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THE INFLUENCE OF THERMAL CYCLES AND POTASSIUM ON THE DAMAGE MECHANICS OF DELAYED ETTRINGITE FORMATION

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Abstract: Delayed ettringite formation (DEF) is a concrete deterioration process that involves the growth over time of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, crystals. This research investigated the effects of two factors, thermal cycling and elevated potassium levels, on the mechanisms and kinetics of this process. The experimental approach involved casting three sets of concrete specimens under different conditions that were designed to either promote or inhibit DEF. These consisted of a control set cured at room temperature, a set that was subjected to thermal cycling and a third set which was made with an elevated potassium content of 1.72% K_2O and also thermally cycled. The measurements included expansion, weight change and compressive strength and were taken periodically up to 350 days. In addition, fractured specimens were examined by Scanning Electron Microscopy (SEM) and Energy Dissipative X-ray (EDAX) which confirmed the presence of ettringite. Only the heat-treated specimens showed significant expansion. Analysis of The correlation of the expansion data with the weight change data revealed that deterioration process occurs in three distinct stages. In the first stage, the ettringite fills the pores with little or no expansion; in the second, the expansion mechanism appears to be creep due to expansive stresses in the filled pores and in the third, ettringite causes crack propagation leading to significant expansion and loss of compressive strength. Pre-existing microcracks are a necessary condition for DEF. The elevated potassum level did not affect the rate of ettringite formation, but resulted in a higher limiting value of the expansion.

1 INTRODUCTION

Delayed ettringite formation (DEF) in concrete and mortars has been associated with deleterious expansion leading to cracking and deterioration and loss of compressive strength [1]. There are various factors that cause the type of damages associated with DEFincluding cement chemistry, the curing method andexposure condition. The mechanism of deterioration involves the growth of ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O]$ crystals in concrete pores and cracks leading to expansion.

The research presented here concerned two of the factors: early age microcracks and elevated potassium in the cement. Previous investigation of DEF using laser shearography has shown that they have the potential to cause serious damage [2]

2. EXPERIMENTAL METHOD

2.1 Sample preparation

Two batches of concrete were made with type III cement (High early strength Portland cement) and a water to cement ratio of 0.5 were prepared in accordance with ASTM C192-16 Standard Practice for Making and Curing Concrete Test Specimens in the laboratory. . The difference between the two batches was the level of potassium in the cement paste. One batch in which potassium carbonate (K2CO3) was added such that the total potassium content was 1.72%, while the other batch in which potassium carbonate was not included had a potassium content estimated to 0.79%. For the purpose of this study, the batch in which potassium carbonate was added was called high potassium batch while the one without potassium carbonate was called normal potassium batch. Fifteen 4”x8” cylinders and five 3”x3”x11.5” prisms were made from the high potassium batch while thirty 4”x8” in cylinders and ten -3”x3”x11.25” prisms were made from the normal potassium batch. Each prism was equipped with steel studs at the ends that were used to measure length changes. After casting, the specimens were cured in a moist room at 70°F and 100% relative humidity (RH) for 24 hours and then demolded.

2.2 Thermal cycling

Upon demolding, five cylinders and fifteen prisms from the batch with normal potassium along with all cylinders and the prisms from the batch with high potassium were subjected to the a set of thermal cycles for 14 days (Fig. 1). in order to initiate cracks and accelerate the formation of ettringite [1].

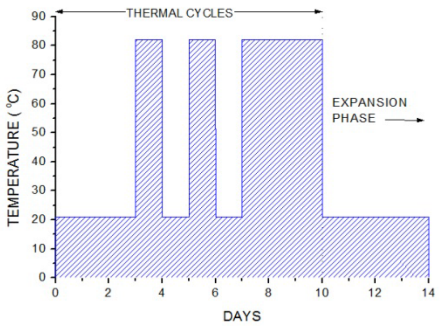

Figure 1 Plot of temperature versus time for the thermal cycles.

