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Limiting Alkali Content in Blended Cement – A Review

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***Abstract* -- The role of blended cements in concrete/mortar etc. to combat alkali silica reaction is very well known. Blended cement is obtained by mixing OPC with mineral admixtures or additives like fly ash, slag or silica fumes and are now being considered superior as compared to conventional OPC category of cements. In India, large amount of flyash is being generated by the various thermal power plants and its storage, disposal and the consequent environmental problems associated with it, is posing a great challenge to one and all. Partial replacement of cement with flyash not only saves the valuable and depleting resources of limestone for the manufacture of cement in the country, but also serves to bring down the cost of concrete production. Flyash with a high pozzolanic activity has the capacity of preventing alkali silica reaction with particular reference to strained quartz in concrete structures. The reaction between silicious glass in blended cements and the alkali hydroxides in Portland cement paste consumes alkalis, thus reducing its availability for expansion reaction with reactive silica in aggregates. It is also well known that not all the alkalis present in the blended is available for the reaction. Hence, it becomes necessary to determine available alkali content and not the total alkali content in flyash or silica fume, which, hitherto, is being carried out in cement. Similarly in slag cement the total alkali content is not considered. The present paper discusses the various approaches, viz. BRE Publication, ACI, BIS, ICOLD etc. for limiting alkali content in concrete with particular reference to contribution from flyash, slag and silica fume.**

I. INTRODUCTION

Flyash from coal burning power plants, silica fume from ferrosilicon industry or the slag from metal industry is used in concrete primarily because of their pozolanic and cementitious properties. These properties contribute to strength gain and improved durability when used with Portland cement[1,2]. Other principle reasons for using blended cement include economy and beneficial modification of certain properties of fresh and hardened cement concrete. The use of adequate amount of flyash/ silica fume or slag can reduce the amount of alkali aggregate reaction and thus reduce the harmful expansion of the concrete.

Alkalis in cementitious materials play an active role in determining the rate at which calcium silicates react with water, which affects significantly both the hydration reaction rate and development of mechanical strength of cements.

Portland cements having more than 0.6% alkali (eq. as Na_2O) are generally vulnerable to attack by aggregates containing reactive amorphous as well as crystalline silica. Alkali silica reaction involves a reaction between hydroxyl (OH^-) ions normally associated with (Na_2O & K_2O) in the cement paste and certain reactive silica minerals present in the coarse or fine aggregate.

The interaction among the alkalis in the cement and the cementitious materials on the one hand and reactive silica in the concrete aggregates on the other and the efficient use of flyash/silica fume/slag in reducing AAR damage in concrete is the subject of study by the research workers world over. The deleterious expansion due to the alkali silica reaction could be reduced using flyash/silica fume/slag or containing silicious materials. If the alkalis are in excess in concrete mix and the aggregate has amorphous or reactive silica component, a swelling gel is formed, which results in expansion, cracking, exudation of gel and finally progressive deterioration of the structure. Hence, it has become mandatory to limit the alkalis in concrete ingredients in order to prevent the alkali silica reaction. In this paper, various approaches of limiting alkali content in flyash has been discussed.

II. ALKALI CONTENT AND ASR

The alkali aggregate reaction was first recognized more than 90 years ago. To minimize alkali aggregate expansion to acceptable limits, the following criteria should be considered.

1. The use of non reactive aggregate
2. The use of cement with less than 0.6% Na_2O eq. total alkali content and
3. Use of pozzolanas to replace a portion of the cement when both high alkali cement and reactive aggregate are used.

The first option though of high utility value, is sometimes out of control of the user in case the nearby quarry sites for aggregates are identified as "reactive" and bringing non-reactive aggregates from far off sites is uneconomical. The third option, the use of pozzollans has become the most suitable material mainly because of its wide spread availability.

However, the beneficial effect of flyash in reducing the damage due to AAR depends on both intrinsic and extrinsic characteristics such as the chemical composition of the fly ash and the amount of the cement being replaced.

