

# TRANSFORMATION OF THE U PHASE INTO ETTRINGITE IN REACTIVE AGGREGATE-CONTAINING MORTARS IMMERSSED IN NaCl SOLUTION

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## Abstract

This study was aimed at elucidating the possibility of the formation of the U phase in a reactive aggregate-containing mortar with a large amount of added NaOH and its transformation into ettringite in the mortar in 1M NaCl solution. We pursued changes in the intensity of X-ray diffraction peaks for the U phase and ettringite in the mortar with time. It was found that the transformation of the U phase into ettringite occurred in the mortar in a moist environment as well as in the NaCl solution. The measured expansions of the mortar in the former were much smaller than those in the latter. A part of the expansion in the mortar must be due to the transformation of the U phase into ettringite. However, judging from the fact that the mortar in a moist environment showed much smaller expansions than in the NaCl solution, the majority part of the measured expansion of the mortar in the NaCl solution may be due to the accentuation of the ASR resulting from the increase in solubility of silica and calcium hydroxide in the strong electrolytes solution with NaCl.

**Keywords:** U phase, ettringite, expansion, ASR, NaCl

## 1 INTRODUCTION

The effects of a deicing salt of NaCl and sea water on ASR damages in concrete is an important consideration in the maintenance of ASR-affected concrete structures. In order to reveal their effects on ASR expansion behavior and the mechanisms, numerous expansion tests for mortars and concretes produced with combinations of various reactive aggregates and alkali contents of cements have been conducted in NaCl solutions and seawater. In most cases, reactive aggregate-containing mortars and concretes in NaCl solution showed greater ASR expansions than those in a moist environment. We also previously reported that reactive aggregate-containing mortars with an extremely high internal alkali content showed far greater expansions in 1M NaCl solution than in 1M NaOH solution [1]. On the other hand, it was reported that expansions in mortars with a reactive cherty aggregate in the saturated NaCl solution were much smaller than those in a moist environment [2]. It appears to depend on the type of reactive aggregate whether immersion of reactive aggregate-containing mortars in NaCl solution increases ASR expansion.

In relation to the elucidation of mechanisms of acceleration of ASR in concretes under a saline environment, some authors suggested that a part of the expansion of concrete in a saline environment might be due to the formation of an expansive chloroaluminates and Aft [3, 4, 5, 6]. However, few studies have directly related the formation of the secondary reaction products to the expansion of the concretes in NaCl solution and sea water. In the present situation of the research, it is significant to see the possibility of the formation of the U phase and its transformation into ettringite in reactive aggregate-containing mortars with extremely high alkali contents in NaCl solution.

Li et al. [7] found that the U phase formed in the cement pastes with extremely high alkali contents produced in the solidification of the low liquid waste in nuclear industry. They also indicated that the secondary formation of additional U phase and the transformation of the U phase into ettringite induced expansion [8, 9]. The production of concretes with such extremely high alkali contents is not general in the usual concrete industry. Recently, however, it was shown that the degradation of concrete pavement due to ASR induced by the de-icing salt of potassium acetate was

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associated with a drastic rise of  $\text{OH}^-$  ion concentration in the pore solutions to higher than about 4M [10].

We examine the formation of the U phase in a reactive aggregate-containing mortar with extremely high alkali content and its transformation into ettringite in 1M NaCl solution and a moist environment by the X-ray diffraction analysis for powdered mortar samples, measuring expansion of the mortar. Effects of the transformation of the U phase into ettringite on the expansion of the mortar in 1M NaCl solution are discussed.

## 2 EXPERIMENTAL WORKS

The calcined flint produced by Lafarge with a size fraction of 0.6 – 2.5 mm and a Japanese standard sand were used as a reactive and a non-reactive aggregate, respectively. An ordinary portland cement with the equivalent  $\text{Na}_2\text{O}$  percentage of 1.12wt% was used. The chemical composition of the cement is given in Table 1. Mortars made with the calcined flint and a cement with 2.93wt%  $\text{Na}_2\text{O}$  showed extremely great expansions in 1M NaCl solution in our previous study [1]. Then, in this study, an amount of NaOH was also added at a dosage level equivalent to a cement with 2.93wt%  $\text{Na}_2\text{O}$ .

Mortar prisms (25 x 25 x 285 mm) for expansion tests were prepared with a water/cement ratio of 0.4 and an aggregate/cement ratio of 0.75. The replacement level of the calcined flint in the mortar was 26wt%.

Mortar prisms immersed in 1M NaCl solution were pre-cured in a moist environment (95% R.H.) at 38°C for 28 days. Expansions plotted in Figure 1 are the average of three measurements.

