Pergamon

Cement and Concrete Research 32 (2002) 585–592

CEMENT AND CONCRETE RESEARCH

Modeling the effects of solution temperature and concentration during sulfate attack on cement mortars

Manu Santhanam, Menashi D. Cohen*, Jan Olek

School of Civil Engineering, Purdue University, West Lafayette, IN 47907, USA

Received 27 June 2001; accepted 30 October 2001

Abstract

Simple chemistry-based empirical models have been developed to assess the role of temperature and concentration of the sulfate solution in the process of expansion of cement mortars that are subjected to external sulfate attack. ASTM Type I PC mortars, prepared according to ASTM C-109, were immersed in sodium and magnesium sulfate solutions at five different concentrations and four different temperatures. For both solutions, the trends in the measured expansion suggested the use of a simple rate law to analyze the effect of concentration. For the effect of temperature, an Arrhenius relationship was developed to determine the activation energy required to initiate expansion in sodium sulfate solution. Regression-based statistical models were found to be sufficient to explain the effect of temperature of magnesium sulfate solution on the expansion. Implications of using these models for developing potential test methods, as well as to enable interpretation of data from nonstandard test methods, are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfate attack; Expansion; Modeling; Temperature; Rate law

1. Introduction

Reliable models, in addition to appropriate laboratory test techniques, are necessary in order to predict service life and to select suitable materials for structures exposed to sulfate-rich environments. It is not always possible to create field-like conditions in the laboratory. The primary difficulties are related to the scale of testing, as well as the need for results within a short time period. However, it is often possible to design adequate accelerated tests, which can mimic, to a certain degree, the behavior of concrete under field conditions. According to ASTM E 632-82 (Standard Practice for Developing Accelerated Tests to Aid Prediction of Service Life of Building Components and Materials) [1], accelerated aging tests are ones in which the degradation of building materials is intentionally accelerated over that expected in service. One basic assumption in this methodology is that the mechanisms of action in the laboratory and the field are identical. In the case of sulfate attack, however, the mechanism of concrete deterioration depends on numerous factors, including the effects of the service environment, such as concentration of sulfate in the solution, and temperature and humidity variations. Thus, in order to predict concrete performance in situations involving sulfate attack, it is essential to incorporate these effects into any model that is developed for prediction purposes.

The current test method for sulfate attack, ASTM C-1012 [2], suggests the use of a 50-g/l Na_2SO_4 solution (5 mass%, or 33,800 ppm SO_4^{2-}). It also states that other sulfate solutions, such as $MgSO_4$, and other concentrations, may be used to simulate the desired exposure conditions. It should be noted that a concentration of 5% leads to a rapid attack, which is desired in the laboratory. Thus, most studies tend to use sulfate solutions that are of nearly the same concentration. The exposure levels commonly found in field conditions are an order of magnitude lower in concentration. The effect of varying concentrations becomes critical especially in field structures where the same concrete column may be attacked in different regions by different concentrations of sulfates due to the development of drying and wetting fronts. Sulfate concentration gradients may also exist through the depth of slabs on grade.

According to Biczok [3], the mechanism of sulfate attack can change with a change in the concentration of the sulfate

---

* Corresponding author. Tel.: +1-765-494-5018; fax: +1-765-496-1364.
E-mail address: mcohen@ecn.purdue.edu (M.D. Cohen).

PII: S0008-8846(01)00727-X

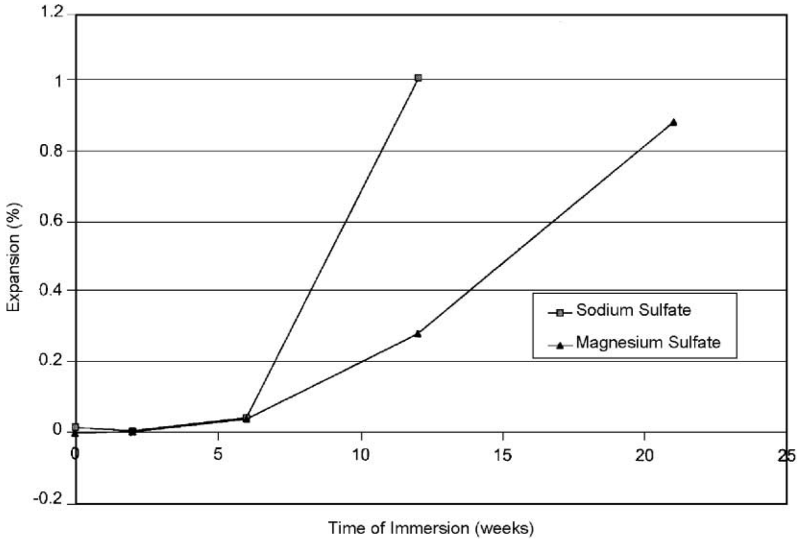

Fig. 1. Expansion of PC mortars in sodium and magnesium sulfate solutions.

