

Analysis of interaction of silica and alkalis in concrete

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In alkali solutions of hydroxides of alkali metals Na and K silica form silicates, as its depolymerization proceeds deeper and fuller. The quantity of soluble silica formed as a result of SiO₂ depolymerization and dissolution as well as subsequent processes are limited on the one hand by alkali concentration and on the other by the amount of reactive silica in concrete aggregates. In hydrolysis and hydration of Portland cement dissolution of alkalis present in it proceeds very rapidly, and in the liquid phase the above mentioned high pH value is established.

Now let us consider the question of the amount of silica that can participate in reaction with alkalis.

Solid silica particles in aggregate grains are in contact with alkali solutions on the total surface S of SiO₂ (cm²) solid phase.

SiO₂ depolymerization and dissolution result in degradation of a silica grain down to the depth δ (cm).

Assuming the specific mass (density) of silica γ = 2.2 (g/cm³) and activity coefficient of this silica modification equal to f one can put down that reacting volume in the given aggregate Q will be

$$Q_{SiO_2} = S_{tot} \delta \gamma f$$

In calculations it is more convenient to assume as an activity value f the relative activity of a silica available in the aggregate with respect to its well known modification, for example, to opal. Then value f will characterize relative activity of the given aggregate expressed in fractions of unity.

Taking into account that the greatest role in subsequent destructive processes is played by silica on the developed surface of the aggregate sand fraction grains, its surface size can be calculated as follows.

The mean surface of one grain with diameter d is S = π d² (cm²) the weight g of one grain is

$$2.2 \frac{\pi d^3}{6}$$

The grain number n of mean diameter d in the weight unit is:

$$n = \frac{1}{g} = \frac{1 \times 6}{2.2 \pi d^3}$$

Then the total surface S_{tot} will be

$$S_{tot} = \Sigma (s n) \text{ (cm}^2\text{)}$$

The depth (δ) of silica depolymerization and dissolution layer varies in a wide range depending on the structure and activity of aggregate silica and time.

Proceeding from conditions of obtaining the maximum of depolymerization products at a certain place - near the aggregate grain (without complete grain destruction) one can assume that the minimum diameter of the reactive aggregate grain for the given calculation can be $d_{\min} \geq 3 \delta$; this conditionally corresponds to retaining SiO_2 solid phase at the place of reaction. Further, if we assume on the basis of a number of papers the value $\delta = 0.02-0.04$ mm, the minimum value d_{\min} appears to be in the order of less than 1 mm.

According to a number of research data considerable strains were observed at d in the order of 0.2-2 mm. At lower values of grain diameters in this aggregate the reactive silica will be more uniformly distributed within the concrete, and being dissolved more rapidly and to a fuller extent will not cause formation of local stress state and concrete degradation points. Moreover, one can hold it proved that in the presence in concrete of fine-ground active silica it is possible to prevent appearance of internal stresses hazardous for concrete - at corrosion centers.

Let us further write down the main conditions for the formation of an expanding complex of stress state centers as a result of development of the depolymerization process and formation of soluble silicates under effects of alkali solutions in concrete on solid silica in concrete aggregates.

Alkali solutions in concrete are formed, as has been shown above, at the earliest stages of cement clinker grain hydrolysis and are retained in the liquid phase. Only their concentration varies with consumption of water added to the concrete mix to form cement stone hydrates.

Under effects of alkali solutions, as has been shown above, gradual layer-by-layer hydration takes place with subsequent silica depolymerization. SiO_2 passes into the solution to form molecular solutions in a quantitatively lesser extent and colloidal solutions on a quantitatively greater extent.

Internal stresses are caused by the increase in the volume at places of $\text{SiO}_2\text{-Na}_2\text{O}$ interaction when viscous colloidal solutions are formed. The greater the amount of such products, the more the probability of appearance of these stresses.