Mortar slices (25 x 25 x 5 mm) were cut from the mortar prisms for expansion tests to make samples for X-ray diffraction analyses. They were dried for about one day by means of ethanol replacement, followed by drying at 50°C in an oven for an additional one day. The whole of a mortar slice was ground in a mortar and pestle. Thus, the intensity of X-ray diffraction peaks for compounds reflects their quantities averaged across the section of mortar prisms with zonal distributions of compounds from surfaces to the core. The discussion on the results of X-ray diffraction analyses in this study was made based on semi-quantitative assessments.

The samples obtained were examined by an X-ray diffractometer, "Geigerflex CN 4057S5, Rigakudenki Co." (Cu-K $\alpha$  radiation under 45kV/40mA, 10s/0.02°).

## 3 RESULTS

In Figure 1 we plot the measured expansions of the mortar made with a cement with 2.93wt%  $\text{Na}_2\text{O}$  immersed in 1M NaCl and a moist environment (95 % RH) at 38°C. As shown in Figure 1, the mortar prisms rapidly expanded with time during the first 28 days of pre-curing in a moist environment. The alkali silica reaction should progress in the mortar during the period. Considerable differences in the expansion recorded during the first 28 days pre-curing period between the two batches are probably due to high rigidity of high alkali-bearing mortar mixtures leading to the production of somewhat inhomogeneous mortar specimens.

After pre-curing, measured expansions were greatly different in different environmental conditions. The expansion rate of the mortar immersed in 1M NaCl solution was much greater than that of the mortar in a moist environment. Eventually, the expansion of the mortar in a moist environment was about one third that of the mortar in the NaCl solution.

Figure 2 shows X-ray diffraction patterns for the mortar with the reactive aggregate cured for 28 days in a moist environment, and then immersed in 1M NaCl solution for 7, 14, 36, 56 and 70 days. A strong peak for the U phase at 1.00 nm had already existed in the X-ray diffraction pattern for the sample taken from the mortar pre-cured in a moist environment for 28 days. After immersion in the solution, X-ray diffraction patterns drastically changed. The peak height of the U phase rapidly decreased with time, and the peak disappeared by 56 days after immersion in the solution. The X-ray diffraction peaks for ettringite at 0.973 nm and 0.561 nm appeared after immersion in the solution for at least 7 days.

The X-ray diffraction patterns for the mortar successively cured in a moist environment are presented in Figure 3. It is seen that there are only minor differences in the X-ray diffraction patterns between the mortar in the NaCl solution and a moist environment. However, precisely comparing the X-ray diffraction patterns in the mortar in the NaCl solution (Figure 2) with the corresponding ones in a moist environment (Figure 3), the intensity of X-ray diffraction peaks for ettringite at 0.973 nm and 0.561 nm in the latter is a little weaker than the intensity of the peaks in the former as a whole. Furthermore, as shown in Figure 3, a broad shoulder is found around 0.973 nm in the 35 days old mortar in a moist environment, but the peak for ettringite at 0.973 nm is conspicuous in the corresponding mortar immersed in the NaCl solution at 7 days (Figure 2). Thus, it is found that the

transformation of the U phase into ettringite was promoted in the mortar in 1M NaCl solution, as compared with the mortar in a moist environment. In Figure 2, it is also seen that the transformation from the U phase into ettringite in the mortar was terminated by the immersion time of 56 days in the NaCl solution. However, even after that, the mortar continued to greatly expand (Figure 1).

#### 4 DISCUSSION

Li and Bescop [8] conducted X-ray diffraction analyses for samples taken from various depths from surfaces of cylindrical cement paste specimens ( $\varnothing 30\text{mm} \times 30\text{mm}$ ) containing the U phase which were immersed in the deionized water for one month. They reported that the transformation of the U phase into ettringite occurred only in the zones up to about 4.5 mm from the surfaces, and no trace of the U phase was detected in the zones. As shown in Figure 2, in this study, a broad shoulder due to the U phase was still found around 1.000 nm in the X-ray diffraction pattern even at 36 days after immersion in the NaCl solution. Since mortar samples used in the X-ray diffraction analyses in this study were prepared by grinding the whole of a slice cut from a mortar prism, this result is not necessarily inconsistent with that obtained by Li and Bescop [8].

