Greywacke, Swedish porphyritic rhyolite, Norwegian mixed aggregate of rhyolite and quartzite and a silicified limestone aggregate from Belgium could be detected within 24 h. This is one of the quickest methods for the evaluation of alkali–silica reactivity of aggregates.

Keywords: Alkali–Silica; Reaction; Mechanism; Aggregate; Testing

1. Introduction

Damage to concrete structures due to alkali–silica reaction and consequent expansion is being observed in more and more countries. Construction engineers and real state owners are demanding better methods of assessing the alkali–silica reactivity of aggregates before they are used in constructions. In most actual structures, it takes a considerable time, after their constructions, before any sign of distress becomes obvious. Furthermore, for a given reactive aggregate the structural expansion depends on a number of factors like the diffusivity of the relevant ions through the structure, state of unsaturation of the structure, source and concentration of

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these ions, environmental moisture and temperature, the presence of a pozzolan, etc. The expansion of a concrete specimen, made with a known reactive aggregate, could be suppressed using a sufficient amount of a pozzolan even when the specimen is stored in an alkaline solution, e.g. so-called ultra-accelerated concrete expansion test. It has to be remembered that a concrete structure is seldom exposed to such concentrated alkaline solution at such high temperature (see also Section 6.2.3).

The engineers and real state owners therefore demand accelerated methods of aggregate testing in the laboratory. A field structure is exposed to fluctuating and changing environments and use, which no accelerated test method can simulate. An analysis of the consumer's requirements shows that actually two, contradictory, demands are made on the test methods. These are: (a) to ascertain alkali–silica reactivity of an aggregate in a reasonably short time and (b) to evaluate and set an acceptable limit of long-term expansion of a reactive aggregate–cement combination. This combination could be a specified sand–cement mortar or a specified concrete mix. In most national specifications, these two objectives are combined in a single test method. The acceptance criterion is often arbitrarily chosen in the sense that a fixed percent expansion at a fixed time is chosen. This criterion disregards that a slower rate of expansion may give much higher final expansion and consequent larger damage of the structure. Use of a specified mortar or concrete mix may even obscure the effect of alkali concentration on expansion capacity of such mix, i.e. so-called pessimum combination. To detect the pessimum combination one has to have a previous knowledge of the nature of the aggregate (see also Section 6.2.3). Furthermore, very few countries have incorporated environmental considerations in their national specifications (see further discussions on Table 1).

Table 1
A comparison between JIS and NaCl bath methods

Sample no.	% Expansion or cracking		
	JIS[a]	NaCl bath[a]	No. of prism cracked in NaCl bath
2–3	0.015	0.201	3
2–4	0.016	0.04	2
2–5	0.017	0.019[b]	1
2–6	0.017	0.017[b]	1
2–7	0.019	0.025[b]	3
2–8	0.020	0.107[b]	3
2–9	0.016	0.029[b]	3
2–10	0.018	0.013[b]	2
2–11	0.016	–	–
2–14	0.198	0.108	3
2–17	–	0.026	–

[a] Three prisms were measured in each set.

[b] In these cases the prisms from JIS test were exposed to NaCl bath.

Like most chemical reactions, the rate of alkali–silica reaction itself is higher at higher temperature. It is therefore easy to detect alkali–silica reaction at a higher temperature than at a lower temperature. However, long-term expansion due to alkali–silica reaction is higher at a lower temperature than at a higher temperature [1,2]. Usually in laboratory testing, the alkali–silica reactivity of an aggregate is evaluated indirectly by measuring expansion of a specified cement-aggregate combination at a specified, often at an elevated, alkali content and a specified environment. It is therefore, necessary to make a compromise (see further the discussion of Table 1). The compromise accepted by ASTM C227 is 38 °C and 100% RH. Some other countries have approved a similar environment. An implicit assumption behind this compromise is that the chemical reaction and expansion is directly related. However, a number of workers have shown that the rates of reaction and expansion are not directly related [1,3]. This testing at an elevated temperature involves a risk that some very reactive aggregate may show less expansion than less reactive aggregates. One has to remember 38 °C is not the most common temperature of concrete use and the alkali content of the structure may change over time. In exposed concrete surfaces, the temperature can easily reach about 50 °C or more.

In a few test methods, potential alkali–silica reactivity of an aggregate is evaluated directly. In these methods, elevated temperature is often used. In these tests, if the alkali hydroxide concentration is kept low then the risk of false negative is low. These methods can only evaluate the reactivity of the aggregate but cannot suggest an acceptance criterion.

