

On the Alkali Content of Cement in AAR

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ABSTRACT

This paper discusses methods for the control of the alkali content of cement in AAR based upon the reaction, product, the type, grain size and content of reactive aggregate and the cement content of concrete. The problems have been theoretically analyzed and several important deductions have been made.

1. Introduction

Because most of the alkali in concrete comes from the cement, the alkali content of the cement is very important in controlling deterioration due to AAR. Problems relating to the control of alkalis are discussed in this paper.

2. Control of the alkali content of cement

2.1 Products in AAR

In early period when the problem on AAR was put forward, most people considered that the product in AAR, which causes failure of concrete, is the alkali-silica gel. Powers (1955) considered that alkali-silica gels were expanding types but that the alkali-calcium-silica gels were not. Diamond (1983) summarizing "energy-dispersive x-ray and electron probe analysis of expanding gels by various workers showed the universal presence of calcium as well as of alkali in these materials".

This means that the products of AAR are all alkali-calcium-silicon complexes. From the analyses presented by Poole (1983), the author calculated the following composition of silica gel: $(0.184-0.709) \text{Na}_2\text{O} \cdot (0.454-1.545) \text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. From probe analyses reported by Oberholster (1983) the author calculated the composition of gel from cores from 5 buildings as follows: $(0.056-0.126) \text{Na}_2\text{O} \cdot (0.161-0.275) \text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. The differences in the above mole ratios indicate that composition of the gel varies with the conditions of reaction which also effect the expanding properties of the gels.

It was known that the alkali-silica complex is a type of expanding gel, but the calcium-silica complex is a nonexpanding gel. Therefore, when the $\text{CaO}/\text{Na}_2\text{O}$ ratio is reduced to certain value, the complex will become expanding gel. Conversely, the complex becomes nonexpanding gel when the ratio is increased to a certain value.

It should be pointed that alkali ions in the liquid phase go into silica when the alkali-silica complex is formed. At the same time, if the calc-

ium ions are abundant, an alkali-calcium-silica complex is formed. Thus the $\text{CaO}/\text{Na}_2\text{O}$ ratio of the complex depends on the concentration of calcium ions in the liquid phase.

Fig. 1 (5) shows that the solubility of calcium hydroxide decreases with the increasing concentration of alkali metal hydroxide. When the alkali content decreases below a critical value, the AAR products will no longer depend on reactive aggregate and the content of cement. The resulting products are all nonexpanding gels with higher $\text{CaO}/\text{Na}_2\text{O}$ ratio and the critical alkali content is called the absolute safety content of alkali.

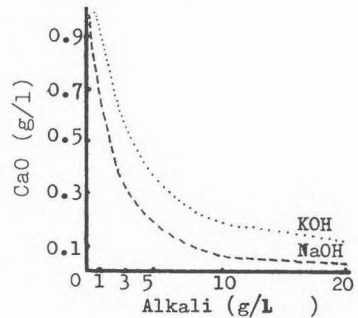


Fig. 1 Solubility of CaO

The critical value of the alkali content of low alkali cement is usually considered to be 0.6%, however, the validity of this concept requires further study. Experience over nearly half a century has shown that the 0.6% value is generally, but not always effective in preventing damage due to AAR.

The author considers that the critical value of the alkali content of low alkali cement should be determined according to the relationship between the alkali content of cement and the $\text{CaO}/\text{Na}_2\text{O}$ ratio of AAR product especially of the non-expanding gel.

2.2 Reactive Aggregate

Generally speaking, the alkali content of cement is always higher than the absolute safety content of alkali. So we call the content of alkali which should not cause dangerous AAR the "Safe content of alkali". Obviously the "safe clean content of alkali" is affected by many factors. The reactivity of SiO_2 is due to non-saturated Si-O bonds. In general SiO_2 is an ordered crystal e.g. quartz with saturated Si-O bonds except for some microamount of non-saturated Si-O bonds on the surface. The opal is disordered crystal. It possesses very high reactivity because of wide spread non-saturated Si-O bonds.

Although the number of non-saturated Si-O bonds existing on the surface of ordered crystalline silica is a small, it increases as the grain size decreases or the specific surface area increases. Grains can become reactive when the grain is smaller than a certain size. Both the gray-white chert and the black chert are reactive. The reactivities S_0 for opal, gray-white chert and black chert are 984.0, 776.0 and 86.8 millimoles per litre respectively.

From the above description and from the results of our experiments, the relationship between the safe alkali content of cement and reactivity of the aggregate can be discussed as follows:

It must be pointed out that alkali not only can combine with non-saturated Si-O in silica to form expanding Na_2SiO_3 gel, but also can break the saturated Si-O bonds in silica to form the same gel if the concentration is high enough. In the reaction between alkali and cryptocrystalline silica the alkali function of cutting Si-O bonds and of dispersing silica, would probably play an important role. As a consequence, the higher the reactivity of aggregate, the lower the alkali content of cement which may cause dangerous AAR.

Fig.2 (Obtained with mortar bar tests) shows that the critical safe content of alkali exists for all types of the reactive aggregate. The critical value does not vary with the content of reactive aggregate but increases as the reactivity becomes lower. For example: the critical values for opal, gray-white chert and black chert are 0.6%, 1.0% and 1.2% respectively.