The use of Portland cement with an alkali content of 0.6% Na_2O eq. or less, is acceptable worldwide as the best means of minimizing the risk of damage due to alkali silica reaction. Mineral admixtures i.e. natural pozollana, flyash and granulated blast furnace slag have been used successfully to control the expansion due to alkali aggregate reaction. The flyash have comparatively high total alkali level but most of this alkali is combined in the glassy structure of flyash and released relatively slowly as the flyash hydrates in the concrete. The alkalies derived from this source do not appear to be available to promote the alkali silica reaction in the manner as the alkalies derived from portland cement. The alkalies present in the flyash are less susceptible to reactive aggregate due to their limited solubility in water and being in combined form unlike the free and water soluble alkalies of portland cement.

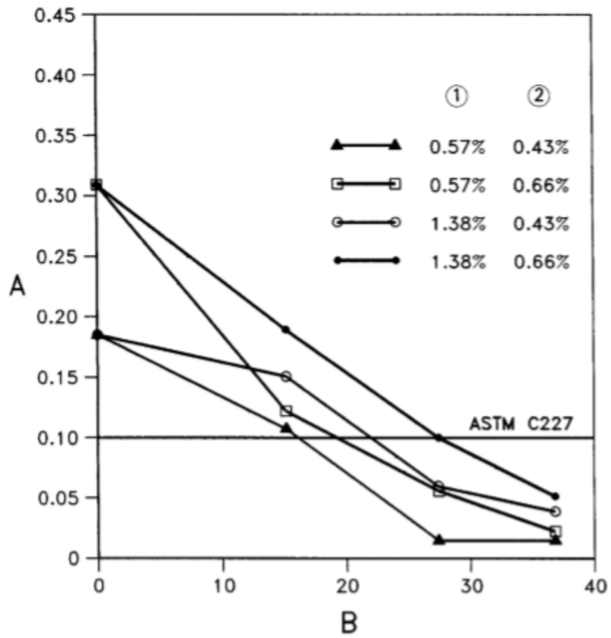
Moreover, the inhibiting mechanism of flyash in alkali silica reaction is well cited in the literature. It states that the reaction between the silicious glass in flyash and the alkali hydroxides in the portland cement paste consumes alkali, which reduces their availability for expansion reactions with reactive silica aggregates. Therefore, unconsumed or the excess alkalies in concrete mix is only available for alkali aggregate reactions, if any. According to an school of thought, the expansion potential is a function of the reactivity of the aggregate and of the total quantity of reactive alkalies available per cubic meter of concrete.

The safe level of reactive alkalies available in the concrete must be determined experimentally for each combination of aggregate and cementitious material.