The heating part of the cycles was performed in an oven at 80°C while the cooling was done in a water bath at 20°C. The remaining cylinders and prisms from the normal potassium batch which will be referred as the control specimens were store in water during this time. After the heat treatment, all the specimens, including control samples were stored in limewater for the

2.3 Measurement Methods

Expansion measurements were taken in accordance with ASTM C 157-14 Standard Test Method for Length change of Hardened Mortar and Concrete with a digital comparator accurate to + 0.0001 inches and a reference 10 –inch Invar bar. The weight change measure-ment was done concurrently with the expansion measurement on the same prism. The specimens were blotted surface dry then measured for expansion and immediately weighed. Measurements were done at regular time intervals of two days up to 150 days and at interval of 4 days thereafter. Testing was stopped once hairline cracks appear on the surface of specimens. The baseline length and weight were taken 1 day after the specimens had been immersed in lime water after heat treatment.

3 RESULTS

3.1 Expansion

Figure 2 presents the results of expansion measurements. Overall, the control samples show little to no expansion throughout the study while samples with high potassium heated and those with normal potassium show significant expansion (up to 1.6% and 0.8% respectively), which confirms the findings of previous studies

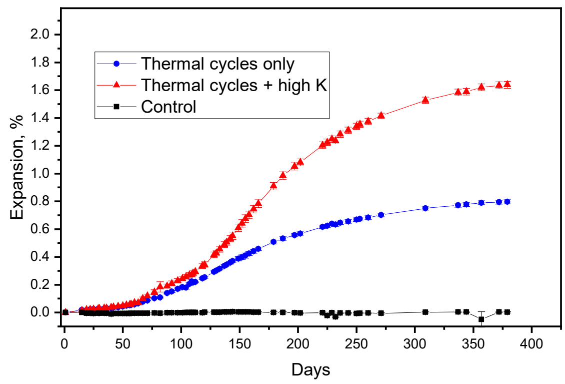

Figure 3: Plot of expansion of concrete samples vs time

that heat treatment has a significant impact on concrete deterioration [1], [2], [3]. Samples with high potassium displayed more expansion than those with normal level of potassium, this also show that additional potassium has an adverse effect on concrete expansion. For both sets of heat treated specimen the rate of expansion reaches its peak between 144 and 150 days with expansion rates of 1.15% and 0.6% per day respectively for sample with highand normal level of potassium.

3.2 Weight change

Average weight change was calculated for each set based on corrected weight changes. Figure 4 presents the results of the weight measurements. All sets had weight gains, but the highest gain was observed with samples heat treated with high potassium content. The overall weight gains for the duration of the experiment were 1.9, 1.3 and 0.35% respectively for the specimen with high

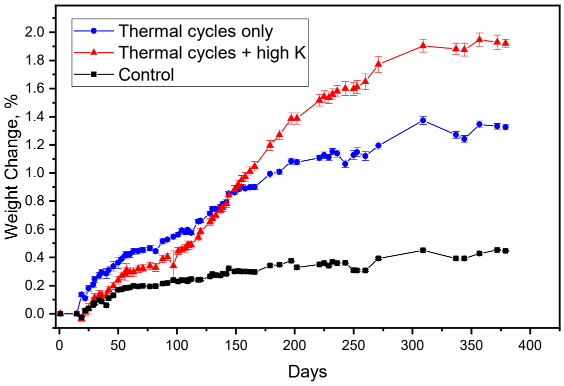

Figure 4: Plot of weight change of concrete specimens vs time

potassium, normal and control specimens. It was observed that the specimens with normal potassium gained weight at a higher rate than those with high level of potassium early in the experiment (up to 55 days) then the situation was reversed. For both sets of heat treated specimens the rate of weight change reached its peak at the same time with the peak rate of expansion between 144 and 150 days with rates of 1.15% and 0.6% per day respectively for sample with high and normal level of potassium. These results are consistent with the expansion results and show the effect of the heat treatment and the addition of potassium to the mix.

3.3 SEM analysis

Samples of concrete broken during compressive strength test were further fractured to obtain specimens for fracture surface SEM. This confirmed the presence of ettringite. Three main morphologies of etteringite were observed: balls filling pores (Fig.5a); blades or lamellae aligned parallel to aggregate surfaces (Fig. 5b) and needles formed in cracks (Fig. 5c)

