STANDARDS FOR EVALUATING THE SUSCEPTIBILITY OF CEMENT-BASED MATERIALS TO EXTERNAL SULFATE ATTACK

James R. Clifton, Geoffrey Frohnsdorff and Chiara Ferraris
National Institute of Standards and Technology

ABSTRACT

In this paper, the current status of standards 1) for specifying cement-based materials to prevent deleterious reactions with external sulfates, and 2) for predicting the performance of concrete exposed to external sulfates, is reviewed. The applicability and reliability of these standards are discussed and deficiencies in them noted. Recommendations for the development of improved standard test methods are presented.

INTRODUCTION

The purpose of this paper is to discuss: 1) the current status of standards for controlling or predicting the durability or service life of portland cement-based materials exposed to aqueous sulfate solutions; and 2) improvements needed in the standards. Deficiencies in current standard tests include lengthy testing periods, the insensitivity of the measurement tools to the progression of sulfate attack, and uncertain relationship to field degradation mechanisms. Ways to erase these deficiencies are discussed based on the application of the methodology outlined in ASTM E 632, "Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials" [1]. To begin with, reliable specifications for selecting durable cements, and test methods for evaluating the sulfate resistance of cements and concrete made from them, should be based on knowledge of the reaction mechanisms. This conference has advanced our knowledge of the reaction mechanisms of external sulfate attack and hopefully will help to establish the agenda for future research leading to improved standards.

MANIFESTATION OF DEGRADATION

The nature of the manifestation of sulfate degradation depends on several factors including the exposure conditions that can range from continuous immersion to cycles of wetting and drying. In the following, rather simplistic descriptions of the manifestation of sulfate attack are related to the exposure conditions.

Continuous Immersion

If the concrete is essentially continuously immersed in a fixed volume of sulfate-containing water and sulfate attack occurs, either cracking or delamination of concrete surfaces or their softening, or all three, are usually observed. The affected area (reaction zone) follows the advancing sulfate interface. The processes result in a reduction of the concrete's mechanical properties, e.g., its load-carrying capacity [2]. Atkinson and Hearne [3] developed a model for predicting the rate of attack of concrete under continuous immersion in an sulfate solution, based on the following assumptions:

- sulfate ions from the environment penetrate into concrete, usually by diffusion,
- sulfate ions react expansively with certain aluminum-containing phases in the concrete,
- to simplify the problem, magnesium ions are not present (however, the effect of magnesium sulfate is predicted by the model) and the precipitation of gypsum does not cause significant expansion,
- the expansion of the surface layers results in stress buildup culminating in cracking and delamination (spalling) of the reacted material from the concrete surface,
- the rate of reaction is sufficiently rapid that there is a well-defined reaction front separating a layer in which the reaction is essentially complete from the inner volume in which it has not started.

The rate of degradation, R, is given by:

$$R = X_{spall} / T_{spall} = E\beta^2 c_s C_o D_i / \{\alpha_o \tau (1-v)\} \tag{1}$$

where X_{spall} is the thickness of a spalled layer,
T_{spall} is the time for a layer to spall,
E is Young's modulus,
β is the linear strain caused by one mole of sulfate ions, reacted in 1 m^3 of concrete,

c_s is the sulfate ion concentration in the bulk solution (which is assumed to remain constant),

C_o is the concentration of reacted sulfate ion from the solution present as ettringite,

D_i is the intrinsic diffusion coefficient of sulfate ions,

α_o is a roughness factor for the fracture path (usually assumed to be 1),

τ is the fracture surface energy of the concrete, and

v is Poisson's ratio

This model predicts that the rate of degradation increases with increases in diffusivity, in the concentration of external sulfate ions in the solution, and in the concentration of reactive species (compounds) in the cement paste matrix. The results of experimental studies and modeling at NIST [4] are in general agreement with the concepts of the formation of a reaction zone that delaminates, exfoliates or spalls. A NIST model [5], developed based on the analysis of experimental data obtained using a constant pH test method, showed that the data was consistent with the occurrence of a two-stage process (Figure 1); with Stage 1 being diffusion-controlled, with little expansion occurring as voids in the concrete
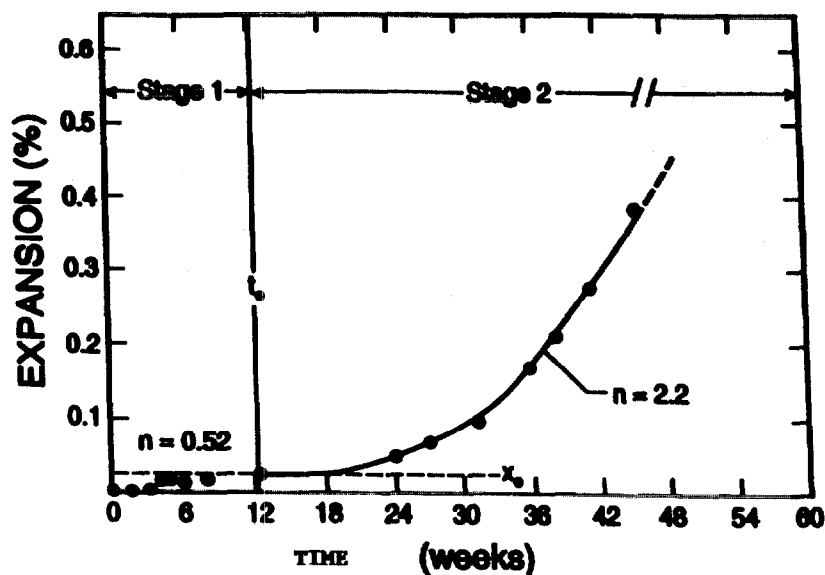