III. Available Alkalies In Flyash And Silica Fume

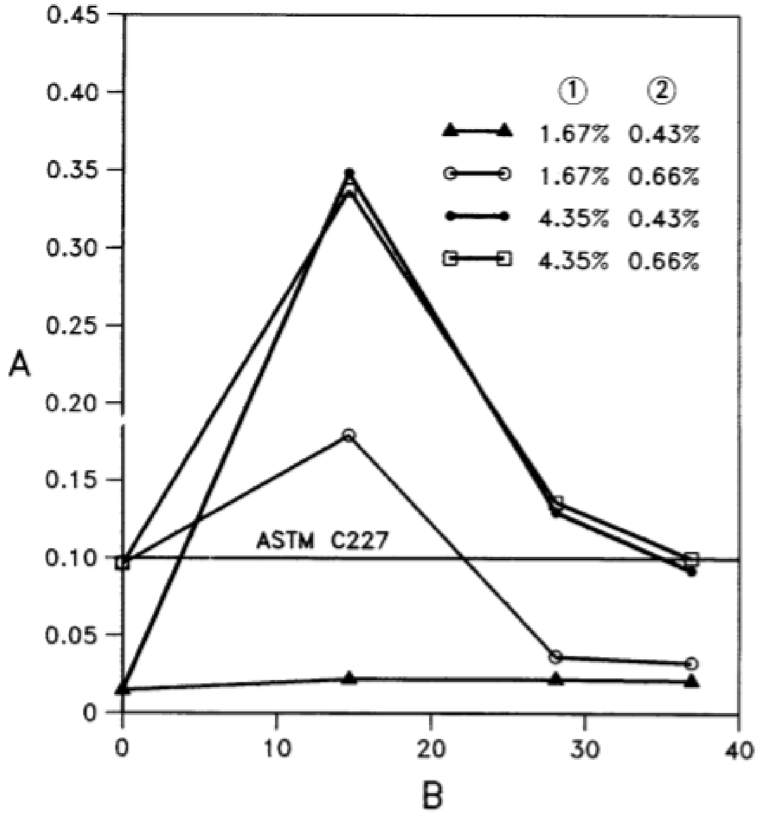
The quantity of alkalies in flyash or silica fume[3] is usually high but limit on their alkali content is expressed in different way in codes and practices, ASTM 618-89 prescribes an available alkali content of 1.5% as Na_2O eq. Available alkalies refer to the amount of alkalies that are released after curing with calcium hydroxide for 28 days at temperature $38^oC\pm2$, according to ASTM C 311-88 procedures. The proportion of the total alkalies that become water soluble when the flyash/silica fume is mixed with lime and water is dependent on temperature and the duration of storage. Flyash with an available alkali content is less than 1.5% showed in increasing beneficial effect with increase in the amount of the cement replaced when mortar bar expansion are conducted. Results of such study are indicated in International Commission on Large Dams Bulletin[4] No. 79 (See Fig. 1). On the other hand, flyash with an available alkali content greater than 1.5% needed a minimum percentage of cement replaced to be effective: small additions of this flyash had caused larger expansion than that of mixture without flyash (Fig. 2).

Accordingly, when using flyash to prevent unacceptable damage in concrete due to alkali aggregate reaction, it is necessary to look at both alkali content of the cement and the available alkali content of the flyash.



A Expansion at 6 months (%) 1 Available alkalis in flyash
B Cement replacement % by weight 2 Cement total alkalis

Fig. 1 Mortar Bar Expansion Test results for Mixes made using Flyashes having an available alkali content of less than 1.5% (Control Aggregate)



A Expansion at 6 months (%) 1 Available alkalis in flyash
B Cement replacement % by weight 2 Cement total alkalis

Fig. 2 Mortar Bar Expansion Test results for Mixes made using Flyashes having an available alkali content of more than 1.5% (highly reactive aggregate)

IV. VARIOUS APPROACHES FOR LIMITING ALKALI CONTENT IN DIFFERENT CEMENTITIOUS MATERIALS BASED CONCRETE MIX

4.1 Flyash Based (Portland Pozzolana Cement) Concrete Mix

The world over, flyash is currently the most abundant and commonly used pozzolana in cement mortar/concrete. Because of the reported difficulty in evaluating degree of pozzolanic activity, most organizations do not even identify flyash as pozzolanic admixture but as mineral admixture in cement concrete. Therefore, various organizations around the world and even different organizations in the United States have their own standards, codes of practices, guidelines and the requirements for the use of the mineral admixtures in cement and concrete.

4.1.1 British Cement Makers' Federation And Building Research Establishment (UK) No. 330 : March, 1998

Recommends one sixth of the alkali content of flyash to be considered as the reactive alkali. Calculation of alkali content in flyash based Portland pozzolana cement may be done as follows:

$$Aeff = \frac{(X \; x \; C)}{100} + \frac{(1 - X)\mathrm{F}}{600}$$

Where,

X = % of OPC/Clinker in Portland Pozolana Cement
C = Alkali content in OPC/Clinker cement (as Na_2O eq.), % by mass
F = Alkali content in flyash (as Na_2O eq.), % by mass
A_{eff} = Effective alkali content in PPC, % by wt.