Increase in the volume of $\text{SiO}_2\text{-R}_2\text{O}$ interaction products is proportional to water absorption by depolymerized silica per unit volume of SiO_2 polymer, i.e.

$$\alpha = \frac{m - m_0}{m_0}, \text{ where}$$

α - swelling coefficient;

m_0 - polymer mass before swelling;

m - polymer mass after swelling.

If swelling occurs in a confined volume, there appears pressure similar by its nature to osmotic pressure.

Now calculate the quantity of silica and alkali participating in formation of the expanding complex.

Concrete composition of the total volume V_0 (in mixing) consists of the volumes of cement, sand, coarse aggregate, water in the dense state. Besides, the concrete contains a certain amount of air.

$$V_0 = V_{\text{cem}} + V_{\text{sand}} + V_{\text{c.agg.}} + V_{\text{water}} + V_{\text{air}}$$

Dividing the both parts of the equality by V_0 we obtain the concrete composition expressed in fractions of unity.

$$\frac{V_{\text{cem}}}{V_o} + \frac{V_{\text{sand}}}{V_o} + \frac{V_{\text{c.agg.}}}{V_o} + \frac{V_{\text{water}}}{V_o} + \frac{V_{\text{air}}}{V_o} = 1$$

The concrete expansion degree in the reaction of alkalis with silica is mostly affected by reactive silica contained in sand that has the largest total surface of interaction with alkali solutions. The total reacting surface of silica in the coarse aggregate is much less and, consequently, its role in expansion is smaller. This has been proved by numerous studies. In addition, the studies of H E Vivian, T Stanton, etc. have established that maximum expansion of concrete can be expected at the content of reactive aggregate (opal) in sand in the quantity of 1% to 10%.

In the general form it can be written that the total content of opal in sand (V_{op}) per unit volume of concrete at certain percentage of opal is

$$V_{op} = V_{\text{sand}} \frac{p}{100}, \text{ where}$$

V_{sand} - volume of sand per unit volume of concrete;

p - percentage of opal in sand.

The total of sand (opal) grains per unit volume of sand is

$$S_{\text{tot}} = S_{\text{dav}} \times n_1, \text{ where}$$

S_{dav} - surface of one grain of the average diameter

$$d_{\text{av}} S_{\text{dav}} = \pi \frac{d^2}{4};$$

n_1 - number of grains with diameter d_{av} per unit volume of opal

The number of grains n_1 in this formula is

$$n_1 = \frac{V_{\text{sand}} p}{100 V_{\text{dav}}}, \text{ where}$$

V_{dav} - volume of one opal grain (before its interaction with alkalis)

$$V_{\text{dav}} = \frac{\pi d^3}{6};$$

$$S_{\text{tot}} = S_{\text{dav}} n_1 = \frac{\pi d^2_{\text{av}} V_{\text{sand}} p}{100 \frac{\pi d^3_{\text{av}}}{6}} = \frac{6 V_{\text{sand}} p}{100 d_{\text{av}}} \text{ (cm}^2\text{)}$$

The reacted volume (V_1) of opal contained in sand in the form of grains of d_{av} diameter is approximately equal to

$$V_1 = S_{\text{tot}} \delta = \frac{6 V_{\text{sand}} p}{100 d_{\text{av}}} \delta \text{ (cm}^3\text{)}, \text{ where}$$

δ - thickness of depolymerized opal layer

A similar formula could be written more accurately by taking instead of d_{av} equal to the grain diameter before the reaction, the value d equal to:

$$d = \frac{d_{\text{av}} + d_1}{2}, \text{ where}$$

d_1 - particle diameter minus the reacted layer thickness δ , but some inaccuracy can be neglected here taking into account non-uniformity of the sand grain shape.

The weight of the silica depolymerized layer (per unit volume of concrete) participating in the interaction reaction and with consideration of activity of reactive aggregate is

$$Q [\text{SiO}_2] = S_{\text{tot}} \delta f 2.2 = \frac{13.2 V_{\text{sand}} p \delta}{100 d_{\text{av}}} \text{ (kg)}$$

where 2.2 - specific mass (density) of opal.