solution. For attack by sodium sulfate solution, at a low concentration of sulfates (< 1000 ppm SO_4^{2-}), the primary product deposited is ettringite, while at high concentrations (> 8000 ppm SO_4^{2-}), gypsum is the main product. In the intermediate range (1000–8000 ppm SO_4^{2-}), both gypsum and ettringite are observed. In magnesium sulfate attack, ettringite production is observed at a low concentration (< 4000 ppm SO_4^{2-}), a mixture of ettringite and gypsum forms at an intermediate concentration (between 4000 and 7500 ppm SO_4^{2-}), and magnesium corrosion dominates at high concentrations (>7500 ppm SO_4^{2-}).

Akoz et al. [4] studied the effect of varying concentrations of sodium sulfate on the sulfate resistance of cement mortars with and without silica fume. At low concentrations (< 18,000 ppm SO_4^{2-}), no significant deterioration of the mortars was observed up to 300 days of exposure. For high concentration solutions, a 'critical time' was defined. Physical properties were seen to change slowly until this time, after which the change observed was large. However, a study of the mechanism was not performed.

Ferraris et al. [5] found that the pH and concentration of the sulfate solution played an important role in the rate of expansion of the specimens. A higher concentration of sodium sulfate in the solution led to quicker expansion of the specimens. Increasing the pH of the storage solution led to a reduced rate of expansion.

Ping and Beaudoin [6,7] proposed a new theory of sulfate-related expansion based on thermodynamics. According to them, 'crystallization pressure', which is a result of the interaction between attack products such as ettringite, and the cement paste, is responsible for expansion. Two conditions are necessary to maintain the crystallization pressure, namely, the growth of the crystal in a confined region, as well as a high concentration of reactants that drive the reaction. Using this philosophy, they suggest that the best way to minimize the expansion is by reducing the concentration of Ca^{2+} and SO_4^{2-} in the solution. However, no experimental evidence was provided related to the effect of SO_4^{2-} concentration. The temperature of the solution was identified as an important factor controlling the expansion of the specimens. Expansion was determined to be proportional to the temperature of the solution. The principal effect of temperature, according to the theory proposed, was to increase the crystallization pressure due to the formation of the solid product.

Lawrence [8], in his comprehensive review of sulfate attack, presented some data regarding the temperature of the sulfate solution. In sodium sulfate, the increase in temperature reduced the time to a given expansion. The effect of increasing the temperature of magnesium sulfate, however, was not very clear. Many other data for slag cements and seawater solutions were also presented in the same publication.

In summary, it is evident from the available literature that an attempt to model the effects of concentration and

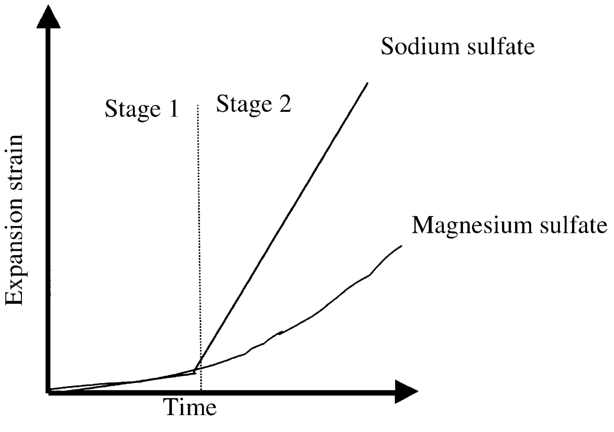

Fig. 2. Observed trends from expansion measurements in the two solutions.