The measured expansion of the aggregate-free cylindrical specimen of a mixture of  $\text{C}_3\text{S}$  and the U phase in water for about 60 days was as much as 2.5%/ℓ/ℓ in the study by Li and Bescop [8]. They reported that considerably great expansions occurred due to the transformation of the U phase to ettringite in the mixture and that this U phase-ettringite transformation was caused by the reduction in alkali concentration due to leaching [8,9]. As shown in Figure 1, however, in this study the expansions recorded after the first detection of the X-ray diffraction peaks for ettringite in the mortar with a reactive aggregate in 1M NaCl solution and a moist environment were about 1.3%/ℓ/ℓ and 0.3%/ℓ/ℓ, respectively. In the mortar stored in the two different environments, the reduction in the alkalinity due to both ASR and leaching is responsible for the transformation of the U phase into ettringite [8]. These results suggest that the amount of expansion arising from the transformation of the U phase into ettringite in the mortar in the NaCl was very small. Judging from the fact that the expansion of the mortar in a moist environment was much smaller than that in the NaCl solution and that expansion greatly increased even after the termination of the transformation of the U phase into ettringite in the NaCl solution, most of the large expansion of the mortar in the NaCl solution is brought about by the accentuation of ASR expansion by NaCl.

#### 5 CONCLUSIONS

- (1) The reactive aggregate-containing mortar with an extremely high alkali content of 2.93wt%  $\text{Na}_2\text{O}$  in 1M NaCl solution showed much greater expansions than those in a moist environment.
- (2) The formation of the U phase was confirmed in the mortar cured in a moist environment for 28 days. The U phase was transformed into ettringite in the NaCl solution as well as in a moist environment.
- (3) Only a small part of the expansion of the mortar in 1M NaCl solution may be due to the transformation of the U phase into ettringite.
- (4) ASR expansion of the mortar in the NaCl solution seems to be greatly promoted by NaCl.

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TABLE 1: Chemical composition of cement.

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	LOI
wt%	20.1	4.7	3.2	62.5	2.5	3.3	0.41	1.08	1.2

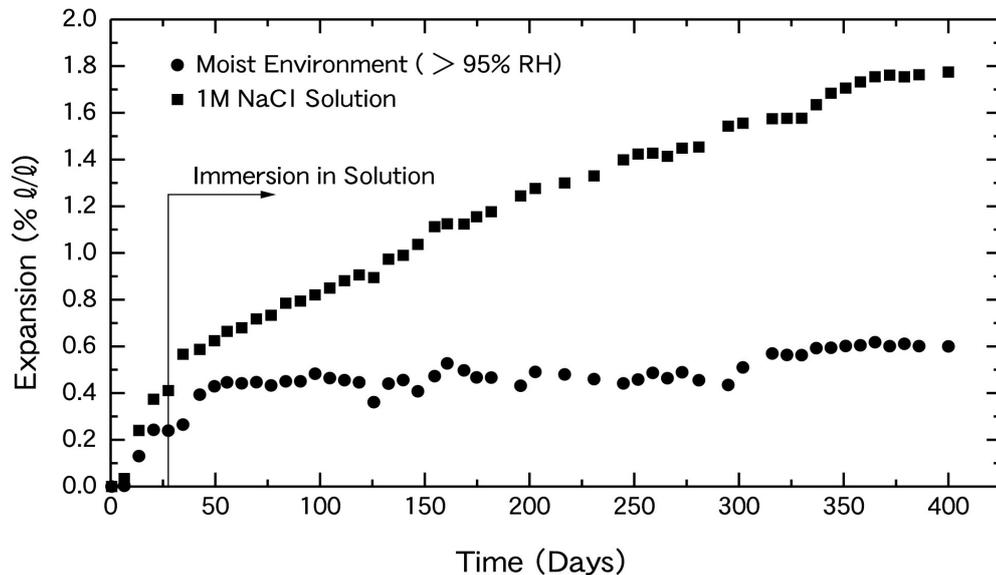


Figure 1: Expansion curves for mortars with a 2.93% Na<sub>2</sub>Oeq cement immersed in 1M NaCl, 1M NaOH and a moist environment.

