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Time to failure for concrete exposed to severe sulfate attack

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Abstract

In the 1940s, the U.S. Bureau of Reclamation (USBR) began a long-term, nonaccelerated laboratory test program to determine the influence of a variety of concrete-mix parameters on resistance to severe sulfate exposure conditions. This paper reports the time of failure of these samples as influenced by their water-to-cement (w/c) ratio, cement composition, and percent replacement of cement with fly ash. The analysis indicates that there is a "safe zone" for concrete made with w/c ratio lower than 0.45 and cement with unhydrated tricalcium aluminate (C_3A) content lower than 8% where failure did not occur within the 40-year exposure period. As expected, concrete samples cast with high amount of C_3A failed after a relatively short time of sulfate exposure. Expansion tests indicated that cements containing high amounts of C_3S may lead to premature failure of concrete, even when moderate w/c ratios are used. Samples prepared with 25% and 45% replacement of cement with fly ash showed significantly less expansion than comparable mixtures containing no pozzolans.

Keywords: Durability; Sulfate attack; $Ca_3Al_2O_6$; Ca_3SiO_5; Pozzolan

1. Introduction

Because of its reputation for strength and durability, concrete is often the material chosen for the construction of structures exposed to severe environmental conditions whether they be offshore oil platforms on icy water or hazardous waste containment vessels buried in the earth. As demand for construction in harsh environments increases, so does the concern for long service lives of these structures. Typically, concrete structures are designed to perform, even in aggressive environments, for 50 to 100 years with minimal maintenance. Construction of chemical and radioactive waste containment vessels from concrete is an example of the selection of concrete for durable structures exposed to aggressive conditions.

Sulfates present in soils, groundwater, seawater, decaying organic matter, and industrial effluent surrounding a concrete structure pose a major threat to the long-term durability of the concrete exposed to these environments. Sulfate attack of concrete may lead to cracking, spalling, increased permeability, and strength loss. Therefore, to ensure long periods of satisfactory performance, concrete in contact with sulfate-containing soil or water must be designed to be resistant to damage by sulfate attack. This is especially important now because the durability of manufactured products is becoming an increasingly serious economic and ecological issue.

Essentially, two forms of sulfate attack are known to exist: (1) reaction with alumina-bearing hydration products, and/or unhydrated tricalcium aluminate (C_3A) to produce ettringite; and (2) reaction with calcium hydroxide to produce gypsum. In hardened concrete, the formation of ettringite by sulfate attack *can*, but does not always, result in expansion. Because of concrete's low tensile strength, expansive strains resulting from ettringite formation during sulfate attack can lead to cracking and reduced performance. Gypsum, in addition to ettringite, can be produced during sulfate attack through cation exchange reactions. Sulfate attack through gypsum formation can result in smaller expansion, but is more generally known to manifest itself through loss of stiffness, strength, and adhesion. Thorough reviews of the mechanisms of sulfate-induced damage can be found in Refs. [1–4].

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To limit the ettringite form of sulfate attack, cements low in C_3A, such as ASTM Type II or Type V portland cement, are recommended where sulfate exposure is expected. However, control of cement composition alone will not ensure sulfate resistance, particularly if the permeability of the concrete is high or if the mechanism of the attack is not due to ettringite formation. For moderate conditions (up to 0.2% sulfate content of the soil or up to 1500 mg/l sulfate in water), Type II portland cement (less than 8% C_3A) can perform satisfactorily if the water-to-cement (w/c) ratio is below 0.50. In severe conditions (0.2–2% sulfate in soil, or 1500–10,000 mg/l sulfate in water), ACI 318 recommends the use of Type V (less than 5% C_3A) cement and a w/c ratio below 0.45. For very severe attack (sulfate content over 2% in soil, or over 10,000 mg/l in water), Type V portland cement plus a pozzolanic admixture should be used with less than 0.45 w/c ratio.