Figure 1. Schematic of sulfate attack model [5]. The value of n is the exponent of time, t.

are being filled with gypsum and ettringite; and, in Stage 2, continuing formation of ettringite causes expansion to accelerate with the resultant formation and propagation of cracks. Atkinson and Hearne [3] observed that only about one twentieth of the solid volume increase due to ettringite formation (also, for brucite) appears as bulk expansion. Therefore, the rate of degradation is not linearly related to the rate of ettringite formation. This is in agreement with a model by Clifton and Pommersheim [6] which predicted that, in the w/c range of normal concrete, sufficient void space is usually available to accommodate the maximum volume of ettringite formed from ASTM Types I and V portland cements. The above studies suggest that if the model is reliable, no testing should be needed for portland cements. If testing is to be accelerated so that the rate of spalling is increased, both the diffusivity of specimens and the exterior concentration of sulfates should be increased. The diffusivity can be increased by adjusting the mixture design, especially the water-to-binder ratio. Also, the measurement of expansion appears to be an insensitive parameter of ettringite formation.

Exposure to Cycles of Wetting/Drying.

Wetting and drying cycles with sulfate-containing water is another form of exposure which can be encountered when water levels rise and drop, e.g., by flooding and runoff of precipitation, and ocean tides. Also, cyclic migration of water into concrete can be induced by capillary flow and cyclic variation in atmospheric relative humidity. The result of such processes is the concentration of sulfates near the free concrete surfaces (at times denoted as "subsurfaces"). When soluble sulfate salts, as well as other soluble salts, are concentrated in sufficient amounts, disintegration of the surface layers can occur. The mechanism of the disintegration is controversial and both topochemical and precipitation/crystallization mechanisms have been proposed. Other possible degradation processes include reduction in the modulus of elasticity of concrete and thermal expansion/contraction incompatibilities of the affected and un-affected concrete [7]. Studies of wet and dry cycling by the U.S. Bureau of Reclamation [8] indicate that the accompanying degradation is more rapid than that associated with continuous immersion.

In a restricted sense, degradation of concrete by concentrating sulfate salts in the outer concrete surfaces through wetting and drying cycling is a physical process and other soluble salts may induce the same type of damage. However, if the wetting and drying processes are gradual then it is likely that both chemical and physical processes are involved in the degradation.

Partial Immersion with Evaporation

A particularly severe condition for sulfate attack is present when the lower portion of a concrete element is in contact with moist soil or ground water containing sulfates and the upper portion is exposed to a drying atmosphere. Damage occurs in areas exposed to the dry atmosphere in the form of spalling and scaling from both chemical and physical processes. Such problems have been observed [9, 10] in basements, foundations, and footings of residential dwellings, and service tunnels and dams. A standard test for concrete partially immersed in a sulfate solution or sulfate-laden soil, combined with drying conditions, was not found during the preparation of this paper.

SPECIFICATIONS FOR SULFATE RESISTANCE

Specifications for selecting cements and concrete resistant to external sulfate attack are numerous; the specifications have been developed by national organizations and local authorities such as highway departments. Rather than making a comprehensive survey of national and regional specifications, we will focus on current ASTM and European standards for concrete performance.

Because of the obvious correlation between the potential for ettringite formation and the amount of tricalcium aluminate (C_3A) in cements, specifications for sulfate resistance of cements usually stipulate limits on the maximum C_3A content. In ASTM C150 [11], Type V portland cement (sulfate resistant) is specified to have a maximum C_3A content of 5.0%, by mass, and Type II (moderately sulfate resistant) a maximum C_3A content of 8.0%, by mass. K. Mather [12] described the lengthy process in which ASTM Committee C-1 on Cement developed the above limits on C_3A contents. She commented on the need for a performance test, especially for evaluating the sulfate performance of blended cements. Through the work by Mather and other members of ASTM C-1, a performance test using mortars was adopted by ASTM and designated as ASTM C 1012 [13], which is applicable to both portland and blended cements. In this test method, the water-to-binder ratio is fixed and the mortar specimens are to attain an average compressive strength of 20 MPa before testing. Therefore, the performance of mortar specimens in the test is usually considered to be dependent primarily on the composition of the cement. The American Concrete Institute Guide to Durable Concrete [14] gives recommendations on durable concrete exposed to aggressive chemicals and salts which depends on severity of the exposure conditions. Based on the sulfate concentration in soil or water, recommendations are given on applicable cements and the maximum w/c ratio. The limit on w/c ratio indicates recognition of the influence of transport properties on the sulfate resistance of concrete.