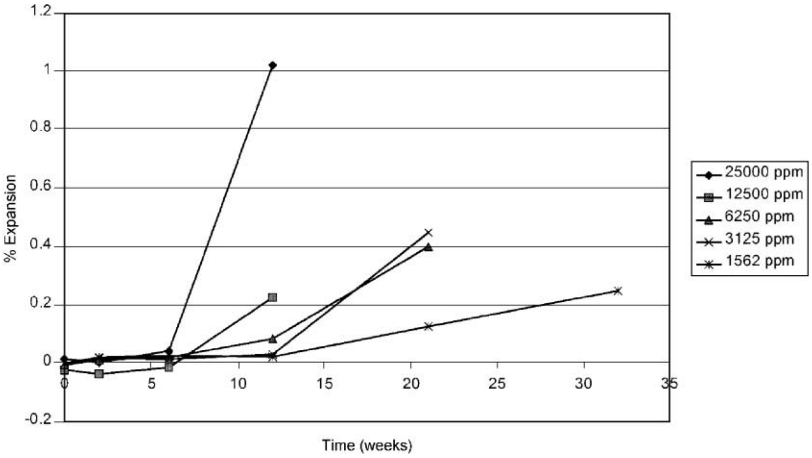

Fig. 3. Expansion of PC mortars immersed in sodium sulfate solutions of various concentrations (expressed in terms of ppm of SO_3).

temperature of the sulfate solution on the performance of cement mortars and concrete has not been made. This article presents an effort to simplify the analysis of these effects, in order to enable design of new test methods, as well as ease the interpretation of results from nonstandard tests. With some additions, such as validation of the results using large specimens, as well as comparison of data from tests using concrete specimens, these models could also help in field performance prediction.

2. Experimental methods

Mortars prepared with ASTM Type I cement, according to the mixture proportions defined in ASTM C-109, and mixing procedures defined in ASTM C-305 were immersed in sodium and magnesium sulfate solutions. The temperatures of storage were 40, 70, 85, and 100 °F (5, 21, 30, and 38 °C). Five different concentrations were evaluated for each type of solution. These had an equivalent SO_3 content of 25,000, 12,500, 6250, 3125, and 1562 ppm (parts per million, or milligrams per liter). The length of 5 × 16 × 80 mm mortar prisms, with acrylic end pieces, was measured periodically. The data presented in the plots are average expansions for each set of three length measurements.

3. Results

3.1. Observations from the research study

The measured expansion of PC mortars in sodium and magnesium sulfate solutions is presented in Fig. 1. The schematic plot shown in Fig. 2 represents the observed trends in expansion.

The expansion of mortars in sodium sulfate solution follows a two-stage process, as shown in Fig. 2. Other researchers, such as Ferraris et al. [5], have reported a similar observation. An initial period of very small expansion (Stage 1) is followed by a sudden increase in the expansion. The rate of expansion in Stage 2 is nearly constant up to the point of complete failure of the specimens. In the case of magnesium sulfate solution, a gradual increase in the rate of expansion is observed.

The expansion of PC mortars immersed in sodium sulfate solutions of various concentrations is presented in Fig. 3, and the corresponding schematic plot showing the dependence of expansion on solution concentration is shown in Fig. 4.

Increasing the concentration of the sodium sulfate solution did not change the length of Stage 1. However, the rate of expansion in Stage 2 was proportional to the concentration, as shown in Fig. 4.

An increase in temperature, however, shortened the duration of Stage 1 expansion without causing any appreciable change in the rate of expansion in Stage 2. The experimental data for the effect of temperature on the

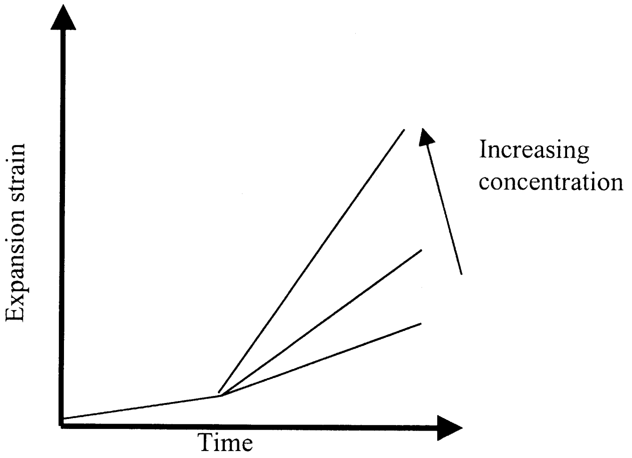

Fig. 4. Observed trends for expansion of PC mortars immersed in sodium sulfate solutions of various concentrations.