Present specifications on cement composition and concrete quality for sulfate resistance are based upon long-term field exposure tests performed by the portland Cement Association, National Bureau of Standards, Corps of Engineers, and the Bureau of Reclamation [5,6]. Because some of these long-term tests were still continuing when the specifications were made [5], a review of the complete data set, such as the U.S. Bureau of Reclamation (USBR) measurements, may yield additional information. Indeed, it is critical to assess the validity of these prescriptions with controlled experiments performed over a long period of time. Accelerated tests that typically do not expose concrete to existing field conditions are of limited value to establish the life prediction of concrete exposed to sulfates.

Over 50 years ago, a program of nonaccelerated laboratory testing was initiated by the USBR to determine the influence of a variety of concrete-mix parameters on sulfate resistance. Concrete specimens continuously exposed to sulfate concentrations typical of field conditions were monitored at regular intervals. Kurtis et al. [7] conducted statistical analysis of a portion of the data to predict the expansion of the concrete as a function of time, w/c ratio, and C_3A content. Corr et al. [8] used the expansion equations to conduct a reliability analysis of concrete exposed to sulfate attack. One of the interesting results of the reliability study was that the effect of w/c ratio on expansion was one order of magnitude higher than the effect of C_3A content (for cements with low C_3A).

The objective of the present paper is to study the time to failure of USBR concrete samples as influenced by w/c ratio, presence of fly ash, and C_3A and C_3S content. The analysis of the results will be done primarily in graphical form to illustrate the general trends by which specific parameters influence performance in severe sulfate environments and to allow identification of those parameters or combinations of parameters which result in clearly improved and clearly poor performance.

2. Data from long-term testing of concrete exposed to sulfate attack

In the early 1940s, the USBR in Denver, CO, began an extensive investigation on sulfate-related durability of concrete. To test the effect of a number of parameters on sulfate resistance, over 100 concrete mixtures were designed with varying cement composition, cement content, cement fineness, w/c ratio, pozzolan type, pozzolan content, air content, admixtures (including air entraining, water-reducing, and set accelerating), mixing temperature and strength. Concrete cylinders (76×152 mm, 3×6 in.) were cast for each mix design and were partially submerged in 2.1% (0.15 M) Na_2SO_4 solution at ambient temperature. As a measure of the effect of sulfate exposure on the concrete, length measurements were made with a length comparator. The length of the cylinders was measured every 28 days initially. After about 5 years of testing, the cylinders were measured biannually. The sulfate solution was replaced as needed to maintain partial submersion of the cylinders, ensuring that the sulfate concentration was maintained. The testing continued, uninterrupted for over 40 years.

These data are important because no comprehensive database has been compiled for concrete exposed to typical field concentrations of sulfates over such a long period. The exposure conditions are similar to severe conditions likely to be encountered in service. Investigations of long-term performance of concrete considering the effect of such a wide variety of mix parameters have not been previously available. However, one shortcoming of the USBR data is that expansion was the only property measured. Sulfate attack of concrete can produce expansion, but decreased stiffness, strength, and impermeability are also important effects. However, the expansion data do provide a general indication of effect of mixture parameters on concrete performance.

3. Discussion of results

Expansion data collected by the USBR have been organized into three databases for analysis. One database includes data for 82 concrete cylinders prepared from 41 concrete mixtures prepared with portland cement with low (< 8%) potential C_3A content. Another contains the data for 33 concrete cylinders prepared from 12 mixtures prepared from portland cement with high (>10%) potential C_3A content. Previous statistical analysis of the data showed distinctly different expansion behavior with time based on potential C_3A content of the cement, as determined by Bogue calculations using data from chemical oxide analyses [7]. This led the research team to differentiate between the mixtures on the basis of the cement composition. A third database contains the data for 80 concrete cylinders prepared from 40 portland cement–fly ash concrete mixtures with fly ash content ranging from