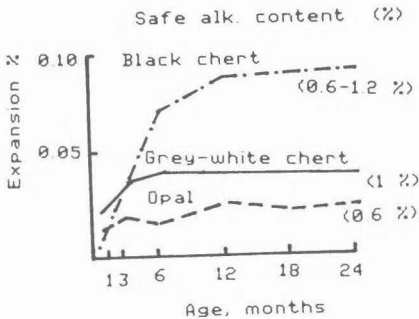


Fig 2 max expansion with 20% reactive aggregate

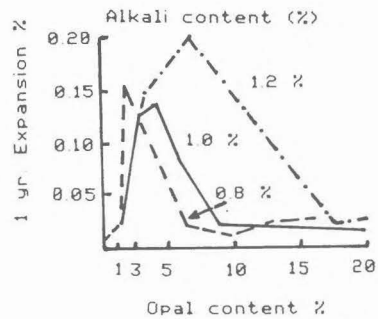


Fig 3. Expansion with opal

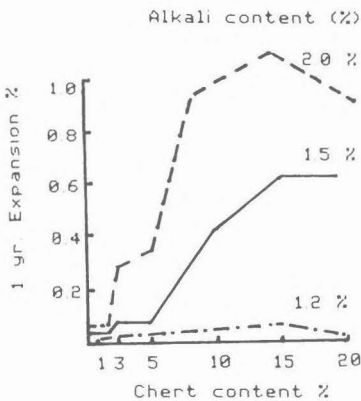


Fig 4. Expansion with grey white chert.

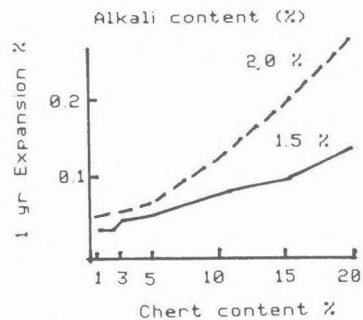


Fig 5. Expansion with black chert

Fig. 2,3,4,5, (Obtained with mortar bar tests) show that the lower limit of dangerous alkali content which can cause harmful AAR decreases as the reactivity of aggregate increases (Expansion greater than 0.1% at one year is taken to indicate a deleterious reaction). On the other hand, for example, the dangerous lower limit value of alkali content in cement is 1.2-1.5%, 1.0-1.2% and 0.6-0.8% corresponding to black chert, gray-white chert and opal respectively.

Fig.3 also shows that when dangerous alkali content reaches a certain value, the content of opal will cause dangerous AAR only within a certain range, beyond this range, all the AAR are safe.

Referring to Fig.4 and Fig.5, it may be seen that the lower limit as well as the upper limit of the dangerous content of reactive aggregate increases as the reactivity of aggregate decreases (Obviously, the upper limits of the dangerous content of the two kinds of chert are both above 20%).

The reason why the reactive aggregate does not cause dangerous AAR when its content is too high or too low may be explained as follows. When the reactive aggregate content is too high, the ratio of alkali to silica in a reaction product is too small, and the ratio of calcium to alkali too large, so the reaction product will be a non-expanding gel. When the reactive aggregate content is too low, at first, the reaction product will not be abundant enough to cause harmful expansion and that the highly fluid products produced owing to the high ratio of alkali to silica may flow into the surrounding pores, so the expanding pressure can be greatly reduced. Although the smaller the grain size of the reactive aggregate, the higher its reactivity, it does not necessarily cause dangerous reaction. It was discovered by Stanton (1940) that when the content of the powdered reactive aggregate such as powdered opal is about ten times that of the reactive aggregate of normal grain size the dangerous AAR can not be caused but is inhibited. This is due to the probability of alkali being absorbed by powdered opal being countlessly larger than that of alkali being absorbed by bigger reactive aggregate grains, with the result that the alkali is soon consumed by the powdered opal.

2.3 The Cement Content

It should be pointed that alkali content in concrete is largely derived from cement and depends not only upon the alkali content of cement but also on the cement content of the concrete. The expansion of mortar bars increases as the cement content increases. When the cement content is increased to a certain value, the original non-dangerous AAR may cause harmful expansion even if the cement is of low-alkali content. For example, the alkali content of cement is only 0.43% but the alkali content in concrete can be doubled if the cement content is increased from 300 kg/m³ to 600kg/m³. As a result, the expansion increases from 0.13% to 1.13%. This example can best explain the importance of cement content in determining the safe alkali content of cement.

It was reported that controlling the alkali content of concrete works well in preventing expansion, so the use of 3 kg alkali/m³ concrete as the critical alkali content was proposed, however the author is not sure that this value is always appropriate.

3. Conclusions

- (1) Cement possesses an absolute safe alkali content which increases as the reactivity of aggregate decreases. Below this critical value, dangerous AAR cannot occur.
- (2) The safe alkali content of cement depends upon the type, the grain size and the quantity of reactive aggregate as well as the content of cement. In order to determine the safe alkali content of cement, it is necessary to make special analysis.
- (3) If the alkali content of cement and the cement content are all fixed, the dangerous AAR can occur only when the content of reactive aggregate is within a certain range. The higher the reactivity of aggregate is, the lower the limitations are. Conversely the lower the reactivity is, the higher the limitations are.

(4) The smaller the grain size of reactive aggregate, the higher the reactivity. When the grain is big enough the dangerous AAR wouldn't occur if other conditions are fixed. When the grain of reactive aggregate is very fine e.g. less than 0.15 mm, effective inhibiting action occurs.

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