It will be desirable to keep in mind the above-mentioned contradictory requirements, i.e. the contradiction between the rates of reaction and absolute expansion. It will also be desirable to distinguish between testing of an aggregate–cement composite and testing of aggregate itself. However, until recently the test methods were based on empirical observations that some aggregates, in a Portland cement matrix, react with alkali hydroxides and cause expansion. In the following presentation, I shall relate recent fundamental understanding of alkali–silica reaction with testing of a suspect aggregate. In this paper, I shall deal solely with the alkali–silica reaction and testing of alkali reactive aggregates. I shall deal with the acceptance criterion of reactive aggregate–cement combinations in a separate paper.

2. Reactants of alkali–silica reaction and the composition of reaction products

To understand the reaction between an aggregate and alkaline pore solution it is necessary to know the nature of the aggregate, the reaction environment including the type of ions present and their concentrations, temperature and the composition of the reaction products. In the following, these will be considered in turn.

2.1. Aggregates

Aggregate constituents, which have been reported to be alkali reactive, include pure SiO_2 like, tridymite, opal, flint or silicates like industrial glasses, partly crystallised volcanic lava, i.e. andesite, rocks like greywacke, rhyolite, etc. or rocks containing opal like opaline limestone. Some of the reactive materials, e.g. andesite may contain substantial amount of alkaline oxide which is released during reaction. All these reactive materials have some common characteristics. All of them contain SiO_2 as the major component and have either a disturbed or open structure, e.g. tridymite, industrial glasses, partly crystallised lava and/or very fine grained, e.g. opal, greywacke, some types of rhyolite, porous flint. Surfaces, both external and internal, of all siliceous materials are covered with silanol, $\equiv$Si–OH, groups.

2.2. Reaction environment

When embedded in a cement paste an alkaline pore liquid surrounds the aggregate particles. The composition of the pore liquid affects the rate and extent of alkali–silica reaction. It is of interest to follow the development of pore liquid composition with time [5]. Up to about 8 h, the pore liquid contains a mixture of Ca^{2+}, K^+, Na^+, OH^- and SO_4^{2-} ions. After that time the concentrations of Ca^{2+} and SO_4^{2-} drop quickly and those of alkali and hydroxyl ions increase sharply. "Thus the pore solution is converted essentially to a concentrated alkali hydroxide solution containing little more that a trace (ca. 0.001 N) of calcium ions and much lower concentrations of silica" [4]. In the absence of moisture ingress from outside, the final alkali hydroxide concentration reflects the alkali content of the cement and the cement content of the concrete. In a high alkali cement–sand mortar, the final alkali hydroxide concentration could be about 0.7 N. The interaction between aggregate particles and the pore liquid will be discussed shortly.

2.3. Composition of the reaction products

Earlier analyses of the reaction products showed them to be gels of alkali silicate hydrates with some $CaCO_3$. These gels were obtained from the surfaces of structures in advanced stages of damage. These reaction products at the surface are already altered by carbonation. The advent of electron probe micro analytical technique made it possible to analyse the reaction products in situ and at an early stage of reaction [5–7]. These workers showed that the reaction products are a lime–silica–alkali–water complex of variable composition. On the dry basis the alkali oxide content of the product could be up to about 20%, CaO content could up to about 20% and the rest is mainly SiO_2. This means there are active transport processes, which transport alkali oxide, CaO and water into the reactive grains.

3. Fundamental aspects of alkali–silica reaction

This section deals with the chemical process that transforms the reactants to the reaction products. In an alkaline solution the surface Si–OH groups on a siliceous mineral grain ionise according to the following Eq. (1):

$$\equiv \text{Si–OH} + \text{M}^+ + \text{OH}^- = \equiv \text{Si} - \text{O}^- \cdots \text{M}^+ + \text{H}_2\text{O} \quad (1)$$

The mineral grain acquires multiple negative surface charges. Only quartz and opal have been studied extensively although other silicate minerals are expected to follow a similar process. Surface charge density on silica or opal grains suspended in different types of electrolyte solutions of different concentrations and pH has been studied by many workers [8–11]. Bolt studied the charge development of solid silica particles over wide range of NaCl concentration and pH values up to 10 [8]. Results of other workers are in broad agreement with those of Bolt's. Fig. 1 shows Bolt's results. From Fig. 1 it can be seen that charge density increases with increasing pH and NaCl concentration, i.e. the ionic strength of the ambient solution. Fig. 1 also shows that in a high ionic strength solution silica acquires high surface charge at a lower pH. In a 4 N NaCl solution at pH 10, the charge density could be higher than −240 mC/M^2. Above pH 10 the solubility of silica increases sharply. Adding a soluble neutral salt like NaCl, $BaCl_2$, etc. or NaOH increases the ionic strength of the ambient solution.