European specifications for sulfate attack are undergoing change. Hobbs [15] has commented that in the forthcoming European Standard pr EN 206, "Concrete - Performance, Production and Conformity," durability of concrete will rely on prescriptive specification of minimum grade, minimum binder content, and maximum water-binder ratio for a series of defined environmental classes. He further comments that "it has not proved possible within the European Committee for standardization (CEN) to agree on common values for the specification parameters to cover the wide range of climates and wide range of cements in use in the EU Member States." Therefore, the standard will likely include indicated (default) values and individual Member States will be able to specify national values, when necessary. The book edited by Hobbs [15] gives minimum requirements for durable concrete considering corrosion, freeze-thaw attack, and chemical attack, which includes sulfate attack, in the U.K. Minimum requirements are given for concrete subject to exposure from sulfate in groundwater or in soil, that are necessary for service lives of 100 years. The recommendations cover the type of cement, cement content, and water-cement ratio. The concrete coarse aggregate should have a nominal maximum size of 20 mm and should conform to BS 882 or BS 1047 [15].

The effectiveness of mineral admixtures such as some fly ashes, silica fume, and granulated blast furnace slag in mitigating sulfate attack is well known [12,15,16] and is recognized in the ACI 201 Durability Guide and in pr EN 206. The type of cement, either portland cement or blended cement, and if needed, the type of mineral admixture to be added to the concrete, depends on the severity of the sulfate exposure. ASTM C 1157M is a recently established standard performance specification for blended cement [17]. It does not give any restrictions on the composition of a blended cement or its constituents. The sulfate performance of a blended cement is evaluated using ASTM C 1012.

In a review of sulfate attack on concrete, Metha [18] commented that the reliability of present specifications and test methods dealing with the resistance of concrete to sulfate attack are subject to question. He cited evidence that control of permeability of concrete is more important than control of the chemistry of the cement for sulfate-resistant concrete. This can be deduced from Eq. 1 since D_i varies by several orders of magnitude in concrete, whereas $[C_3A]$ only varies between about 1 and 12 percent.

TEST METHODS

Analysis of Standard Test Methods and Other Proposed Test Methods

Two ASTM test methods are available and other test methods have either been implemented or proposed by other organizations. Before reviewing the most widely used methods, the requirements for an acceptable test are explored. A reasonable approach for analyzing the reliability of test methods for determining sulfate resistance of concrete is to follow the generic procedures in developing accelerated tests described in ASTM E632 [1]. The major elements of ASTM E632 are applied to ASTM C452 [19] and C1012 [13] (both test methods are described in Section 4.2) in the following:

- PROBLEM DEFINITION - Define what the test should do and the degradation factors that should be included in the accelerated test.
  COMMENT - The purpose of the ASTM sulfate resistance test methods is well-defined - determine the performance of a cement paste matrix of concrete when exposed to sulfates at concentrations expected to be encountered in service.

- PRE-TESTING - Design and perform preliminary accelerated aging tests to demonstrate that rapid failures can be induced and measured and identify the main degradative factors.
  COMMENT - The work leading to the development of ASTM C452 and C1012 is reviewed by Mehta [18] and by Cohen and Mather [20]. Several ways to accelerate sulfate attack have been used or proposed [20, 21] including increasing reaction surface of test specimens (small specimens with large surface area); increasing the concentration of sulfate; increasing crystal pressure (i.e., continuous wetting-drying cycles); and raising the temperature of the solution. Acceleratory factors used in the ASTM tests are restricted to elevated concentrations of sulfates.

- TESTING - Design and perform predictive service life tests using the degradation factors of importance to determine the dependence of the rate of degradation on exposure conditions. Also, determine if the mechanisms of degradation in the accelerated test are representative of those observed in-service.
  COMMENT - This workshop should be a good starting point in determining if the conditions and procedures used in current test methods give rise to degradation mechanisms occurring in the field. If the field mechanisms are not being produced in the accelerated tests, then new test methods need to be developed.

• INTERPRETATION OF DATA - Develop mathematical models of degradation and compare rates of change in service life tests with those from in-service tests. Establish performance criteria for predictive service life tests. An alternative to actually predicting service life is to compare the relative behaviors of a number of materials based on the results of the same test.

COMMENT - Failure criteria in the ASTM tests appear to be empirically based which are only useful in making relative durability predictions, i.e., Cement A is potentially more durable than Cement B. Cohen and Mather [20] suggested that a wide spectrum of properties should be measured including changes in visual appearance, in size and mass, and in mechanical properties.

In addition to the generic criteria of ASTM E632, Mehta [18] recommended that for an acceleratory test for sulfate attack to be meaningful: (a) it should give reliable results within a relatively short time (e.g., 4 weeks or less) if the test is to be of practical benefit to a cement manufacture or user; and (b) it should be applicable to both portland and blended cements. ASTM C452 is reasonably rapid, completed within 14 days, however, it is not considered to be applicable to blended cements [13, 18]. ASTM C1012 is applicable to both portland and blended cement; however, a cement meeting the performance criteria will require 6 months of testing.