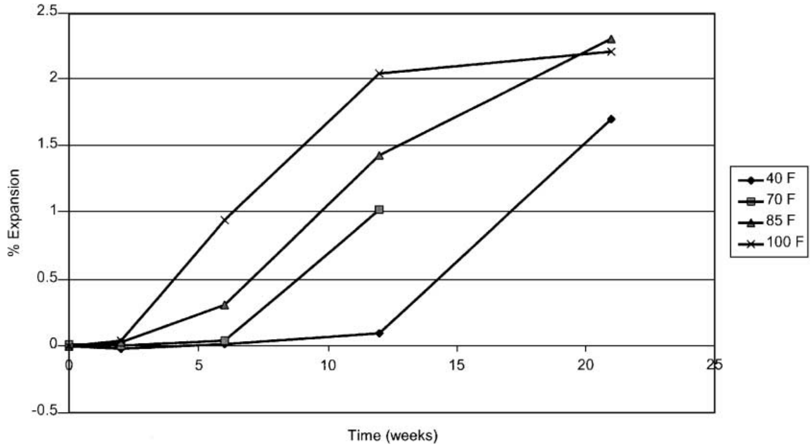

Fig. 5. Expansion of PC mortars immersed in sodium sulfate solutions at various temperatures.

expansion of PC mortars stored in sodium sulfate solution and the corresponding schematic plot are presented in Figs. 5 and 6, respectively.

The experimental data for the variation in expansion of PC mortars subjected to attack by magnesium sulfate solutions at different concentrations and temperatures are plotted in Figs. 7 and 8, respectively. The corresponding schematic plot showing the effect of temperature and concentration is presented in Fig. 9. According to the observed trends, an increase in the temperature, or in the concentration, of the magnesium sulfate solution results in an increase in the rate of expansion.

3.2. Rate law models for the effects of solution concentration

The rate of expansion in the concentration study was calculated as the slope of the line representing the relationship between expansion, in percent, and time, in weeks, during Stage 2, for sodium sulfate solution. In the case of magnesium sulfate solution, the rate of expansion was simply taken as the expansion at a particular time period divided by the time elapsed in weeks. The rate law for this study may be written as (Eq. (1)) [9]

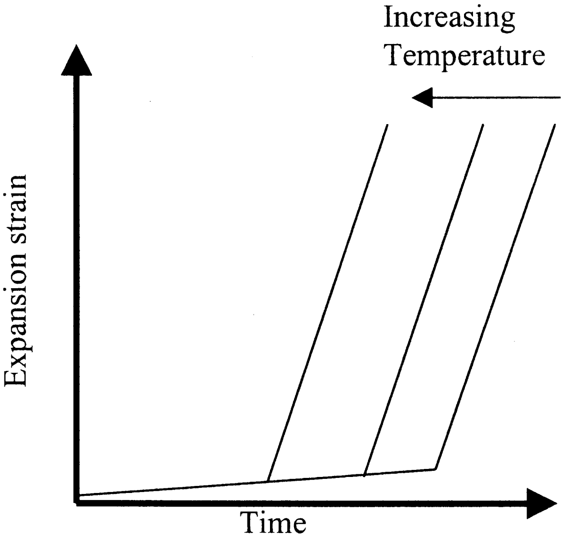

Fig. 6. Observed trends for expansion of PC mortars immersed in sodium sulfate solutions at various temperatures.

$$\text{Rate} = k[\text{SO}_3]^n \tag{1}$$

where $[\text{SO}_3]$ is the concentration of SO_3 in the solution (in ppm), k is the rate constant, and n is the order of the reaction. Taking the natural log on both sides, we get Eq. (2).

$$\ln(\text{Rate}) = \ln(k) + n\ \ln([\text{SO}_3]) \tag{2}$$

Hence, a plot between the natural log of rate and the natural log of concentration would yield a straight line, with a slope of n units, and an intercept of $\ln(k)$.

3.2.1. Sodium sulfate

The data from the results collected for sodium sulfate agree with the straight-line relationship suggested by the rate law theory, as seen in Fig. 10. Using this plot and the regression equation, predictions about the rate of expansion during Stage 2 can be made for an unknown concentration.

