

Should Acid Soluble Sodium Equivalent Alkali Be the Measure of Potential Portland Cement Reactivity?

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ABSTRACT

This paper examines some of the variables in the composition of cement that can affect the reactivity of the metal alkali components. The author suggests that recent changes in the design and operation of cement plants have exacerbated the problem of alkali-aggregate reactivity, for when kilns that incorporate preheaters or precalciners are operating efficiently, most of the sodium and potassium will be in the form of sulphates, and so are readily available for conversion to hydroxides as a part of the hydration process. The author suggests that the chemical analyses of cements should have a percentage availability factor applied to the total equivalent alkali figure in order that the user shall be able to compare the reactivity potential of the various products available.

Author's Experience with Alkali-Silica Reactivity: Our company is a manufacturer of precast concrete products, such as steps, patio slabs and pavers. We used the same brand of cement for steps from 1958 to 1979, and our coarse aggregate was local limestone. We did not have cracking problems during the '60s, but had trouble periodically during the '70s. This cracking showed up in the concrete after about 18 months exposure and it appeared to be worse in some locations than others, often being noticed after hot summer weather. Thirteen years ago, we were sued by one builder because steps had cracked before the warranty period on houses had expired. We were fortunate to be able to settle the action out of Court.

We changed to four different local limestone aggregate producers in the '70s in order to try to find a non-reactive cement-aggregate combination. Finally, we switched to a gravel aggregate from outside the Ottawa area. We checked the chemical analyses of the cement supplied to us by the manufacturer. There was virtually no change in total equivalent alkali based upon acid extraction between 1969 and 1979. About three years ago, we found out that the manufacturer had changed fuel from oil, to gas and then to coal during this period, and that he had installed a new modern kiln complete with preheaters. We had not realized that

the reactivity of the cement might have been increasing despite the constant level of total equivalent alkali reported.

Availability of Metal Alkalis: Metal alkali compounds combined in cement must undergo chemical change during hydration in order to be available to enter the pore solution. Alkali sulphates dissolve readily upon mixing with water; the double sulphates being the most soluble. The sulphates then interact with tricalcium aluminate to form ettringite or monosulfoaluminate, while the sodium and potassium ions form sodium hydroxide and potassium hydroxide. The behaviour of the complex alkali compounds in the clinker phases is less understood. A percentage of these will become available as hydroxides.

In South African cements (Brandt and Oberholster 1983), the "Active" alkali content gives a better indication of potential reactivity with Tygerberg formation aggregate than either total equivalent or 10 minute soluble alkali content. Examination of 6 South African cements showed that the "Active" alkali content varied from 71 to 93% of the total equivalent alkali (Putterill and Oberholster 1985). I believe that our experience indicates that the reactivity or "Active" alkali content of a cement can alter with changes of material, equipment or operational procedures, even though the total equivalent alkali remains constant. We need to be aware of the variables in the manufacture of cement that can change reactivity.

CEMENT MANUFACTURE AND ITS EFFECT ON ALKALI COMPOUNDS

Kiln Operation: Major changes have taken place in kiln design and operation during the past 20 years, mainly as a result of the energy crisis and increases in the cost of fuel. Oil was cheap and generally had a low alkali content. Gas was cheap, and had both a low alkali and a low sulphur content. Price increases for oil and gas in the '70s saw conversion of fuel feed to coal, and the installation of energy efficient kiln systems using pre-heaters, pre-calciners and satellite cooling systems. The use of pre-heaters requires that a proper alkali-sulphur balance be maintained within the kiln. Modern "dry" kilns with preheaters require only half the energy "wet" kilns built 40 years ago used (Ferguson 1986), but these energy efficient systems will convert most alkali to sulphate as an operational necessity.

Thirty years ago, the white plume from kiln stacks contained a percentage of the volatile alkalis. Environmental regulations forced the installation of precipitators, and the return of some of the alkali dust to the kiln as the "external cycle". The modern kiln has been designed to be environmentally acceptable as well as energy efficient.