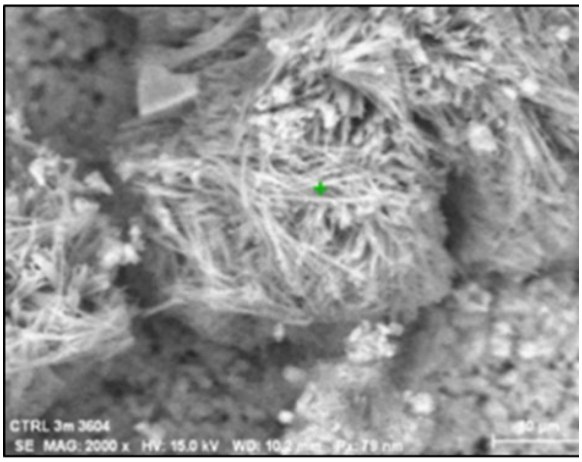

Figure 5a: Ball of ettringite filling a pore

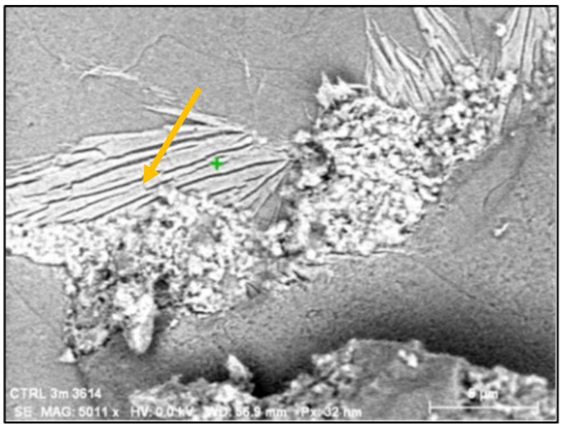

Figure 5b Blades of etttingite (arrow) growing along aggregate surface

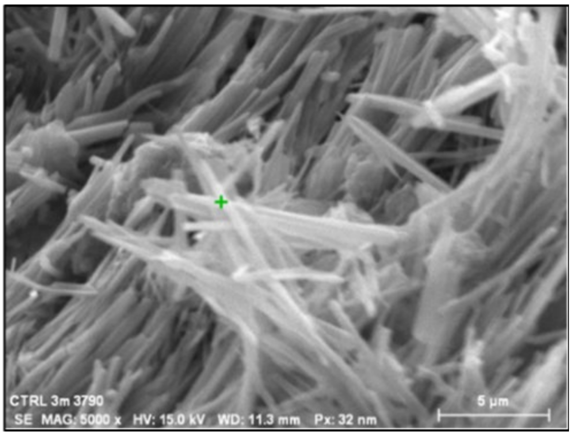

Figure 5c: Needles of ettringite growing in a crack.

4 DISCUSSION

5.1 Correlation of expansion vs weight change

Both the expansion and the weight change data have a non-linear relationship with time (Figs. 3 and 4). However, when they are plotted against each other a linear relationship appears (Figs. 6 and 7). This is confirmed by a piecewise linear regression analysis with R^2 values of 0.99 or 0.98. The results are summarized in Table 1.

The lines for the two potassium batches at the later stage appear to have very similar slopes. As shown in Fig. 8, they can be made to coincide by simply subtracting a lag in weight gain from the normal potassium data. Consequently, the data were pooled into a single set which to which linear regression analysis was applied. The resulting R^2 value was also very high, 0.976. These results are also included in Table 1.

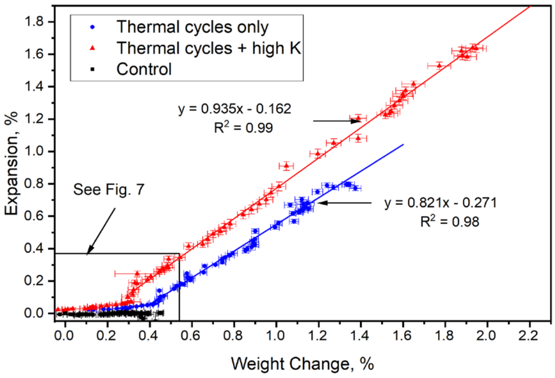

Figure 6: Plot of expansion vs normalized weight change of concrete specimen

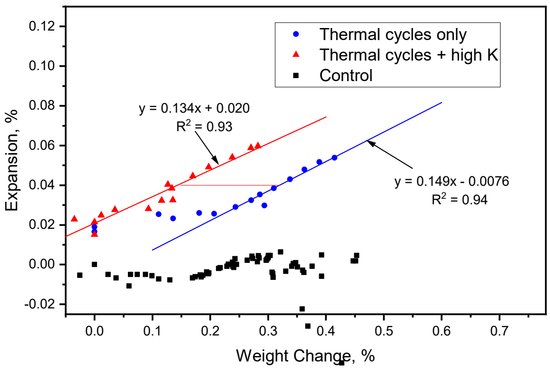

Figure 7: Enlargement of the rectangular area in Fig. 6 showing the correlations at early times.