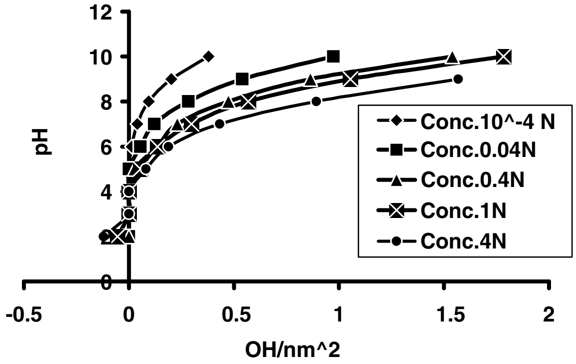

Fig. 1. Charge density on silica surface in different NaCl solution. Drawn after Bolt.

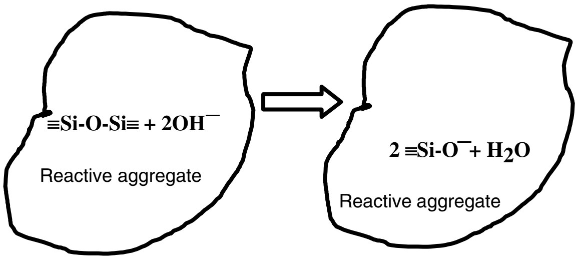

Fig. 2. Breakdown of internal Si–O–Si bonds due to the ingress of OH^- ions.

The negative charges were originally thought to reside only on the outer surface as ionised $\equiv$Si–O^- groups. However, in an alkaline solution of high ionic strength, ionising OH^- ions enter the grains to cleave and ionise the inner $\equiv$Si–O–Si$\equiv$ bonds [9]. Fig. 2 depicts the process. At constant pH and ionic strength, this penetration of OH^- ions decreases with increasing size of accompanying hydrated cation, i.e. decreases in the series K^+ to Na^+ to Li^+ and Ca^{2+} to Ba^{2+}. This lowering of OH^- penetration decreases the rate of reaction. In a mixed electrolyte environment, e.g. $Ca(OH)_2$ and NaCl both the cations penetrate the reactive grains. It appears that about half of the measured charge on reactive grains lies within the grains [12]. The last point is important for silicas with disordered, or metastable or porous structure. Very few, if any, of the inner $\equiv$Si–O–Si$\equiv$ bonds of quartz are cleaved. Note that in the process of cleaving of inner $\equiv$Si–O–Si$\equiv$ bonds external materials, e.g. hydrated cation, water and OH^- ions are pumped into the grains.

The cleavage of inner $\equiv$Si–O–Si$\equiv$ bonds opens up the reactive grains for further attack by OH^- ions and liberates some silica from their original sites. This liberation of silica assumes increasing importance at pH 10 or higher. In Ca^{2+} free solution, higher pH increases this liberation of silica. The liberated silica remains in solution and can diffuse out [13]. Diffusion of silica out of the reactive grains is mainly controlled by Ca^{2+} concentration of the ambient solution. High concentration of Ca^{2+} lowers diffusion of liberated silica. In solution of high OH^- concentration, i.e. high pH, the concentration of Ca^{2+} is depressed; liberation and diffusion of silica are increased.

From the above it can be seen that reactive aggregate grains continue to receive OH^-, Na^+, Ca^{2+}, and H_2O from an ambient solution of low alkalinity provided the ambient solution has high ionic strength and reserve sources of the ions are present. The reserve sources need not have to be in solution; the presence of a sparingly soluble salt like $Ca(OH)_2$ acts as the source of OH^- and Ca^{2+} ions. It is also obvious that for alkali–silica reaction to proceed the presence of alkali hydroxide is not necessary. An external source of alkali halide is all that is necessary.