In addition to effective alkali, the BS 3892 suggests[6] that the damage to concrete is unlikely to occur if any ordinary portland cement is replaced by 25% or more pulverized fuel ash, provided that the alkali content of the concrete is not more than 3.0 Kg/M^3.

*4.1.2 ICOLD Bulletin – 79 On "Alkali Aggregate Reaction In Concrete Dams***"**

The limits for the available alkali content in flyash are suggested on the basis of a curve (Fig. 1) drawn after a series of mortar bar expansion test. The mortar bar expansion test results for mixes made using flyash having an available alkali content of less than 1.5% plotted. A study of this figure shows that replacement of cement by 30% of flyash by weight in quite effective for reduction of the expansion due to alkali silica reaction to be within allowable limits.

4.1.3 ASTM C – 618 -1994 " Standard Specification For Coal Flyash And Raw Or Calcined Natural Pozzolan For Use As A Mineral Admixture In Portland Cement Concrete"

The specification covers coal flyash and raw or calcined natural pozzolan for use as a mineral admixture where cementitious or pozzolanic action, or both, is desired, or where other properties normally attributed to finely divided mineral admixtures may be desired, or where both objectives are to be achieved.

The optional chemical requirement for available alkali as Na_2O eq. is 1.5% max. It is applicable only when specifically required by the purchaser for mineral admixture to be used in concrete containing reactive aggregates and cement to meet a limitation on content of alkalies.

ACI manual of concrete practice (232.2R-15) "Flyash in concrete" also suggests use of pozzolan meeting ASTM 618 requirements to prevent excessive expansion due to ASR.

4.1.4 IS : 3812 – 1981 " Specification For Flyash For Use As Pozzolana And Admixture"

(First Revision)

This standard covers the physical and the chemical requirements for flyash for use as a pozzolana for part replacement of cement, for use with lime, for use as an admixture and for the manufacture of Portland pozzolana cement conforming to IS : 1489 (Part 1)[7] – 1991.

As per this code, available alkalies as sodium oxide (Na_2O eq.) in flyash shall not exceed 1.5% by weight. It is applicable only when the reactive aggregates are used in concrete and are specially requested by the purchaser.

4.2 Slag Based (Portland Slag Cement) Cement Concrete

In case of Portland Blast Furnace Slag Cements[10], a distinction is needed between those with a medium slag content[5] more than 50% and those with a high slag content more than 65%. To be considered "Low alkali", they must meet the following requirements :

More than 50% slag	Less than 0.9 % Na_2O (eq.)
More than 65% slag	Less than 2.0% Na_2O (eq.)

Though a series of expansion tests, an empirical formula was derived for computing an "Effective Alkali (Aeff)" for the Blast Furnace Slag Cement, which could be directly compared to the 0.60% Na_2O (eq.) limit for the Portland cement. The proposed formula is :

$$Aeff = A\left\{1 - (\tfrac{H}{H_0})^2\right\}$$

Where

A = Alkali content of Portland Blast Furnace Slag Cement

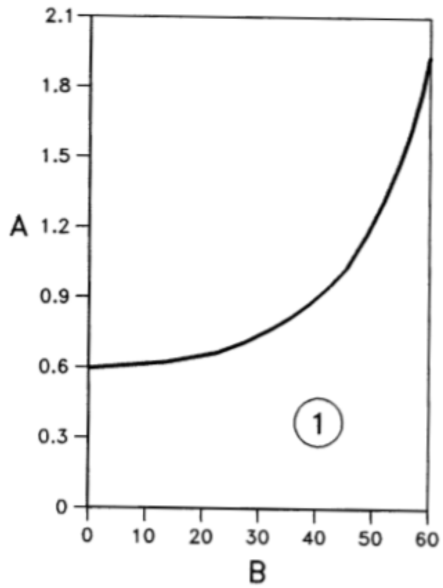
H = Slag Component in % by weight

H_0 = An experimental constant representing the slag content, in % by weight, which will not produce any expansion (72% was found from experimental data to satisfy this condition).