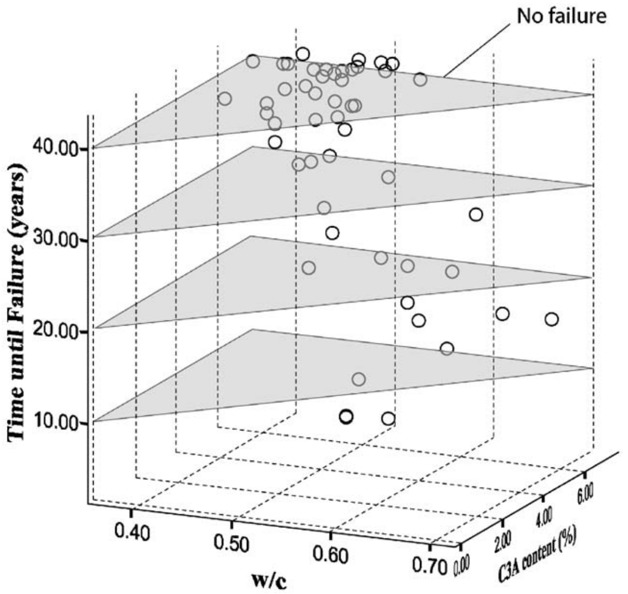

Fig. 1. Time to failure described as a function of both w/c ratio and potential C_3A content of the cement.

25% to 45% by mass of cement. For the portland cement–fly ash concrete mixtures, the water-to-cementitious materials (w/cm) ratio ranges from 0.44 to 0.58, and C_3A contents range from 4.2% to 6.0%. These three databases have been used to generate graphical representations to illustrate the effect of w/c ratio, C_3A content, and fly ash content on the time to failure, which was defined by the USBR to be 0.5% expansion.

Figs. 1 and 2 are based on the database describing time to failure for concrete prepared using cement with C_3A content below 8%. The time to failure as a function of w/c ratio and C_3A content is shown in a three-dimensional plot in Fig. 1. The time to failure was measured as the reading where the expansion first exceeded the failure criterion established by the USBR (i.e., 0.5% expansion). From Fig. 1, it is apparent that, as expected, time of failure decreases with increasing w/c ratio and C_3A content. However, three-dimensional plots can be misleading because the view depends on the position of the observer. Therefore, it is more useful to develop two-dimensional plots, as shown in Fig. 2.

Time of failure is shown as a function of w/c ratio in Fig. 2. Different markers are used in this plot to correspond to different ranges of C_3A content. Because the duration of the USBR test program was approximately 40 years, those markers placed at *y*-axis locations corresponding to time to failure beyond 40 years may be assumed to have *not* failed within the test period. Like Fig. 1, this plot also shows that, as expected, those samples with higher w/c ratio and C_3A content tend to fail at earlier ages. However, it is important to note the presence of a "safe zone" for w/c ratio < 0.45. For w/c ratio below 0.45, the concrete samples do not fail during the test period—*independent* of the C_3A content of the cement. In this region, the markers show that samples have been prepared with cements with C_3A in the range 4–5%, 6–7%, and 7–8%, but that none of the samples prepared with w/c ratio lower than 0.45 fails within the test period. These observations make evident the importance of concrete permeability and confirm the current