4. Electrical double layer formation round reactive grains and the composition of the double layer solution

This section deals with the factors that determine the composition of alkali–silica reaction products. The pore solution of a high alkali Portland cement mortar or concrete has low calcium ion content (ca. 0.001 N Ca^{2+}). It is not obvious that this low calcium ion concentration is sufficient to explain about 20% CaO content of the alkali–silica reaction product. The following considerations clarify the situation. Due to the ionization of $\equiv$Si–OH groups on individual reactive grains, they acquire negative charges. These negative charges on individual grains are balanced by accumulation of excess positive ions round the individual grains, i.e. an electrical double layer forms round each reactive grain. The distribution of ion in the double layer is schematically shown in Fig. 3. Fig. 3 shows that within the double layer the concentration of positive ions exceeds that of negative ions. However, some negative ions are present even near the surface of a grain. If the ionic strength of the ambient solution is high then a fraction of OH^- ions from the near surface layer penetrates the grain. Fig. 3 also shows that the composition of the double layer solution, which is in contact with the grain, is different from that of the bulk solution.

The electrical potential created by a negatively charged reactive particle brings the positive ion in the double layer. This negative potential causes a preferential migration of divalent ions, i.e. Ca^{2+} in the double layer. In a Portland cement paste Ca^{2+}/M^+ ratio in the double layer could range from 2 to 100 depending on the alkali content of the cement and the ionic strength

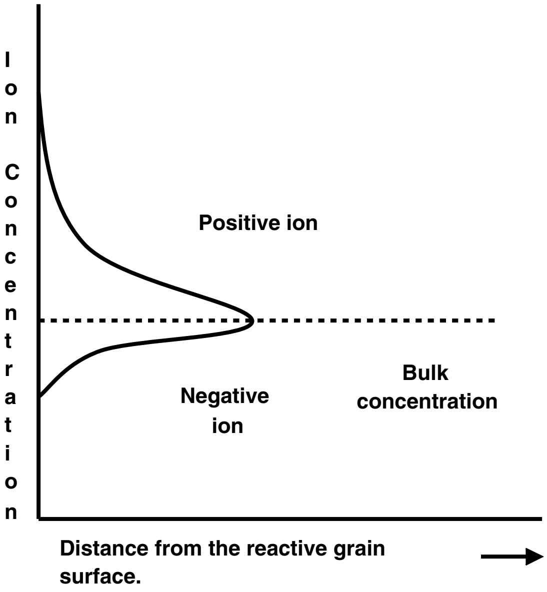

Fig. 3. A schematic representation of ion distribution round negatively charged silica grain.

of the pore solution [14]. At high Ca^{2+} or Ba^{2+} ion concentration Ca^{2+} or Ba^{2+} ion often bind chemically to negative surface sites and may even change local surface charge from negative to positive [15]. This charge decrease or reversal decreases the rate of alkali–silica reaction still further. The high concentration of Ca^{2+} ion in the double layer explains why the reaction products have high CaO contents.

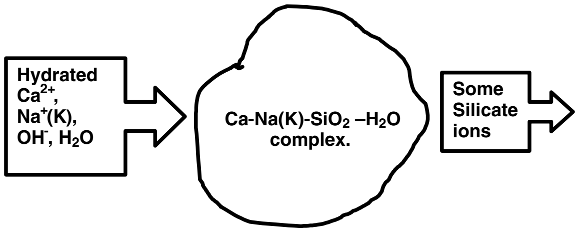

Fig. 4. Mechanism of pressure generation.

5. Important points of the above reaction mechanism

At this stage, it will be useful to recapitulate the main points of the reaction mechanism.