ASTM C452

ASTM C452 [19] involves accelerating the expansion of mortar bars by adding gypsum to a portland cement prior to making the mortar bars and thus its rate is not controlled by the transport properties of the mortar. In the test procedure, sufficient gypsum is added to dry portland cement so that the mixture has a sulfur trioxide (SO_3) content of 7 percent, based on mass of the mixture. Then, mortar bars (25 x 25 x 285 mm) are made, cured in their molds for around 23 hours, demolded and their lengths measured, before they are immersed in water, and their 14-day expansions measured. This test is rapid and does differentiate between high-C_3A and low-C_3A portland cement. However, it is not considered to be applicable to blended cements as the reaction between gypsum and portland cement has been found to be essentially completed before the mineral admixture portion of the blended cement has appreciably reacted with the hydroxide ions liberated by the hydration of the portland cement fraction [22].

Contrary to recommendations of ASTM E632, even with portland cement, the test conditions of C452 do not simulate field exposure of concrete to sulfate, which involves the ingress of sulfates into concrete and the subsequent exfoliation of the attack layers, opening up free surfaces and accelerating the

ingress of sulfate into the concrete. Therefore, as presently constituted, while C452 can be used to differentiate between the potential reactivity of portland cements, it cannot be used to differentiate between portland and blended cements (also, probably not between different blended cements), nor for predicting the sulfate resistance of concretes which depends on the rate of ingress of sulfates.

ASTM C1012

In the immersion test of ASTM C1012 [13], mortar bar specimens are immersed in a sulfate solution, 50 g/L, sodium sulfate, Na_2SO_4, (magnesium sulfate $(MgSO_4)$ may also be used) and their expansions periodically measured for periods of 6 months, or less, if the expansion criterion is exceeded earlier. Expansion limits depend on the severity of anticipated exposure conditions; (a) for moderate sulfate exposure conditions, the maximum expansion is 0.10% after 6 months and (b) 0.05% after 6 months for cements for use in severe exposure condition. Prior to being immersed, mortars should achieve a compressive strength of 20 MPa.

ASTM C1012 clearly more closely simulates field exposure conditions than does ASTM C452, in that sulfates penetrate the mortar prior to reacting with calcium hydroxide $(Ca(OH)_2)$ and the hydration products of C_3A. Also, in C1012 the cement is cured to an extent that most of C_3A is considered to have hydrated [22].

How well does C1012 simulate the field process? A possible significant problem is a change in the chemistry of test solutions. The test procedures stipulated that the beginning and replacement test solutions of Na_2SO_4 should have a pH of between 6 to 8. The test solution should be replaced when expansions are measured at specific periods. However, the pH rapidly rises approaching that of saturated calcium hydroxide, after a solution is replaced. In a report by Romanoff [23], the pH of 124 soils distributed throughout the United States averaged about 7 and ranged from 3.1 to 10.2. The pH of seawater is approximately 8 [24]. Reardon [25] modeled the effect of pH on phase changes of sulfoaluminate in concrete and found that ettringite decomposes at a pH<10.6 into gibbsite and gypsum. Along with a change in pH, the sulfate concentration decreases with time. Again following ASTM E632, the pH of the test solution should be close to the pH of the exposure, otherwise the degradation mechanisms could be different. Also, in an accelerated test, the sulfate concentration should either remain relatively constant or changes in concentration monitored so that reaction rates can be determined.

The model by Atkinson and Hearne [3] would predict that the results of C1012 should be sensitive to the diffusivity coefficient which is controlled by the curing of the mortar. Consistent with the modeling prediction, we have observed lengthy curing has significantly improved the sulfate resistance of test specimens. If curing is not well-controlled so that a specified diffusion or absorption is achieved, the test results will likely be too variable for a standard test method.

Constant-pH Test

Mehta and Gjorv [26] developed an immersion test in which the pH and the sulfate concentration were kept constant at a desired level, with the specimens being 10 mm cubes of high w/c paste. The idea of using a constant pH eliminating some of the problems associated with ASTM C1012. In their early experiments, Mehta and Gjorv kept the pH of the immersion solution at the original pH by manual titration with sulfuric acid (H_2SO_4); later the titration was automated by using a pH-stat [27]. Brown [28] further developed the test and investigated the effects of pH of the sulfate solution on strength and expansion. He found that control of the pH at 7 significantly increased the rate of sulfate attack, as measured by either strength loss or expansion, as compared to ASTM C 1012. The effect of controlling pH at 7 and simultaneously the sulfate concentration upon expansion is shown in Figure 2 [4].