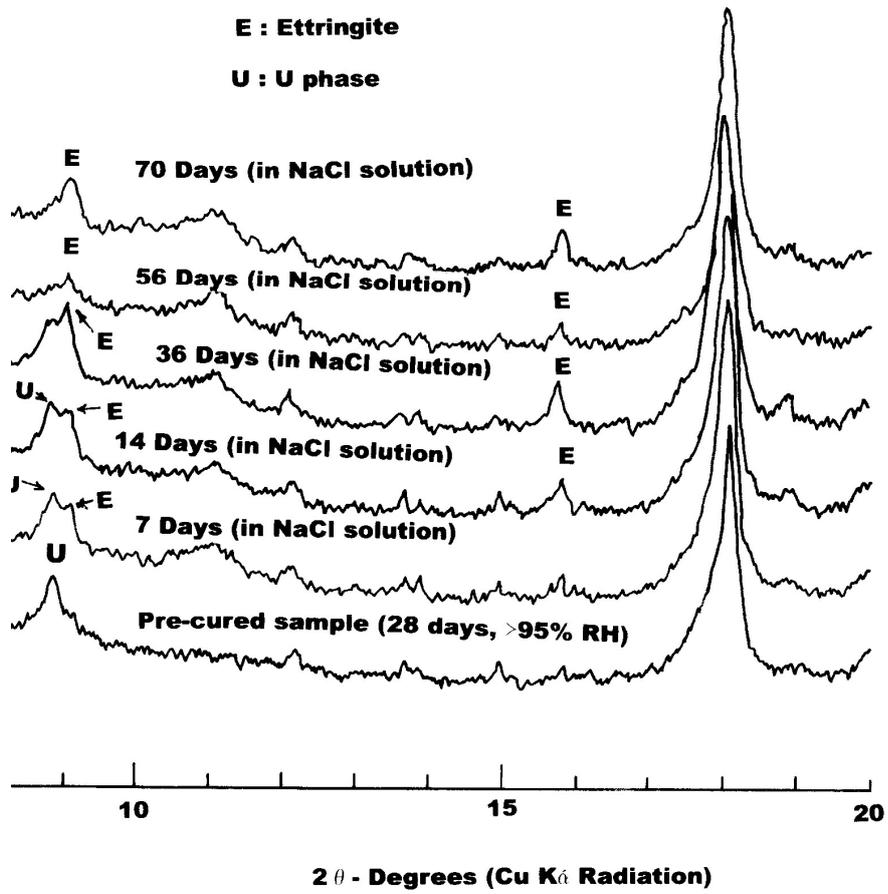


Figure 2: X-ray diffraction patterns for mortars with a reactive aggregate immersed in 1M NaCl solution.

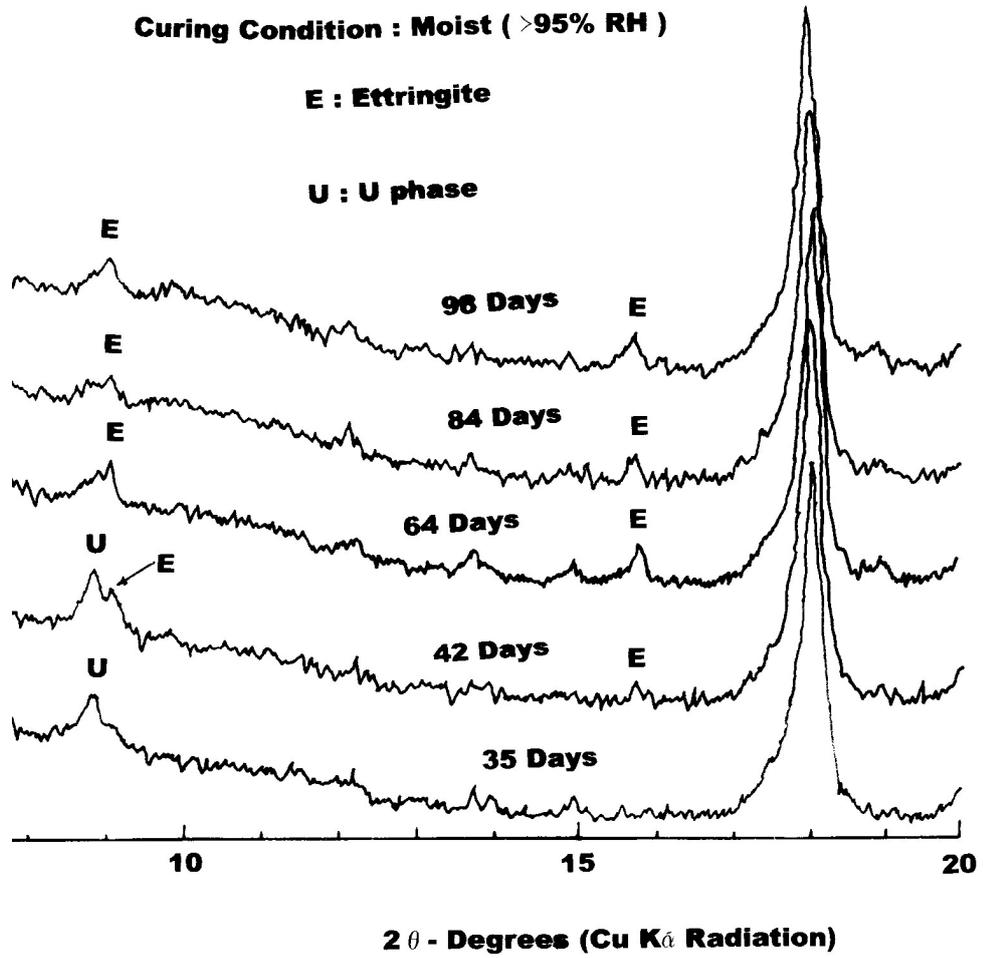


Figure 3: X-ray diffraction patterns for mortars with a reactive aggregate stored in a moist environment.