(a) In an alkaline medium, $\equiv$Si–OH groups on the surface of reactive particles ionise. The reactive particles acquire a negative charge density.
(b) The charge density of a particle increases with increasing pH and ionic strength of the ambient solution. This increase is due to surface adsorption and penetration of OH^- within the particle. This penetration of OH^- within the particle is determined by the size of the accompanying hydrated positive ions. The penetration decreases from K^+ to Na^+ to Li^+ and Ca^{2+} to Ba^{2+}. During this process materials, e.g. Na^+, Ca^{2+}, OH^- and water is pumped within the particle.
(c) Ionic strength of a solution can be increased by adding an "indifferent" electrolyte like NaCl to the ambient solution. An addition of NaOH also increases the ionic strength of solution. However, at pH 10 or higher solubility of silica is increased by NaOH addition. In the Portland cement–water system, NaOH decreases the concentration of Ca^{2+} in pore solution by the common ion effect.
(d) The penetration of OH^- within the particle is accompanied by a breakdown of inner $\equiv$Si–O–Si$\equiv$ bonds and liberation of some silica. The liberated silica can diffuse out of the particles. This diffusion of silica is hindered by Ca^{2+} ion.
(e) An electrical double layer forms round each negatively charged reactive particle. In Portland cement environment the double layer solution has higher Ca^{2+} concentration than the pore solution. The high Ca^{2+} concentration in the double layer explains the high CaO content in the reaction products.
(f) During alkali–silica reaction an explosive pressure is generated by the ingress of materials, Ca^{2+}, Na^+, OH^- and water from outside the particle, into the reactive grains. Dissolution and diffusion of silica oppose the pressure generation. The net expansive pressure is the sum of the above two processes. Fig. 4 schematically depicts the process of pressure generation. The pressure generation could be avoided either (i) by decreasing the ingress of materials from outside by decreasing the ionic strength of the pore solution or (ii) by increasing the dissolution and diffusion of silica by increasing OH^- ion concentration or (iii) by removing Ca^{2+} ion from the reaction environment by using high volume of a reactive pozzolan (even finely ground reactive aggregate) or high slag Blast furnace-slag cement. These react with $Ca(OH)_2$ of the paste and thereby reduce Ca^{2+} concentration in the pore solution. If free $Ca(OH)_2$ is completely removed from the cement paste by adding sufficient volume of finely divided reactive aggregate then expansion could be completely eliminated. In a concrete structure one has to be careful not to use a pozzolan of improper grading and reactivity. Small addition of an improper pozzolan to a concrete structure may increase expansion by enhancing ion diffusion from outside.

The required conditions for an explosive alkali–silica reaction are the simultaneous presence of reservoirs of Ca^{2+}, Na^+, OH^-, water and high ionic strength of the ambient solution. The presence of NaOH is not essential. Concentrated NaOH solution actually decreases the alkali–silica expansion.

6. Evaluation of testing methods for aggregates in view of above fundamental aspects

In the following different testing methods will be evaluated in the light of the above fundamental aspects.

6.1. Methods of direct evaluation of aggregates

6.1.1. Petrographic method

This method will not be discussed in this paper. A trained petrographer conversant with the local aggregates may identify reactive aggregates confidently and estimate quantitatively. His knowledge of the local aggregate may even enable him to suggest the acceptance limit of the reactive aggregate in the total aggregate content.

6.1.2. Chemical methods

All the chemical methods are carried out in solution so that shortage of soluble reactants at the reactive particles does not affect the result. Diffusion of ions is of less importance.

6.1.2.1. In this category, ASTM C 289 is the first [16]. This is a purely empirical method. In this method, 25 g of crushed and sieved sample is digested in 1 N NaOH at 80 °C for 24 h. After this period the amount of NaOH fixed in the grains and the amount of silica dissolved out are estimated. These values are plotted one against the other. Acceptance criterion was determined by comparing the service records of the tested aggregates. There are certain uncertainties. Calcium, magnesium and ferrous carbonates interfere with this method. Very fine-grained cocolithic limestone is rather troublesome. Further complication arises from the crushing of the aggregate. Some non-expansive silicates also react with 1 N NaOH at 80 °C. Intra-laboratory reproducibility of alkali fixation is about 12%. Any alkali containing reactive material like andesite will fix less alkali and may give misleading results.

6.1.2.2. The simple chemical method [17]. It is based on a fundamental consideration of the reaction mechanism of alkali–silica reaction. In this method 100 g aggregate, in its natural state, is digested at 70 °C in a suspension of $Ca(OH)_2$ in saturated KCl for 16 h. In the mixture the following reaction occurs

$$\begin{aligned}&\text{Reactive silica} + Ca^{2+} + 2OH^- + K^+ + Cl^- + H_2O\\&\quad\Rightarrow \text{Hydrated lime–alkali–silica complex} + Ca^{2+} + 2Cl^-\end{aligned} \tag{2}$$

The nascent $CaCl_2$ depresses the solubility of $Ca(OH)_2$ in solution. The difference in $Ca(OH)_2$ contents of the test mixture and a control mixture with a non-reactive quartz sand corresponds to the amount of K^+ that has entered in the hydrated lime–alkali–silica complex. The difference is determined by titrating the two solutions with HCl.