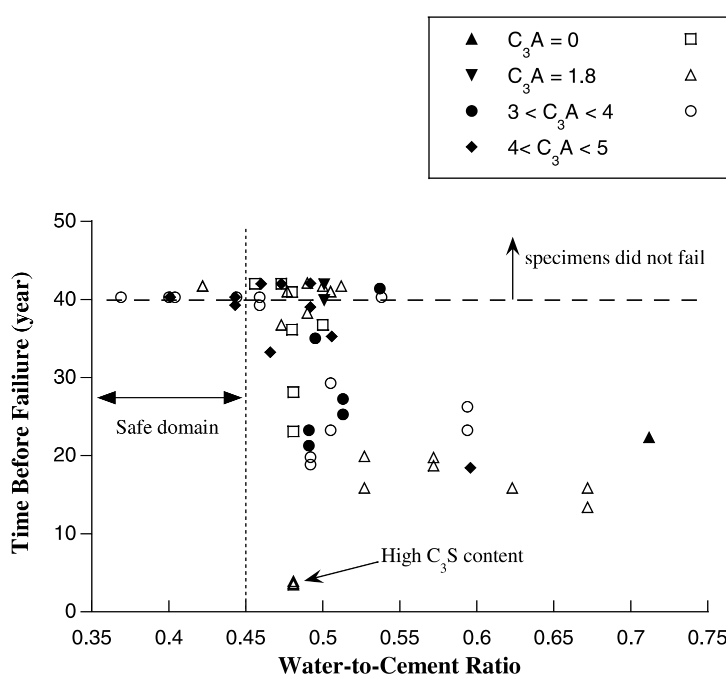

Fig. 2. Time to failure as a function of w/c ratio, with ranges of C_3A content in the range 0–8% shown by the shape and color of the markers.

recommendation that w/c ratio < 0.45 for severe sulfate exposure.

While expansion-based failure for mixtures with w/c ratio less than 0.45 appears to be independent of C_3A content, it is worthwhile to examine more closely the effect of C_3A content when the w/c ratio is slightly greater than 0.45. For example, from Fig. 2 it can been observed that those concrete cylinders prepared from cement containing ~2% C_3A experienced failure near the end of the test period or did not fail, while those concretes prepared from cement with C_3A content of 6–7% are more likely to fail and to fail much earlier. Failures for samples with C_3A of 6–7% were recorded as early as after only 4 years of sulfate exposure. Thus, it is clear that the amount of C_3A in the cement may have a large effect on sulfate-related durability when w/c is increased by 10% from the safe zone.

It is remarkable that the concrete samples that had the earliest failure (3.5 years) were cast with a fairly low w/c ratio of 0.48. However, these samples were prepared with cement containing a high amount of C_3S (73.7%). Data for these samples and a set of samples with comparable w/c ratio and C_3A content but with lower C_3S content are shown in Fig. 3. For the samples with higher C_3S content that failed early, the sulfate attack may have involved a complex mechanism of ettringite expansion, gypsum formation, and decalcification of the C-S-H. The results confirm earlier investigations performed by Mehta et al. [9] that showed that mortars prepared with alite cement had inferior performance compared to other cementitious systems.

The fact that C_3A is not the only compound responsible for the expansion of concrete is evidenced by the experimental results shown in Fig. 4, where the concrete samples failed in less than 25 years even though they were prepared with cement containing *no* C_3A. The high porosity of the concrete resulting from casting with a high w/c ratio and the high contents of C_3S and C_4AF may account for the resulting expansion. When exposed to sulfate attack, cements with high C_3S show a softening in the matrix, which cannot restrain the expansion caused by the reactions with C_4AF. It should be noted that limits on C_3S content are not included in the ACI 318 recommendations, the Canadian Standard CSA A23.1, or ASTM C150.

The database describing expansion behavior with time for concrete prepared from high (>10%) C_3A cement is depicted in Fig. 5. The w/c ratio ranges from 0.45 to 0.51. The plot shows that all of the concrete samples fail in less in less than 5 years exposure time. Fig. 5 shows that there is no question that high amounts of C_3A lead to premature failure. While the deleterious effect of high C_3A content is not disputed, few have recognized that high C_3S content may lead to similar degrees of distress, even though the chemical mechanisms leading to distress are different. This is shown in Fig. 6 which compares the expansion of concrete samples made with the same w/c ratio of 0.48 and two different cements, one with a relatively high C_3A content and the other with a relatively high C_3S content.

Examination of the database for those concrete mixtures containing fly ash shows that the partial replacement of cement with fly ash significantly improves sulfate resistance as measured by expansion. None of the samples containing fly ash fails during the long-term sulfate testing. Thus, plotting time to failure as a function