From the plot in Fig. 10, the values of n and k are determined to be 0.89 and 1.44×10^{-5}, respectively. Therefore,

$$\begin{aligned}&\text{Rate of expansion (\%/week)}\\&\quad = 1.44 \times 10^{-5}(\text{Concentration of SO}_3,\ \text{in ppm})^{0.89}\end{aligned} \tag{3}$$

3.2.2. Magnesium sulfate

The plot and the regression equation for expansion in magnesium sulfate solutions are shown in Fig. 11. From the plot, the values of n and k are determined to be 0.23 and 6.07×10^{-3}, respectively. The fit of the model, as meas-

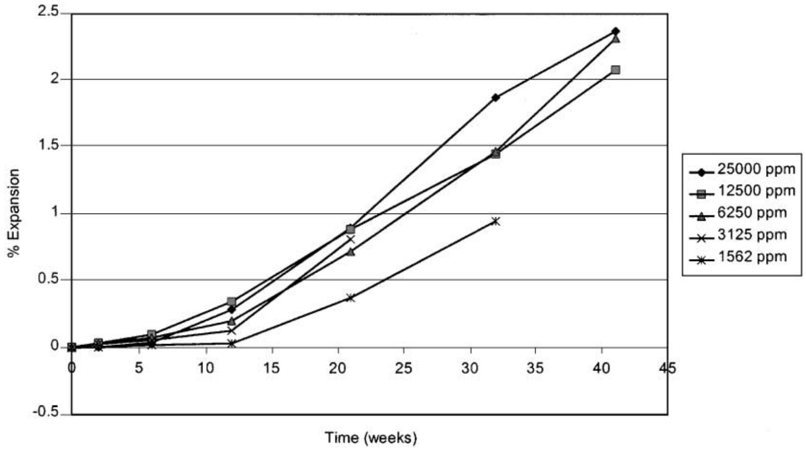

Fig. 7. Expansion of PC mortars immersed in magnesium sulfate solutions of various concentrations (expressed as ppm of SO_3).

ured by the R^2 value, is not as good as the model for expansion in sodium sulfate. The discrepancy is caused by the data point for the solution with a concentration of 6250 ppm SO_3. Therefore, for magnesium sulfate solution, Eq. (4) holds.

$$\text{Rate of expansion (\%/week)} = 6.07 \times 10^{-3}(\text{Concentration of SO}_3,\ \text{in ppm})^{0.23} \quad (4)$$

3.3. Models for effects of temperature

3.3.1. Sodium sulfate

The prediction from the concentration model would only be able to give the rate of expansion during Stage 2. In order to determine the duration of Stage 1, the activation energy of the reaction has to be determined. This is done using the data from temperature studies.

The Arrhenius relation for the activation energy of a chemical reaction may be written in the following form (Eq. (5)) [9]:

$$k = A\exp(-E_a/RT) \quad (5)$$

where k is the rate constant, A the 'frequency factor' (which is related to the frequency of interatomic collisions), E_a the activation energy, R the universal gas constant, and T the temperature in Kelvin.

In the present study of the effect of temperature, k is defined as the inverse of the time taken to complete Stage 1, or t_1 (in days) (Eq. (6)).

$$k = 1/t_1 \rightarrow t_1 = A_1\exp(E_a/RT) \quad (6)$$

where A_1 is another constant.

Taking the natural log on both sides, we have Eq. (7).