A curve no 1 showing relationship of blast Furnace slag content with 0.6% effective alkali content is shown in Fig. 3. All cements that fall below the curved line would behave like Portland cement with alkali contents between 0 and 0.6% Na_2O equivalent.

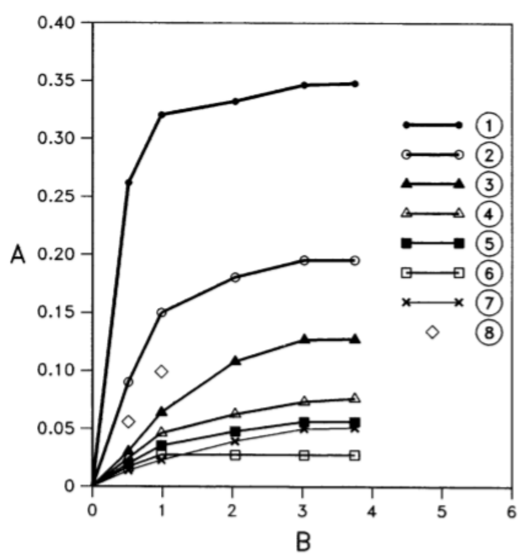
4.3 Silica Fume Based Cement Concrete

Silica fume is an ultrafine powder consisting of spherical particles mainly amorphous silica with an average diameter of 0.1 µ obtained as byproduct of silicon and ferrosilicon electrometallurgical industries. For reducing alkali silica reaction to a safe limit, small amount of silica fume as pozzolana is needed as compared to other materials such as flyash & blast furnace slag. Fig 4 shows expansion curves for mortar containing a reactive aggregates and and various amounts of silica fume. Ordinary Portland Cement incorporating Silica Fume will thus not require any restriction of alkali content in cement to be within 0.6% Na_2O(eq.). In the BIS specification of Silica Fume as per IS: 15388-2003 "Silica Fume- Specification[8]" and ASTM C 1240-43 "Standard Specification For "Silica Fume for Use in Hydraulic – Cements Concrete and Mortar" the available alkali is an optional requirement. The limits given in both the codes are 1.5% by weight.



A = Na_2O eq. of cement in weight (%)
B = Slag content of Cement in weight (%)
1 = Field of Cement with low effective alkali

Fig. 3 Influence of Blast Furnace Slag on Alkali Limit of Cement with low effective alkali content



A Expansion %
B Age in years
(1) OPC
(2) OPC + 10% Rhyolite
(3) OPC + 5% SF
(4) OPC + 15% Rhyolite
(5) OPC + 7.5% SF
(6) OPC + 10% SF
(7) OPC + 25% Rhyolite
(8) Code requirement (Iceland)

Fig. 4 Rhyolite and Silica Fume versus mortar bar expansion

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V. CONCLUSION

It is well known that flyash/slag/silica fume is an effective part replacement of cement for reducing alkali silica reaction. Since these materials itself contains sizeable amount of alkali, it is essential that the nature of these alkalies be well understood in order to put it to good use. The demarcation between normal alkalies and the available alkalies should be clearly understood in case of flyash and silica fume, since the various codes and practices use these terminologies inter changeable for limiting the alkali content in cement/mortar/concrete. The general consensus approach to be

- Use of flyash/silica fume with an available alkali less than 1.5 % as Na_2O eq.
- In case of Portland Blast Furnace Slag Cements to be considered "Low alkali", they must meet the following requirements :

  More than 50% slag: Less than 0.9 % Na_2O (eq.)

  More than 65% slag: Less than 2.0% Na_2O (eq.)

- Limiting the overall alkali content in the concrete to 3.0 Kg/M^3 taking into consideration contribution from all the ingredients including flyash/silica fume/slag. The contributions of alkalies from flyash in this type of calculation should be restricted to 1/6th of the value.

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