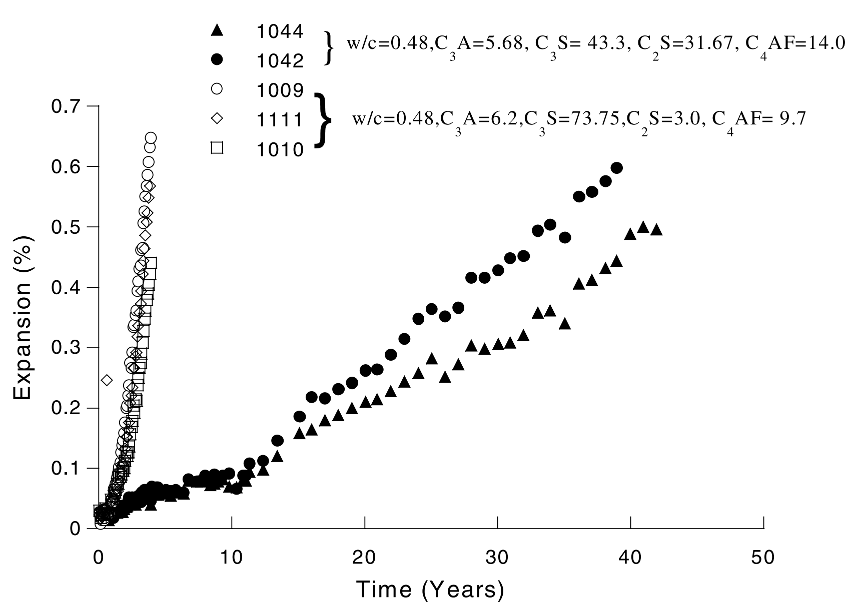

Fig. 3. Effect of C_3S content on the expansion of the concrete. In a concrete mixture with 0.48 w/c ratio, the concrete made with cement containing a high amount of C_3S failed in 3.6 years while a similar concrete made with similar mix proportions but with low C_3S content does not fail in 40 years.

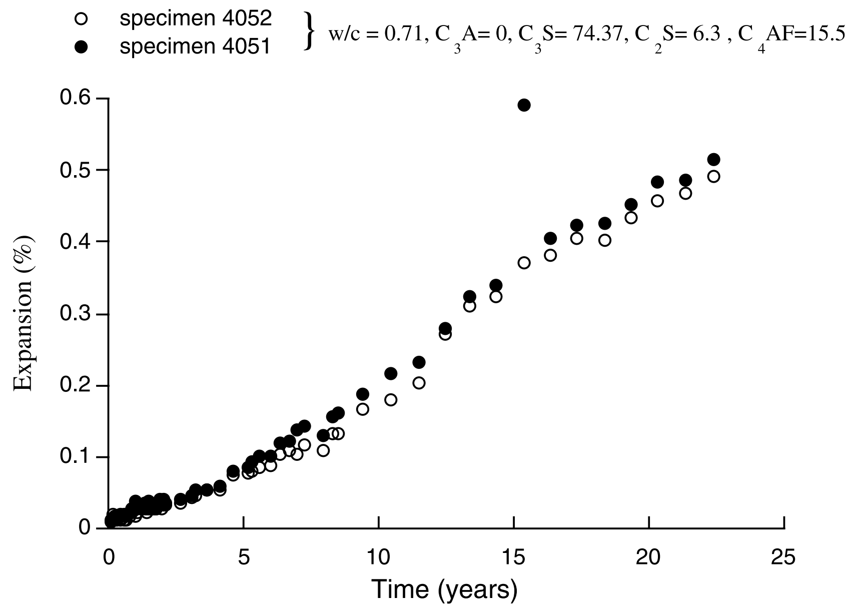

Fig. 4. Concrete made with cement containing no C_3A but with high C_3S failed in less than 25 years (the outlying data point appears to be a measurement error).

of mixture design parameters for these samples does not yield meaningful information. However, by comparing expansion vs. time plots for concrete mixtures containing fly ash to those containing no pozzolans, it is clear that long-term expansion is significantly decreased when fly ash is used as a partial replacement for cement, within the range investigated by the USBR. The graphs in Fig. 7a and b show typical data for those mixtures containing fly ash as compared to typical data for those concretes containing no pozzolanic admixtures. Fig. 7a shows expansion over a 40+-year period for six concrete cylinders prepared from three different mixtures. For these samples, the w/c or w/cm ratios (both represented as w/c ratio in Fig. 7a and b) and C_3A content are comparable, but the amount of fly ash included varies. Fig. 7b shows that after only several years of exposure, the expansion