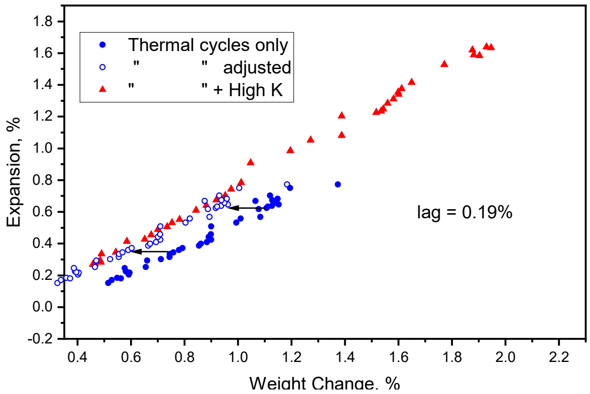

Figure 8: Plot of heat-treated sample data adjusted for lag.

Table 1: Summary of Linear Regression Analysis

	Early Stage	
Condition	Onset, Days	Slope
Thermal only	30	0.14 ± 0.01
Thermal + High K	25	0.13 ± 0.01
	Late Stage	
Condition	Onset, Days	Slope
Thermal only	57	0.82 ± 0.02
Thermal + High K	57	0.93 ± 0.01
	Late Stage	
Conditiom	Onset, Days	Slope
Pooled data	57	0.84 ± 0.02

The fact that both sets indicates that potassium content does not influence the rate-controlling mechanism.

4.2 The three-stage model of DEF expansion

The results of the regression suggests that the damage processes in the heat treated specimens occur in three stages These are indicated in Fig. 9.

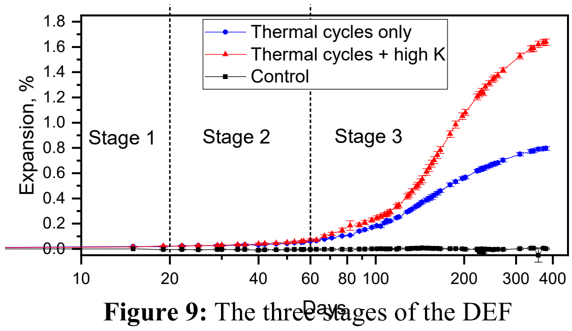

Figure 9: The three stages of the DEF damage progression

4.2.1 Stage 1: Pore filling

From 0 days to 20 days the weight gain observed in the concrete specimen does not result in observable expansion. This is interpret ed as ettringite being formed but simply filling the available porespace.

4.2.2 Stage 2: Creep

During 20 days to 60 days the pores become mostly filled with ettringite, and swelling pressure creates creep stress. However, the concrete at this stage has a low creep resistance and can accommodate these stresses. The curve at thus tage shows a strong linear correlation between weight gain and expansion but with a small slope (0.13 to 0.14).

4.2.3 Stage 3: Crack propagation

Beyond 60 days Fig. 6 shows that the weight gain is accompanied by significant expansion of the specimen. Concrete strength has increased to the point where resistance to creep develops. At the same time further ettringite deposition takes place in cracks that grow wider and longer. More moisture becomes then available and fuels the growths of ettringite crystals that in turn lead to more cracking. There is a strong correlation at this stage between weight gain and expansion for specimen heat treated with R^2 of 0.99 and 0.98 for those with high level of potassium and normal potassium content respectively. It can also be observed at this stage that there is a steady decrease in the compressive strength of the specimen, because micro-cracks and voids in the concrete become interconnected, which weakens the microstructure and lead to decrease in concrete strength (figure

4.3 Kinetics of ettringite nucleation and growth

The time-dependence of concrete specimens' expansion due to DEF can be found by fitting the data to a well-known exponential equation 1 of phase transformation kinetics known as the Kolmogorov-Avrami-Johnson-Mehl (KAJM) model [3]. It describes the transformation of the volume of one crystal phase into another as a function of time. The model can also be extended to the nucleation and growth of secondary ettringite in concrete. It provides a set of parameters to characterize the process which are more reliable than the expansion observed at a fixed time as presently used in the ASTM. This approach can also be used to isolate individual expansion mechanisms if they occur on different timescales. This analysis thus resolves the contribution of DEF to the overall expansion results. In this research the basic KAJM model has been modified to have the form :

$$\varepsilon(t)-\varepsilon_o = A\left(1-e^{-[K(t-t_o)]^n}\right) \qquad (1)$$

where:

$\varepsilon(t)$ = Expansion at time t
ε_o = Expansion at onset time t_o
A = Asymptotic expansion coefficient
K = Rate constant
t = Time
n = Dimensionality

The modification is the introduction of the parameter A which was found to be necessary to scale the data. In the basic KAJM model this has the value of unity.

The sexpansion data in Stage 3 (after 60 days) were fitted to the KAJM equation using a MATLAB nonlinear fit routine, and the results are listed in Table 2 below.

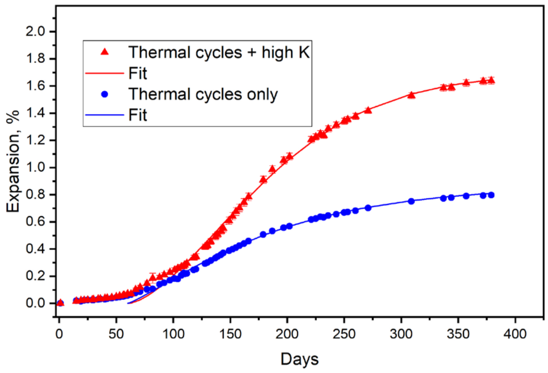

Figure10: Plot of curve fitting of the expansion data with the modified KAJM model

Table 2: Kinetics parameters

Condition	Normal K	High K
A	0.86	1.69
K, $days^{-1}$	7.5 $\times 10^{-3}$	7.0 $\times 10^{-3}$
n	1.2	1.6
R^2	0.995	0.995

4.3.1 Physical interpretation of the kinetics parameters

4.3.1.1 Rate constant *K*

The rate constant *K* incorporates the rate of nucleation and growth. It therefore reflects the rate at which reactions are occurring in the concrete specimen. The value of *K* observed in the high potassium specimens is similar to that of the specimens with the normal level (7×10^{-3} vs 7.5×10^{-3}). This means that in both specimens, the reaction resulting in ettringite occurred at the same rate. Therefore the reaction is not controlled by the potassium content. Since potassium was designed to initiate cracks, it also suggests that the rate of reaction does not depend on the number of initial cracks in the specimen or the amount of water reaching nucleation sites through those cracks.

4.3.1.2 Asymptotic Expansion Coefficient: A

The coefficient A is the limiting value for $\varepsilon(t)$ when t goes to infinity. A is characteristic of the amount of cracks that was initiated in concrete specimens by the heat cycles at the beginning of the experiment. The value of A for specimen containing additional potassium (A=1.69) is nearly double that of specimens with normal level of potassium (A=0.86) and this suggest that more cracks were initiated in the former by the heat cycles. Since the only difference between the two batches is the amount of potassium, we can hypothesize that additional potassium led to more microcracking during thermal cycling. This can be explained by the fact that potassium makes concrete more brittle and therefore more prone to cracking.

4.3.1.3 Dimensionality: *n*

The parameter n expresses the dimensionality of the transformation and phase change that takes place in the concrete specimen. For $n = 1$, the transformation takes place along a line; for $n = 2$ it occurs on a surface and for $n = 3$ throughout a volume. Tthe values obtained by fitting expansion data are $n \approx 1.2$ and $n \approx 1.6$ respectively for the normal potassium specimens and high potassium specmens respectively. These values are somewhere between a line and a full surface, which is a definition that can be applied to microcracks. The larger value for the high potassium specimens implies a greater density of microcracks which is consistent with findings for the *A* parameter.

5 CONCLUSIONS

Pre-existing microcracks are a necessary condition for DEF. The major part of the expansion observed with DEF occurs by filling and widening these crack rather than initiating new cracks, For the microcracked concrete the DEF damage process occurs in 3 stages: initial pore filling, creep and finally crack propagation. The elevated potassum level did not affect the rate of ettringite formation, but results in a higher limiting value of the expansion. This suggests that potassium content influences the amount of micro-crack formation during the heat cycles.

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