This proposed method has a number of advantages. The method is simple and does not need complicated instruments. It can be carried out in a quarry and result is obtained generally within 24 h. Since the OH^- concentration is low, it avoids many of the problems connected with 1 N NaOH solution, i.e. the result is not affected by the presence of calcium, magnesium or ferrous carbonates. The sample size could be adjusted depending up on the size of the aggregate. The method has been tested with Danish aggregates and an acceptance criterion has been suggested. Preliminary experiments show that the reactivity of samples of Japanese andesite, British Greywacke, Swedish porphyritic rhyolite, Norwegian mixed aggregate of rhyolite and quartzite and a silicified limestone aggregate from Belgium, France and Italy could be detected within 24 h. Some of the European aggregates have been tested under the auspices of a project funded by the European Community under the "Competitive and Sustainable Growth Programme" (Contract No. G6RD-CT-2001-00624 Acronym: "Partner" Title: "European Standard Tests to Prevent Alkali Reaction in Aggregates"). The above results indicate that a concrete sample made from any one of the above aggregates and a Portland cement with zero percent alkali content will expand if exposed to a marine environment. Another advantage of this method is that once an aggregate has been chosen its quality could be controlled quickly, regularly and cheaply. This method is not affected by the presence of divalent metal carbonates.

A note of caution: Andesite and aggregates containing andesite may contain up to about 4% Na_2O. During alkali–silica reaction, this alkali is liberated and is consumed to form the reaction products. In other words, the reaction, once started, becomes partly independent of any external alkali source. Since the simple chemical method depends on the utilization of alkali from an external source, it is also only partially successful. *It can detect the alkali–silica reactivity of this type of aggregates*. However, the grading of aggregates is vitiated by their varying andesite content in an aggregate and alkali content of andesite.

6.2. Indirect methods of aggregate evaluation

These methods depend on expansion measurement on mortar bars or concrete prisms made with a high alkali Portland cement. ASTM C227 is the prototype [18]. Recommended alkali content of cement is higher than 1% Na_2O equivalent. Some national test methods allow an addition of NaOH solution to raise the alkali content to a higher value. The test specimens are cured for 24 h in their moulds. After demoulding the specimens are stored in containers maintained at 100% RH at 38 °C. Care is taken such that the specimens are never in contact with liquid water. The lengths of the specimens are measured at regular intervals.

This type of testing has certain drawbacks.

(i) It is known that mortar or concrete specimens undergo self-desiccation during cement hydration. The transport of water vapour from a reservoir to a specimen is a very slow process and as a result, specimens become internally unsaturated. This unsaturation slows down the rate of alkali–silica reaction firstly by reducing the necessary water flow to the reactive grains and secondly by restricting the diffusion of ionic reactants to the reactive grains. This internal unsaturation is one of the reasons why a mass structure takes a long time to show signs of alkali–silica distress.

(ii) Other conditions remaining unaltered a high specific surface cement Portland cement causes a higher degree of unsaturation. This means that the rate of expansion becomes cement dependent.

(iii) The ionic strength of the pore solution in a high alkali Portland cement mortar or concrete is about 1 N NaOH. From Fig. 1 it can be seen that this ionic strength is not the optimum for aggregate testing. For a maximum acceleration of alkali–silica reaction, it will be preferable to elevate the ionic strength of the pore solution without increasing OH^- ion concentration.

(iv) 1 N alkali hydroxide concentration depress Ca^{2+} ion concentration in pore solution especially at temperatures above 40 °C. This depression is particularly effective when NaOH is added to the cement. This lowering of Ca^{2+} concentration enhances the rate of silica diffusion and thereby decreases the expansive pressure. It is obvious that the part of silica that has diffused out of the reactive grains does not contribute to expansion. For the maximum acceleration of alkali–silica reaction, it will be preferable to use a combination of a low alkali cement and high ionic strength pore solution (see also Section 6.2.3).

It is now possible to discuss different test methods critically.

6.2.1. *ASTM C 227 (and its derivatives) was designed to simulate the conditions of inside of mass concrete structures suffering from alkali–silica distress*

The ionic strength of the pore solution and its composition are not optimised for the detection of alkali–silica reactivity of aggregate. Furthermore, a concrete prism test should strictly specify the size of the prism, cement type and its specific surface and the water/cement ratio otherwise the unsaturated part will be higher in larger specimens than in smaller specimens [19]. The rate of expansion will be lower in larger specimens than in small specimens.