$$\ln(t_1) = \ln(A_1) + E_a/RT \quad (7)$$

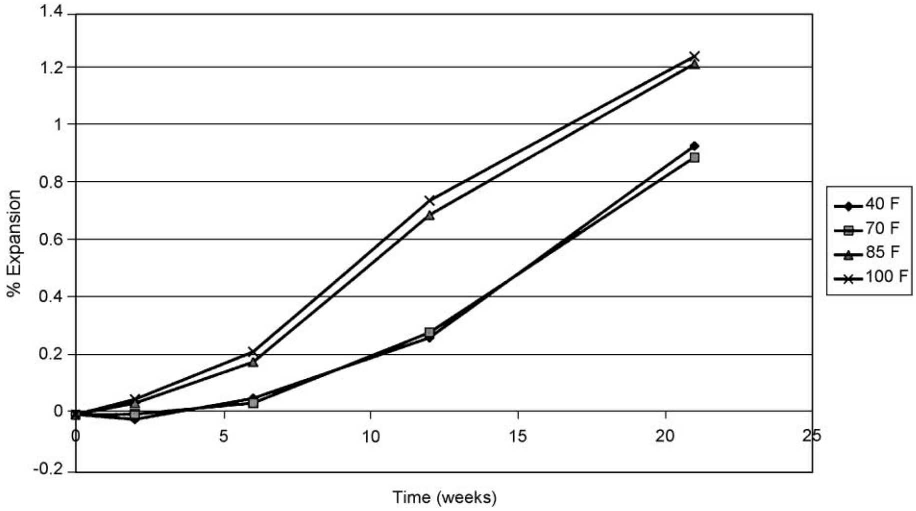

Fig. 8. Expansion of PC mortars immersed in magnesium sulfate solutions at various temperatures.

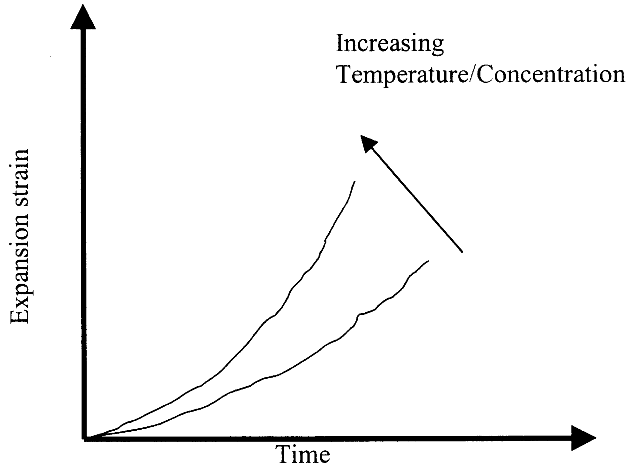

Fig. 9. Observed effects of changing temperature or concentration of magnesium sulfate solution on the expansion of mortar specimens.

Thus, a plot of the natural log of the time for completion of Stage 1 versus the inverse of the temperature in Kelvin would yield a straight-line relationship with a slope equal to E_a/R. The activation energy can then be calculated from the slope. The Arrhenius plot for the current temperature study is presented in Fig. 12. The experimental data satisfies a straight-line relationship with a high degree of correlation (R^2=.96). This indicates that the mechanism driving the reaction at all temperatures should be the same.

As per the regression equation, the slope of the plot is $E_a/R = 4430.7$ K. Hence, using $R = 2$ cal/K mol, the calculated activation energy is $E_a = 8861.4$ cal/mol, or 8.9 kcal/mol. In addition, $\ln(A_1) = -11.45 \rightarrow A_1 = \exp(-11.45)$.

Thus,

$$t_1 \text{ (in days)} = \exp(-11.45)\exp(4430.7/T) = \exp(4430.7/T - 11.45) \quad (8)$$

where T is the immersion temperature in Kelvin.

For example, for a temperature T of 25 °C, t_1 is calculated to be equal to 30 days. Suppose the expansion at 20 weeks for a PC mortar in a sodium sulfate solution of 20,000 ppm SO_3 concentration at 25 °C is desired. From Eq. (8), the duration of Stage 1 is 30 days, or approximately 4 weeks. According to Eq. (3), the rate of expansion (in %/week) is given by:

$$\text{Rate} = 1.44 \times 10^{-5}(20,000)^{0.89} = 0.097\ \%/\text{week}$$

Hence, total expansion at 20 weeks is $(20-4) \times 0.097 = 1.552\%$.

3.3.2. Magnesium sulfate

The pattern for the expansion in magnesium sulfate solutions at different temperatures suggests that a simple regression relationship would sufficiently explain the data. For the current study, the regression model was fitted using the Statistical Analysis Software (SAS) and gave the following results (Eq. (9)):

$$\text{Expansion} = 0.005(\text{Temperature}) + 0.062(\text{Time of immersion}) - 0.529 \quad (9)$$

The R^2 value for the regression was .97, which suggests a good fit. The P value for the model, at a 95% confidence level, was <.0001.