An apparatus used by this paper's authors, similar to that used by Brown [28], is shown in Figure 3; it consists of a pH controller that measures the pH of the solution and, when the pH has decreased by a selected interval, the solenoid valve is opened to allow a dilute solution to sulfuric acid to flow at a low rate until a selected pH is attained. The solution is continuously circulated to mix each addition of sulfuric acid. In different series of experiments, we maintained constant sulfate concentrations and pH at 7, 9, and 11 units with an average deviation of ± 0.5 units.

The constant-pH appears to be a desirable feature of testing, since among other benefits, it allows simulation of field exposure conditions, e.g., the pH can be maintained at that of seawater, and if necessary a variable pH environment can be simulated. It can also accelerate the sulfate degradation process. However, its reproducibility has not been determined by inter-laboratory testing. The same comments made relative to curing in the analysis of C1012 are applicable to the constant-pH test.

Cyclic Wetting and Drying.

Even though degradation of concrete exposed to cycles of wetting (or soaking) and drying associated with a sulfate-containing water is likely to be more severe than continuous immersion [8], a standard wetting and drying test has not yet been developed. A soaking and drying sulfate test for high-strength concrete was described by de Almeida [29]. Cube specimens, 150 mm on edge, were immersed for 2 h. in a 16% Na_2SO_4 aqueous solution, followed by being dried at 105°C for 10 to 15 h. Then they were cooled to room temperature, their masses measured, and returned to the test solution for another test cycle. Performance was also measured by testing selected specimens in compression and by visual inspection. The results of the visual inspection were reported to be consistent with changes in mass and strength. In general, it was found that the porosity and capillary absorption controlled the performance of concrete more than the addition of mineral admixtures. Almeida suggested that, in rapid wetting and drying processes, the precipitation of soluble sulfate salts and accompanying phase changes control the degradation rather than the formation of calcium sulfate and ettringite.

In order to predict the service life of concrete exposed to sulfates, the Bureau of Reclamation [8] carried out a program lasting some 20 years in which the length change of 150 mm diameter, 300 mm long (6" x 12") concrete cylinders exposed to wetting and drying cycles were compared to length changes of companion concrete specimens exposed to continuous immersion. In both types of exposures a 2.1% Na_2SO_4 immersion solution was used. A wetting and drying
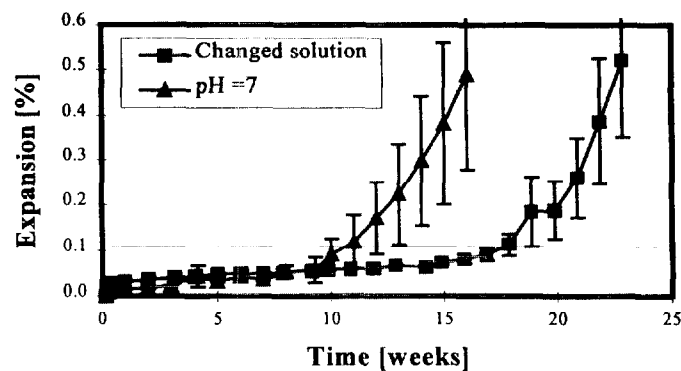
Figure 2. Comparison of expansion using ASTM C 1012, with 5% Na$_2$SO$_4$ solution changed each time a measurement was made, with a pH-controlled test at pH 7. [4].
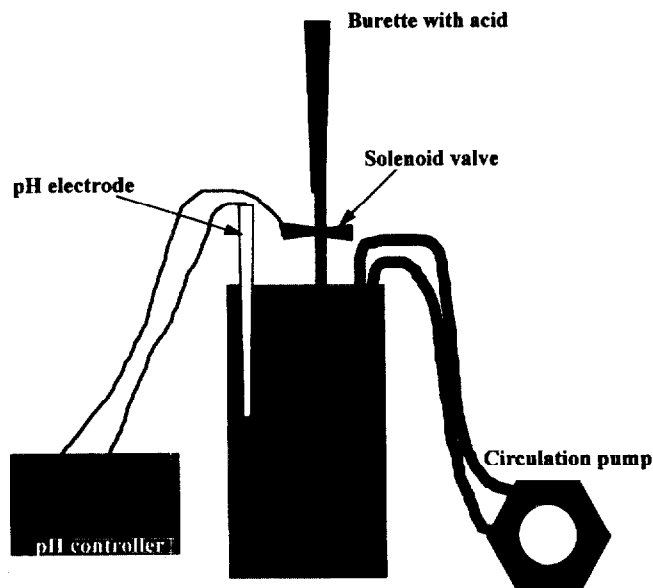

Figure 3. Schematic of pH-controlled test apparatus.

cycle consisted of immersing specimens in the 2.1% Na$_2$SO$_4$ solution for 16 hours at 21° to 27°C followed by forced air drying at 54°C for 8 hours. In the continuous immersion test, specimens were immersed at a temperature between 21° and 27°C and only removed when length measurements were made. From a comparison of the times for specimens to reach an expansion of 0.5% in both tests, it was estimated that 1 year of accelerated testing (i.e., wetting and drying) equaled 8 years of continuous immersion. The expansive mechanisms were not identified; however, the researchers concluded that imposing limits on C$_3$A and C$_4$AF were not the ultimate solution for preventing sulfate attack. Nevertheless, cements, portland or blended, with a maximum C$_3$A content of 6.5 % and a maximum C$_4$AF content of 12 % were recommended for making sulfate-resistant concrete.