6.2.2. *Saturated NaCl bath method*

In this method, three mortar prisms are first water cured for 27 days. After that, they are stored in a saturated NaCl solution bath at 50 °C. The size of the prisms is fixed at 40 × 40 × 160 mm. Sand/cement ratio is fixed at 3 and the water/cement ratio of the mortar is fixed at 0.5 [20]. The expansions of the prisms are measured at regular intervals. The ionic strength is thus optimised for the detection of alkali–silica reactivity of the aggregates. The prisms are stored under solution so the problem of unsaturation is also reduced. If low alkali cement is used to make the mortar then OH^- ion concentration in the pore solution will also be optimum. In Denmark, a low alkali-sulphate-resistant Portland cement is recommended for this test. An advantage of this method is that sand is used as received. This method was introduced to test reactive sand. Only limited amount of research has been carried out with concrete samples. It is obvious that concrete prisms will take longer time to show expansion. Since introduction of this testing method in Denmark, no new structure has developed alkali–silica reaction and distress.

Elevation of alkali level by adding NaOH to a cement-aggregate mix will not necessarily identify reactive aggregates. The results of such tests may give a false assurance especially if the intended structure is exposed to a marine environment. Taguchi's results show this aspect very clearly [21,22]. Taguchi studied 11 Japanese sand samples for their alkali–silica expansivity using both the Japanese Industrial Standard (JIS) and NaCl bath methods. In the Japanese Industrial Standard method the alkali content of the cement is adjusted to 1.2% by adding required amount of 1 N NaOH to mixing water. Table 1 shows Taguchi's results.

Prisms made with six sand samples, i.e. 2–5 to 2–10 were first tested with JIS method and then exposed to the saturated NaCl bath. Sand samples 2–3 to 2–11 passed the JIS requirement of non-expansive sands. Only 2–14 failed the JIS requirement. However, the third and fourth columns of Table 1 show that samples 2–3 to 2–11 are reactive to the extent that the prisms were further expanded and cracked. One has to be careful in interpreting the test results where alkali level is elevated by adding NaOH solution to the mixing water. Table 1 also illustrates the importance of the environmental conditions. Aggregates 2–3 to 2–11 are safe to use in normal constructions but not in constructions exposed to marine environment.

6.2.3. *Ultra accelerated test methods*

These include ASTM C1260 [23], and CSA A23.2–5A. These methods are based on the South African NBRI/CSIR method In these methods 25 × 25 × 250 mm mortar specimens of specified mix design and fixed water/cement ratio of 0.5 are exposed to 1 N NaOH solution at 80 °C. Lengths of the prisms are measured at intervals. The suggested acceptance criterion is 0.1% expansion at 14 day exposure.

It is expected that in the operating conditions of high temperature and high NaOH concentration, the concentration of Ca^{2+} will be low in the pore solution and the solubility and diffusion of silica will be high. These will reduce the expansion of the prisms. The solubility and diffusion are so high that " varying amount of a colourless gel appeared in the storage solutions during the test, indicating that a chemical reaction was occurring rather than expansion..." [24]. It is highly probable that the colourless gel is silica gel. This means that reactive silica has dissolved in hot 1 N NaOH and has migrated out of the specimen and did not take part in expansion. There are some indications that highly reactive, porous aggregates may lose more silica in hot 1 N NaOH than non-porous reactive aggregates. This may give rise to misleading results. It is not known if divalent metal carbonates affect the expansion or not. In somewhat similar operating conditions of ASTM Quick Chemical Tests [16] the presence of divalent metal carbonates affects the evaluation of aggregate reactivity.

Verbeck and Gramlich have earlier reported migration of considerable quantities of sodium silicate through cement paste in their osmotic cell experiments [25]. Verbeck and Gramlich used 0.75 N NaOH at room temperature in their experiments. One would expect that with higher NaOH concentration and high temperature this migration of sodium silicate would be more pronounced. The enhanced sodium silicate migration at higher NaOH concentration may explain Vivian's observation that alkali–silica expansion reaches a peak at NaOH addition of about 1%; further NaOH addition reduces the expansion sharply [26].

7. Conclusion

Alkali–silica reactivity of an aggregate is best evaluated in a solution of moderate OH^- ion concentration and high ionic strength. The solution should also contain a reservoir of $Ca(OH)_2$. Based on these requirements a simple chemical test method has been proposed to test directly the alkali–silica reactivity of aggregate themselves. This simple method is very fast and can also be used to control the quality of a chosen aggregate on a daily basis.

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