4. Discussion

4.1. Reasons for the observed trends

In both solutions, the expansion is a result of the formation of products, like ettringite and gypsum, which result from the reactions between sulfate solutions and hydrated cement paste. For sodium sulfate, the presence of

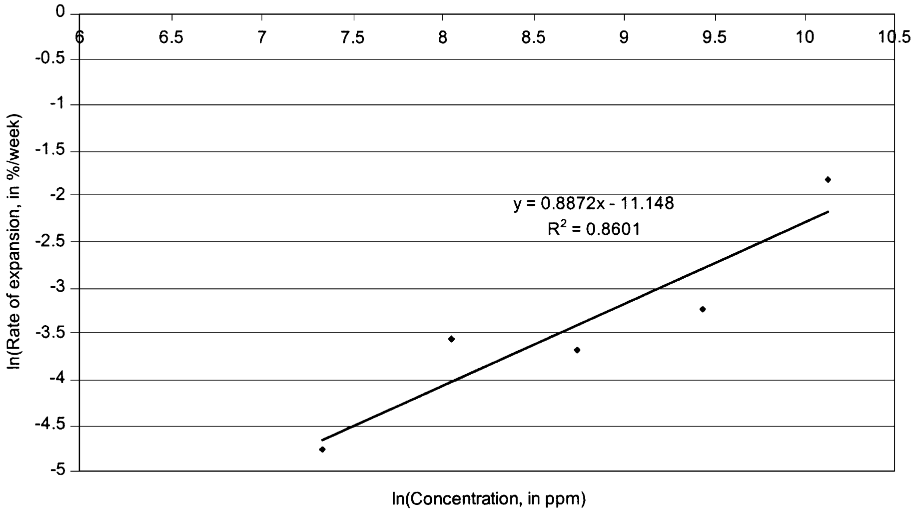

Fig. 10. Rate law study for the effect of concentration on expansion in Na_2SO_4 solution.

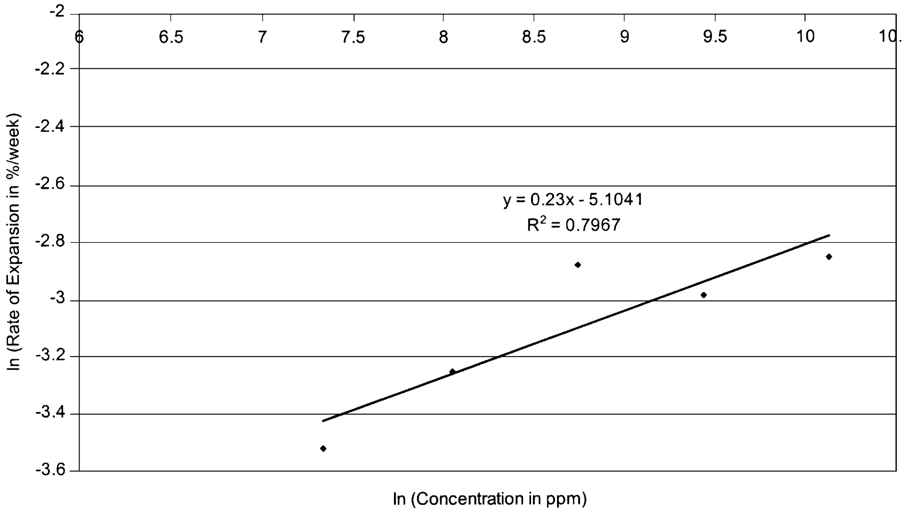

Fig. 11. Rate law study for effect of concentration on expansion in $MgSO_4$ solution.

the initial period of low expansion (Stage 1) could be explained by the ability of the mortars to accommodate the attack products. When the level of attack products in the matrix crosses a critical value, expansion occurs. An increase in temperature would cause a quicker deposition of attack products and thus lead to a shortening of the duration of Stage 1. The change in concentration, however, does not cause a change in the duration of Stage 1. Once the initial level of disruption is achieved, the rate of attack is proportional to the concentration.

For magnesium sulfate, the immersion of specimens in the solution causes a layer of brucite ($Mg(OH)_2$) to form on the surface almost immediately [10]. Thus, the reaction proceeds by the diffusion of sulfate ions across this barrier. The rate of diffusion increases with the time of immersion, and, hence, the rate of expansion also continuously increases. An increase in temperature or concentration causes the rate of diffusion to increase. Thus, both these parameters have the same effect of increasing the rate of expansion.