Before we reject the wetting and drying test as not being applicable to sulfate attack in the field, more knowledge on the process should be obtained. None of the above studies were concerned with identifying the mechanisms of degradation by wetting and drying cycles, which poses the question "in these studies was the

degradation process purely physical involving crystal pressure or were chemical processes also involved, e.g., formation of ettringite?" Depending on the time of drying, both physical and chemical processes may be involved, with the chemical processes likely dominating with slower drying rates.

Notched Beam Test.

The sulfate test methods described so far involve either the measurement of linear expansion or the compressive strength. As discussed previously, the model developed by Atkinson and Hearne [3] indicates that such expansion and strength measurements are insensitive indicators of the progress of sulfate attack. For example, the voids in specimens are nearly filled with ettringite before appreciable expansion is measured. Since sulfate attack involves a moving interface [3,5], only the degraded zone will contribute to expansion or to the loss of strength (actually the compressive strength first increases as voids in a specimen are being filled with reaction products or by the precipitation of penetrating soluble salts [28]). Hughes and Grounds [30] suggested that a more sensitive indicator would involve monitoring microstructural changes in the degraded zone and they explored the use of notch beam specimens. The notched beam test was found to give an earlier indication of sulfate attack than expansion measurements, while giving the same ranking of relative durability. A notch beam test should be sensitive to surface and subsurface discontinuities which arise from the delaminating of layers, from the outside surface inwards, during external sulfate attack. Similar to the results observed with other test methods, the maximum load for notched beam specimens was dependent on the period of curing, with blended cement specimens being especially sensitive.

DISCUSSION AND RECOMMENDATIONS

Based on our analysis, it appears that two rather distinct standards/specifications appear to be needed: 1) a rapid standard test for determining the potential reactivity of cements to sulfates; and 2) a standard method for the service life design of concrete in which sulfate attack is a one of the major degradation processes. Even if these needs are fulfilled, prescriptive specifications will likely continue to be used.

Test Methods for Determining the Potential Sulfate Reactivity of Cements

The present test ASTM C 1012 [13] for evaluating the sulfate resistance of mortars can require up to 6 months testing, which may not impede the introduction to the market place of new cements as numerous other tests would

need to be performed. However, if the composition of a mineral admixture used to produce a blended cement is changed, the manufacturer may be required to subject the blended cement to the ASTM C 1012 test, to demonstrate performance equivalency. For example, for blended cement Types MS and HS, ASTM C1157 requires re-testing of sulfate resistance if analysis shows the change mass of any oxide of the blended cement or any constituent making up 10% or more of the cement is $\geq$ 3%; or if the oxide composition changes by $\geq$ 5% for constituents making up less than 10% of the blended cement. In such a case, 6 months of testing would almost certainly cause problems to a company striving to maintain its production. It follows that, for such cases, a new accelerated test should be developed, possibly based on the methodology outlined in ASTM 632 [1]. For example, combining the constant pH test, with a more sensitive monitor of sulfate attack than the measurement of expansion, appears to be a reasonable approach. Application of fracture mechanics techniques may offer a way to develop a more sensitive monitoring tool. Details such as the curing regime so that the test mortars have the same transport properties would need to be worked out. Other possible ways of accelerating the tests such as changing the dimensions (surface to volume ratio) and shape (tubular, cylindrical or spherical) of test specimens, as well as optimizing the mixture design should be explored. The possibility of modifying ASTM C452 [19] could be explored as it is more rapid and more closely evaluates the potential reactivity of cements than does ASTM C1012. One approach would be to combine gypsum with a partially hydrated cement paste and make compressed specimens that are exposed to a sulfate solution. By this approach, ASTM C452 may become applicable to all types of hydraulic cements. A similar test method used in some European countries, the Anstett test, has been described by Mather [12]. Hopefully, these suggestions will stimulate the development of new test methods that overcome the deficiencies recognized in the existing methods.

Service Life Design of Concrete.

One of the major concerns to an engineer/designer specifying a concrete that will be exposed to an aggressive sulfate environment, is its service life. Our present test methods and specifications for concrete only provide a qualitative basis for ranking relative durability with no quantitative assessment of service life. The model by Atkinson and Hearne [3] has been used in predicting the service life of underground concrete vaults [31] and appears to give predictions that relate to experience, which suggests that further improvements in the model should be pursued. A significant problem of using the model is the lack of validated sulfate diffusion data as such a standard test has not been developed [32]. A computer model has been developed [33] to predict the chloride ion

diffusivity of concrete, which in principle could be used to predict the potential diffusivity of sulfate ions.

Prescriptive Standards versus Performance Standards.