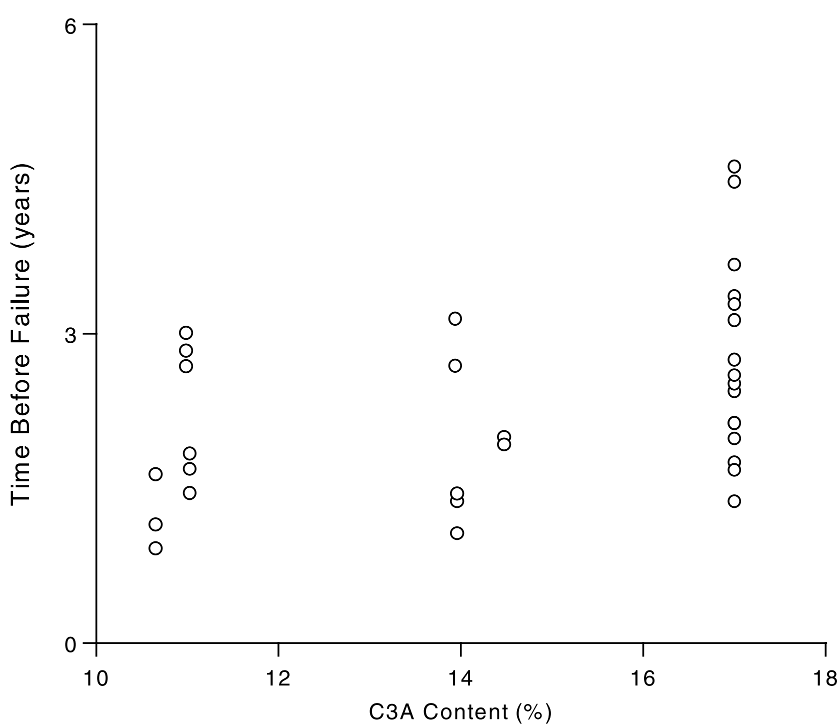

Fig. 5. Time to failure for concrete prepared from high (>10%) C_3A cement.

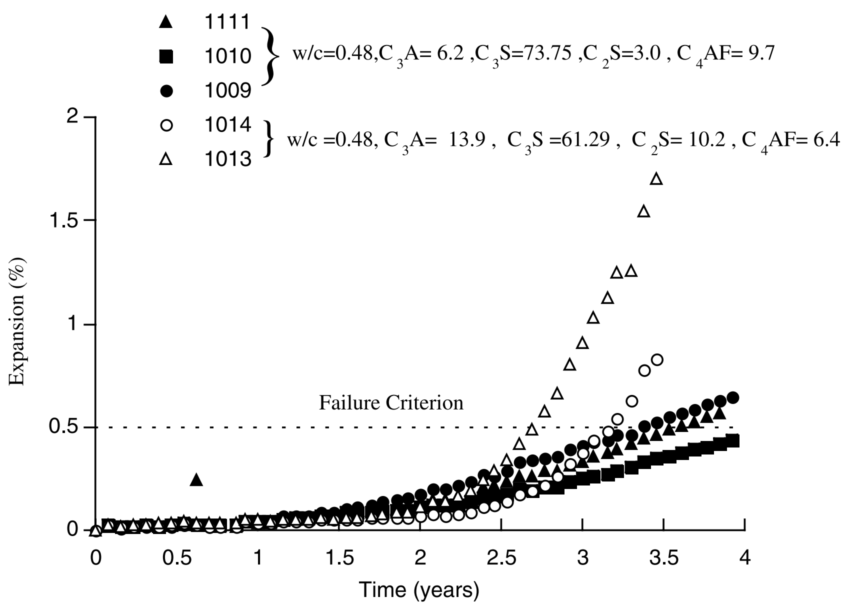

Fig. 6. Concrete samples made with the same fairly low w/c ratio show large expansion at early exposure times when the cement contains high amounts of C_3A or C_3S (the outlying point for sample 1111 appears to be a measurement error).

behavior for all three mixtures is virtually indistinguishable. It is not until after 4–5 years of exposure to the 2.1% Na_2SO_4 solution that the effect of fly ash replacement is obvious. This observation indicates that even for severe exposures, the external manifestations of damage may not be obvious for several years after construction. This observation also emphasizes the need for long-term, nonaccelerated testing such as the USBR test program.