4.2. Potential applications of the models

Researchers tend to use various nonstandard test methods to investigate sulfate attack. The results from the models described in this study could help in interpreting the data from these nonstandard tests. The methods that have been outlined here are fairly simple to perform. Modifications of the current ASTM test procedure [2] are also possible. In order to accelerate the reaction, an increase

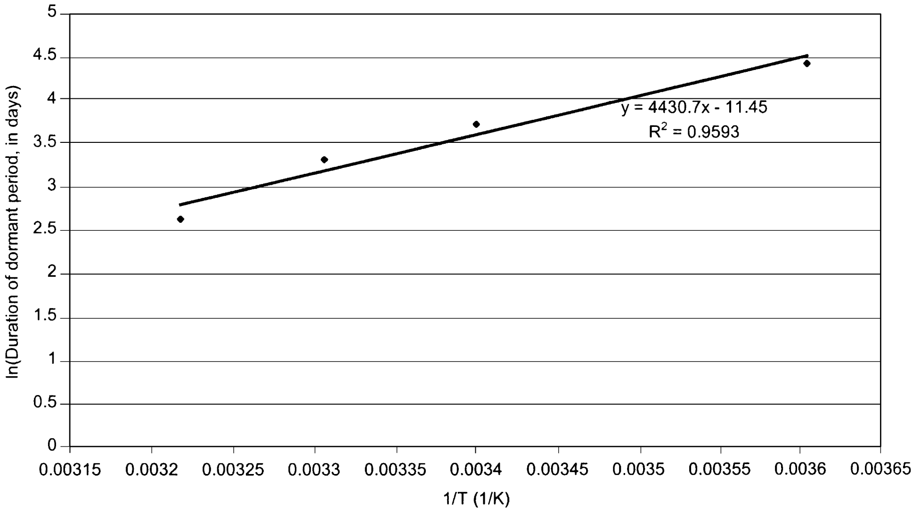

Fig. 12. Modified Arrhenius plot for the temperature effect study for Na_2SO_4 solution.

in the temperature or concentration can produce results in a shorter duration.

4.3. Additional studies needed

The work described in this study was based on small mortar specimens. Size and shape effects also need to be considered in order to make these models more reliable. Another important addition could be the use of a different physical parameter, such as mass change, or compressive strength.

5. Summary

The effects of concentration and temperature of sodium and magnesium sulfate solutions on the expansion of cement mortars were modeled using simple chemistry-based relationships. The concentration effect for both solutions was modeled as a rate law, while a modified Arrhenius relationship was used to account for the temperature of sodium sulfate solution. Simple regression models were sufficient to explain the variation in expansion with the temperature of magnesium sulfate solution. Using the results from these models, modification of current procedures to evaluate sulfate resistance is possible. In addition, the models make it easier to interpret data from nonstandard test methods.

References

[1] ASTM Standard Designation E 632, Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials, American Society of Testing and Materials, Philadelphia, PA, USA, 1995.

[2] ASTM Standard Designation C 1012, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution, American Society of Testing and Materials, Philadelphia, PA, USA, 1995.

[3] I. Biczok, Concrete Corrosion Concrete Protection, Chemical Publishing, New York, 1967.

[4] F. Akoz, F. Turker, S. Koral, N. Yuzer, Effect of sodium sulfate concentration on the sulfate resistance of mortars with and without silica fume, Cem. Concr. Res. 25 (6) (1995) 1360–1368.

[5] C.F. Ferraris, J.R. Clifton, P.E. Stutzman, E.J. Garboczi, Mechanisms of degradation of portland cement-based systems by sulfate attack, in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Systems, E & FN Spon, London, 1997, pp. 185–192.

[6] X. Ping, J.J. Beaudoin, Mechanism of sulfate expansion: I. Thermodynamic principle of crystallization pressure, Cem. Concr. Res. 22 (1992) 631–640.

[7] X. Ping, J.J. Beaudoin, Mechanism of sulfate expansion: II. Validation of thermodynamic theory, Cem. Concr. Res. 22 (1992) 845–854.

[8] C.D. Lawrence, Sulphate attack on concrete, Mag. Concr. Res. 42 (153) (1990) 249–264.

[9] S.S. Zumdahl, Chemistry, third ed., D. C. Heath and Co., Lexington, MA, 1993.

[10] D. Bonen, M.D. Cohen, Magnesium sulfate attack on portland cement paste: I. Microstructural analysis, Cem. Concr. Res. 22 (1992) 169–180.