A recommendation from the workshop on *Cement and Concrete Standards of the Future* [34] was that performance test methods, performance standards and performance prediction methodologies should be developed for assessing and quantifying the performance of cement-based materials. However, it was recognized that prescriptive criteria will continue to play an important role far into the future. Regarding prescriptive specifications for C_3A contents of cements, Bryant Mather in a keynote presentation at the workshop, commented that while performance standards are preferred, if satisfactory performance can be ensured more quickly and simply by placing a limit on C_3A calculated from chemical analysis, then such specifications should be invoked. In addition, however, he commented that performance tests are needed so that cements and concretes with novel compositions can compete and innovated materials or systems can be evaluated.

Prescriptive specifications for cements pose barriers to innovation because they put rigid limits on the range of permitted compositions. However prescriptive specifications can reduce risks that may arise from using cements with an unrestricted range of compositions, especially if there are not reliable performance tests. It has been suggested [35] that performance-based specifications be developed with optional prescriptive criteria. Assuming that prescriptive specifications will continue to be used in the future, we suggest that to be reliable and widely applicable, they should be based on a materials science perspective, rather than being based upon empiricism. An example of such a materials science approach is the computer modeling of microstructural and associated properties of hydrating portland cement deveoped by Bentz [36].

SUMMARY

The purpose of this paper is to discuss: 1) the current status of standards for controlling or predicting the durability or service life of portland cement-based materials exposed to aqueous sulfate solutions; and 2) improvements needed in the standards. Both standard performance tests and criteria, and prescriptive specifications, are available for selecting cement-based materials when sulfate attack is of concern. Some of the deficiencies in performance tests include lengthy testing periods, the insensitivity of the measurement tools to the progression of sulfate attack, and failure to simulate field degradation

mechanisms. Ways to overcome these deficiencies are discussed based on the application of the methodology outlined in ASTM E 632, "Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials" [1]. Prescriptive specifications for sulfate resistance usually pose restrictions on the C_3A content of cements. Also, depending on the severity of the sulfate exposure, the use of blended cements or mineral admixtures may be specified.

Three major types of exposure conditions are associated with sulfate attack: 1) immersion in sulfate-containing water; 2) wetting and drying cycles; and 3) partial immersion with evaporation. Standard test methods, e.g., ASTM C 452 and C 1012 only address the immersion process, while no standard tests exist for exposure conditions 2 and 3, even though they may be more destructive than the immersion exposure condition. It is generally assumed that the destructive process in exposure conditions 2 and 3 involves precipitation/crystallization processes; however, this assumption does not appear to have been rigorously validated.

Based on our analysis, two rather distinct standards/specifications appear to be needed: 1) a rapid standard test for determining the potential reactivity of cements to sulfates; and 2) a standard method for the service life design of concrete in which sulfate attack is a one of the major degradation processes. Recommended approaches for developing such standards include modification of existing test methods and application of modeling based on material science principles.

ACKNOWLEDGEMENTS

REFERENCES

[1]   ASTM Designation E 632, "Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials" (ASTM, Philadelphia, PA).
[2]   P.K. Mehta, "Mechanisms of Sulfate Attack on Portland Cement Concrete-Another Look," Cement and Concrete Research, V.13, pp. 401-406, 1983.
[3]   A. Atkinson and J.A. Hearne, "Mechanistic Model for the Durability of Concrete Barriers Exposed to Sulphate-Bearing Groundwaters," Materials Research Society Symposium Proceeding, V. 176, pp. 149-156, 1990.

[4]   C.F. Ferraris, J.R. Clifton, P.E. Stutzman, and E.J. Garboczi, "Mechanisms of Degradation of Portland Cement-Based Systems by Sulfate Attack," in *Mechanisms of Chemical Degradation of Cement-based Systems*, eds. K.L. Scrivener and J.F. Young, E&FN Spon (London, 1997).

[5]   J.M. Pommersheim and J.R. Clifton, "Expansion of Cementitous Materials Exposed to Sulfate Solutions," Materials Research Society Symposium Proceedings,V. 333, pp. 363-368, 1994.

[6]   J.R. Clifton and J. Pommersheim, "Sulfate Attack of Cementitous Materials: Volumetric Relationships and Expansions," NISTIR 5390, National Institute of Standards and Technology (Gaithersburg, MD 1994).

[7]   J.R. Clifton and L.I. Knab, "Service Life of Concrete," Report No. NUREG CR-5466, U.S. Nuclear Regulatory Commission (Washington, D.C., 1989).

[8]   G.L. Kalousek, L.C. Porter, and E.J. Benton, "Concrete for Long-Term Service in Sulfate Environment," Cement and Concrete Research, V.2 (1), pp. 79-90 (1972).

[9]   G.C. Price and R. Peterson, "Experience with Concrete in Sulphate Environments in Western Canada," pp. 93-112, in Performance of Concrete, ed. E.G. Swenson, University of Toronto Press (1968).

[10] J.J. Hamilton and G.O. Handegord, "The Performance of Ordinary Portland Cement Concrete in Prairie Soils of High Sulphate Content," pp135- 158, *ibid.* 9.

[11] ASTM Designation C 150, "Standard Specification for Portland Cement" (ASTM, Philadelphia, PA).