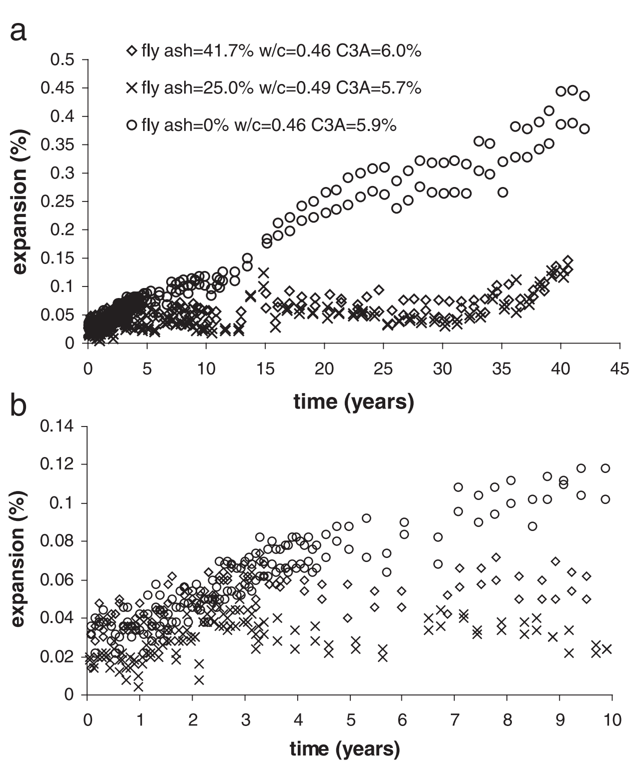

Fig. 7. (a) Long-term expansion vs. time data for comparable mixtures with varying amounts of fly ash. (b) Closer examination of the early (< 10 years of sulfate exposure) expansion behavior of these samples.

By examining the total expansion after 40+ years of sulfate exposure in Fig. 7a, it is seen that the samples containing no fly ash have expanded about 0.40%, while those prepared with 25% and 41.7% fly ash have expanded only about 0.15%. It is interesting that for this range of w/c or w/cm ratio (i.e., 0.46 to 0.49) and C_3A content (i.e., 5.7–6.0%), the expansion behavior of the 25% and 41.7% fly ash mixtures are essentially indistinguishable. The number of samples prepared with 25% fly ash by the USBR was unfortunately quite small, with only a limited range of w/cm ratio and C_3A contents examined. As a result of the limited data at 25% replacement, further relationships among sulfate resistance, w/cm ratio, and fly ash replacement percentage cannot be established from this data set.

4. Conclusions

Examination of the time to failure for concrete prepared from various mixtures and exposed to severe sulfate conditions reveals the following:

- Time to failure, as measured by expansion, decreases with increasing w/c ratio and C_3A content.
- A “safe region” appears to exist for mixtures with w/c ratio below 0.45, where C_3A content is 8% or less.
- Cements containing high amounts of C_3S may lead to premature failure of concrete.

- Where C_3A content is 10% or more, data where w/c ratio is in the range 0.45–0.51 indicate that failure is expected to occur in 5 years or less.
- Partial replacement of low C_3A cement with fly ash in the range 25–45% results in considerable improvements in sulfate resistance.

These observations are mainly consistent with the recommendations found in the existing building code for severe sulfate exposure. It is recommended that additional research be performed to assess specifically the influence of high C_3S content on sulfate resistance, particularly as C_3S content is known to be increased in modern cement manufacture. Overall, however, these results provide a basis for continued reliance upon the recommendations regarding cement type, w/c ratio, and use of pozzolans, and have particular relevance for severe sulfate conditions.

Acknowledgements

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