The weight quantity of alkalis contained in cement and participating in interaction with indicated amount of silica is

$$Q [\text{R}_2\text{O}] = \frac{V_{\text{cem}} \gamma_{\text{cem}} a}{100} \text{ (kg)}, \text{ where}$$

$V_{\text{cem}} \gamma_{\text{cem}}$ - cement content by weight per unit volume of concrete;

$\frac{a}{100}$ - per cent content of alkalis in cement

Then the above indicated principal condition of concrete expansion appearance can be written as follows:

$$K = \frac{Q [\text{SiO}_2]}{Q [\text{R}_2\text{O}]} = \frac{13.2 V_{\text{sand}} p \delta f}{100 d_{\text{av}}} : \frac{V_{\text{cem}} \gamma_{\text{cem}} a}{100} = \frac{13.2 V_{\text{sand}} p \delta f}{V_{\text{cem}} \gamma_{\text{cem}} a d_{\text{av}}}$$

The minimum value of this criterion K is indicative of those conditions when readily soluble sodium ortho- and metasilicates are formed, while K_1 is equal or less than 2. The maximum value of this condition, i.e. $K_2 \geq 4$ when colloidal solutions of silicates of rather high viscosity are formed. The quantity of alkalis contained in the unit volume of cement as has been shown above is

$$\frac{V_{\text{cem}} \gamma_{\text{cem}} a}{100}$$

Hence the quantity of opal can be calculated with observance of the first condition (K_1), i.e.

$$\frac{V_{\text{cem}} \gamma_{\text{cem}} a}{100} = \frac{13.2 V_{\text{sand}} p \delta f}{100 d_{\text{av}} K_1}$$

$$\frac{p}{100} = K_1 \frac{V_{\text{cem}} \gamma_{\text{cem}} a d_{\text{av}}}{13.2 V_{\text{sand}} \delta f}$$

With this amount of alkalis, presence of opal in sand and the value of criterion $K \geq 2$ the conditions for hazardous concrete expansion would not take place. At the value of criterion on $K \geq 4$ the conditions for hazardous expansion of concrete would not take place either.

A hazardous situation due to the above reasons occurs only in cases when the criterion value will be in the range from $K=2$ to $K=4$.

In this way one can also solve a problem on allowable content of alkalis in cement if the content of reactive rock in sand is known:

$$\frac{a}{100} = \frac{13.2 V_{\text{sand}} p \delta f}{100 V_{\text{cem}} \gamma_{\text{cem}} d_{\text{av}} K}$$

The maximum allowable value of alkali content in cement is obtained at $K = K_1 = 2$, i.e. at the minimum value of criterion K , while the minimum allowable value - at $K = K_2 = 4$, respectively.

Conclusions

The analysis of the above formulas for criterion K shows that there are two ways to either reduce the size or even eliminate possibility of the formation of expanding complex centers in the concrete.

The first way is introduction into a concrete mix of fine-ground additive of reactive silica (for example, opal) - with a large reacting surface obtained by fine milling.

With such an additive the amount of which can be calculated using the same formulas, the value of criterion K can be increased up to the values higher than 4 thereby virtually eliminating the hazard of an expanding complex formation.

This method described here for the first time has already been used in practice. The formulas presented make it possible to calculate the required amount of fine-ground silica introduced into the mix.

The second way is introduction into the concrete of a certain amount of alkali to reduce value K down to the value less than 2.

The resulting solutions of sodium and potassium metasilicate and orthosilicate being mainly molecular solutions of low viscosity are relatively easily moved in the capillary-porous structure of concrete causing no internal local stresses in the latter.

In both cases a possibility of emergence in concrete of hazardous internal stresses due to the increase in the system volume under depolymerization of silica in reactive aggregates is diminished (or even completely eliminated).