[12] K. Mather, "Tests and Evaluation of Portland and Blended Cements for Resistance to Sulfate Attack," pp. 74-86, in Cement Standards Evolution and Trends, ed. P.K. Mehta, ASTM STP 663 (ASTM, Philadelphia, PA, 1977).

[13] ASTM Designation C 1012, "Standard Test Method for Length Change of Hydraulic-Cement Mortar Exposed to a Sulfate Solution," (ASTM, Philadelphia, PA).

[14] ACI 201 "Guide to Durable Concrete," AC I Manual of Concrete Practice: Part 1-1998 (American Concrete Institute, Farmington Hill, MI).

[15] Minimum Requirements for Durable Concrete: Carbonation- and Chloride-induced Corrosion, Freeze-Thaw Attack and Chemical Attack, ed. by D.W. Hobbs, British Cement Association (1998).

[16] P.K. Mehta, "Effect of Fly Ash Composition on Sulfate Resistance of Cement," Journal of the American Concrete Institute, V83 (6), pp. 994-1000 (1986).

[17] ASTM Designation C 1157M, "Standard Performance Specification for Blended Hydraulic Cement [Metric] " (ASTM, Philadelphia, PA).

[18] P.K. Mehta, "Sulfate Attack on Concrete-A Critical Review," pp. 105-130, Material Science of Concrete III, ed. by J. Skalny, American Ceramic Society (1992).

[19] ASTM Designation C 452, "Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate" (ASTM, Philadelphia, PA).

[20] M.D. Cohen and B. Mather, "Sulfate Attack on Concrete - Research Needs," AC I Materials Journal, V.88 (1), pp. 62-69 (1991).

[21] I. Biczok, Concrete Corrosion and Concrete Protection, Chemical Publishing Company, Inc., NY (1967).

[22] T. Patzias, "Evaluation of Sulfate Resistance of Hydraulic-Cement Mortars by the ASTM C 1012 Test Method," pp. 92-99 in Concrete Durability, ACI SP-100, American Concrete Institute (Farmington Hills, MI, 1987).

[23] M. Romanoff, "Underground Corrosion," National Bureau of Standards Circular 579 (1957): [Now the National Institute of Standards and Technology].

[24] Handbook of Chemistry and Physics, 73rd edition, CRC Press (1992).

[25] E.J. Reardon, "An Ion Interaction Model for Determination of Chemical Equilibra in Cement-Water Systems," Cement and Concrete Research, V.20, pp. 175-192 (1990).

[26] P.K. Mehta and O.E. Gjorv, "A New Test for Sulfate Resistance of Cements," Journal of Testing and Evaluation, V.2 (6), pp.510-514 (1974).

[27] P.K. Mehta, "Evaluation of Sulfate Resistance of Cements by a New Test Method," Journal of the American Concrete Institute, V.72 (10) pp. 573-75 (1975).

[28] P. Brown, "An Evaluation of the Sulfate Resistance of Cements in a Controlled Environment," Cement and Concrete Research, V.11, pp. 719-727 (1981).

[29] I.R. de Almeida, "Resistance of High Strength Concrete to Sulfate Attack: Soaking and Drying Test," pp. 1073-1092 in Concrete Durability, ACI SP-100, American Concrete Institute (Farmington Hills, MI, 1987).

[30] D.C. Hughes and T. Grounds, "The Use of Beams with a Single Edge Notch to Study the Sulphate Resistance of OPC and OPC/PFA Pastes," Magazine of Concrete Research, V.37 (131), pp. 67-74 (1985).

[31] K.A. Snyder and J.R. Clifton, "4SIGHT Manual: A Computer Program for Modelling Degradation of Underground Low Level Waste Concrete Vaults," NISTIR 5612, National Institute of Standards and Technology (Gaithersburg, MD, 1995).

[32] J.R. Clifton, D.P. Bentz, and J.M. Pommersheim, "Sulfate Diffusion in Concrete," NISTIR 5361, National Institute of Standards and Technology (Gaithersburg, MD, 1994).

[33] D.P. Bentz, E.J. Garboczi, and E.S. Lagergren, "Multi-Scale Microstructural Modeling of Concrete Diffusivity: Identification of Significant Variables," Cement, Concrete, and Aggregates, V.20 (1) pp. 129-139 (1998).

[34] G. Frohnsdorff and J. Clifton, "Cement and Concrete Standards of the Future: Report from the Workshop on Cement and Concrete Standards of the Future - October 1995," NISTIR 5933, National Institute of Standards and Technology (Gaithersburg, MD, 1997).

[35] G. Frohnsdorff, P.W. Brown, and J.H. Pielert, "Standard Specifications for Cements and the Role in their Development of Quality Assurance Systems for Laboratories," *Proceeding*, 8th International Congress on the Chemistry of Cement, Vol. VI, pp. 316-320 (Rio de Janeiro, Brazil, 1986).

[36] D.P. Bentz, "Three Dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development," Journal of the American Ceramic Society, V.80 (1), pp. 3-21 (1997).