Preheater Clogging: This is brought about, in essence, by the appearance of micro-melts from the intermediate phases and their subsequent consolidation as solid particles. Alkalis sublime at 1100°C and pass into the gaseous phase. As volatiles, they react first with any chlorine available and then with sulphur dioxide (Kurdowski 1983). These chlorides and sulphates condense on dust and raw material in the cooler regions of the kiln, the condensates on the raw

material returning to the sintering zone and the dust to the extractors. If there is excess sulphur, it will combine with calcium at between 600 and 900°C and the hemihydrate formed will block preheater ducts. One remedy is to add higher alkali content raw meal so that the extra alkali will balance the sulphur to form alkali sulphate (Frankenburger and Matejka 1977). An alternative is to change some or all of the energy feed to a fuel with a lower sulphur content, such as natural gas. If there is insufficient chlorine and sulphur, the alkalis will condense in the preheater ducts as carbonates or oxides. An answer is to add gypsum to the raw meal, converting the alkali to sulphates.

Equilibrium of Volatile Constituents: Equilibrium for each is reached when quantities entering with kiln feed and return dust are equal to quantities leaving with clinker, exit gases and wasted dust. This leads to the generation of the so-called "external" and "internal" cycles. The "external" cycle is the amount leaving and re-circulated back into the kiln with the dust; the internal cycle is the condensation and evaporation of alkalis within the kiln.

Volatile Cycles: When a kiln is started up, the alkali level of the gases of the internal cycle will be a minimum, and so will the alkali sulphates entrapped in the clinker. The alkali volatiles will build up in the gas stream by evaporation and condensation to a maximum level after several hours; thereafter they will decrease to a lower level before building up to the maximum again. A study of one cement kiln has shown the cycle time from peak to peak to be between five and six hours, with alkali sulphate content built up in the clinker corresponding to the decrease in the kiln gas (Chatterjee 1983). The alkali variation in the clinker was between 0.7 and 1.9% sodium oxide equivalent. Assuming a kiln capacity of 300 tons per hour, this would give maximum and minimum alkali sulphate content in the clinker every 1650 tons.

Grinding of Clinker: The effect of cement particle size must be considered. The finer particle size fractions have a high alkali sulphate content because the latter is soft and easy to grind (Locher 1977). Particle sizes above 30 microns are of little value in the hydration process (Dimitriev, Vlasova and Yudovich 1977), and so it is unlikely that alkali compounds contained therein will become available for conversion to hydroxides. Most grades of cement are ground finer today than they were 30 years ago so there is a smaller percentage above 30 microns.

Dicalcium Silicate-Tricalcium Silicate Ratio: A method for preventing alkali silica reaction is to combine hydroxides produced by cement hydration with reactive silica in fly ash, slag, etc. Tricalcium silicate produces double the amount of calcium hydroxide on hydration compared to dicalcium silicate. There is also the question of the amount of sodium and potassium that can be combined in the lattice structure of hydrated calcium silicate. Dicalcium silicate will retain more metal alkali than will tricalcium silicate upon hydration (Bhatty and Greening 1978). For these two reasons, the ratio of tricalcium silicate to dicalcium silicate is a contributing factor when determining the potential reactivity of a particular cement. Tricalcium silicate levels have been increasing at the expense of dicalcium silicate over the past thirty years, so increased

tricalcium silicate ratios mean that more alkali is available for interaction with unstable silica.

Conclusion: There are many temporary monuments in Eastern Ontario that show the extent of the alkali-silica reactivity problem. Concrete producers have assumed that the reactivity of a cement is related to the total sodium equivalent alkali content obtained by acid extraction and expressed as the oxide. It is on this basis that we have compared the potential alkali reactivity of brands of cements and assessed the past performance of aggregates. This can only be justified when we compare cements that have the same equivalent alkali, a similar phase chemistry and equal amounts of volatile compounds. It is unlikely that a cement produced today will have all of these three factors the same as one manufactured thirty years ago, and so it is not realistic to assess suitability of an aggregate on the basis of past performance, even when the cements have the same total equivalent alkali. I recommend that chemical analyses be required to show an efficiency figure against alkali content; this being the percentage of "active" alkali determined by the South African method in the total equivalent acid soluble alkali. This would help the concrete manufacturer to monitor changes in cement reactivity. As the test for "active" alkalinity takes time and is relatively expensive, I suggest that cement producers be asked to carry out representative testing of each grade of cement every two months and that the report state the date on which the test samples were taken.

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