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EXPANSION MECHANISM ASSOCIATED WITH THE SECONDARY FORMATION OF THE U PHASE IN CEMENT-BASED SYSTEMS CONTAINING HIGH AMOUNTS OF Na_2SO_4

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ABSTRACT

The degradation of concrete by sulfates is generally related to the formation of AFt, but in some cases such as the cement stabilised wastes with a high amount of sulfates, the U phase is formed. This paper studies the influence of the U phase formation on the expansion of the C_3A+C_3S+Na_2SO_4 system. It is shown that the U phase is formed by an external water supply and this reaction process results in a large expansion.

Introduction

Sulfate attack of concrete is a complex process. The major well-accepted process involves the reaction of sulfate ions with calcium aluminate hydrate and the formation of the ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$, which in most of the cases, appears to be the cause of expansion and deterioration of concrete by both internal and external sulfates. Many papers have contributed to the research on the expansion mechanism associated with ettringite formation and two schools have appeared: expansion by crystallisation pressure and expansion by water absorption of colloidal ettringite (1–2).

However, in a recent work, a mineral called U phase was evoked (3). This sodium-substituted AFm phase was observed for the first time by Dosch and zur Strassen in 1967 (4), in their study of the chemical system Na_2O-CaO-Al_2O_3-SO_3-H_2O. It has never been detected in traditional cement pastes, because of its special conditions of formation, that are very high contents of alkalis and sulfates. On the contrary, those particular conditions are compatible with the cement-stabilised wastes containing very high amounts of Na_2SO_4 (10~15% in weight) and the U-phase formation was indeed confirmed for the first time in such a cement-based system (3). In addition, the expansion tests on the simulated samples showed large cracks, or even complete destruction under water.

As it is known, when the water/cement ratio is lower than a critical value, cement hydration reactions stop as soon as the porosity is filled, leaving anhydrous cement grains in the matrix, even after immersion. However, for certain deleterious phases, such as ettringite, the formation continues in the presence of sulfate and external water supply. By creating necessary space for accommodating the new solid phase in the cement matrix, expansion occurs (5). Such an expansion phenomenon can also be induced by a secondary gypsum formation (6), but in the case of the U phase, no information is presently available in the literature. This paper focuses on the expansion phenomenon produced by secondary formation of the U phase. Systematic expansion tests and XRD analysis were carried out on the samples $C_3A+C_3S+Na_2SO_4$ in conditions close to those of cement-stabilised waste systems.

Experimental

A simple system containing $C_3A+C_3S+Na_2SO_4$, hydrated by alkaline solutions, was studied: C_3A and C_3S were synthetized in laboratory. To estimate the amounts of hydrates, the following assumptions were made:

1)the chemical composition of the U-phase is $4CaO \cdot 0.9Al_2O_3 \cdot 1.1SO_3 \cdot 0.5Na_2O \cdot 16H_2O$ according to (2),
2)C_3A reacts directly with Na_2SO_4 and forms the U phase; the necessary $Ca(OH)_2$ is supplied by C_3S hydration,
3)the C-S-H from C_3S was taken in the form of $C_{1,5}SH_{2,3}$ in these alkaline solutions (7). Higher values 1.8~2.0 were published and more particularly at early stage in normal conditions (8-9).

The potential reactions in the system under these considerations are:

$$2.7\ C_3A + 3.3\ Na_2SO_4 + 45.9\ H_2O + 3.9\ Ca(OH)_2 \rightarrow 3.0\ U + 3.6\ NaOH \qquad [1]$$

$$1.0\ C_3S + 3.8\ H_2O \rightarrow 1.0\ C_{1.5}SH_{2.3} + 1.5\ Ca(OH)_2 \qquad [2]$$

TABLE 1

Stoechiometric Calculation of the System $C_3A+C_3S+Na_2SO_4$

Reaction	Reagent				Product				
type	C_3A	C_3S	Na_2SO_4	H_2O	$Ca(OH)_2$	U	NaOH	$Ca(OH)_2$	C-S-H
a	2.70	/	3.30	45.90	3.90	3.00	3.60	/	/
b	/	2.60	/	9.88	/	/	/	3.90	2.60
a+b	2.70	2.60	3.30	55.78	/	3.00	3.60	/	2.60

Critical ratios	C_3S/C_3A	C_3A/Na_2SO_4	H_2O/Na_2SO_4
in mole (in weight)	2.60/2.70 (0.814)	2.70/3.30 (1.556)	55.78/3.30 (2.144)

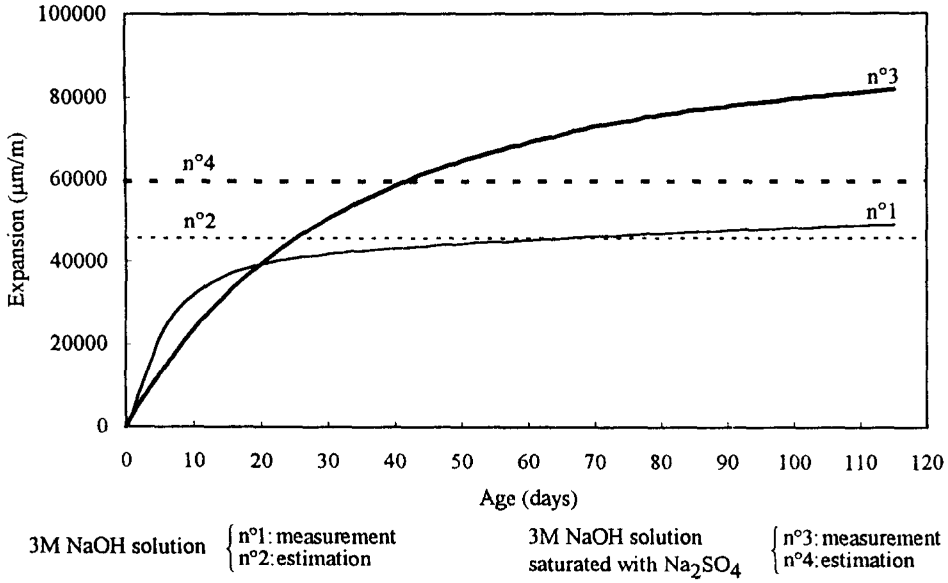

FIG. 1.

Expansion in 3M NaOH solution and 3M NaOH solution saturated with NA_2SO_4.

Based on the reactions [1] and [2] and considering the complete hydration of C_3A and C_3S, the stoechiometric calculation gives three critical ratios C_3S/C_3A, C_3A/Na_2SO_4 and H_2O/Na_2SO_4. The results are presented in Table 1.

The secondary U phase formation can proceed by different ways. Two cases were considered as follows:

(i): by an external water supply,
(ii): by both external water supply and external sulfate supply.

For both cases, the C_3S/C_3A ratio must be taken higher than the critical value for an available amount of $Ca(OH)_2$ necessary to the formation of the U phase as described in the reaction [1].

In the first case, an external water supply appears necessary as C_3A and Na_2SO_4 consume a large part of the mixing water. In the second case, after the C_3A-Na_2SO_4 reaction has been completed, more C_3A is necessary if there is a secondary supply of sulfate as an external agent.

Based on these considerations, the following ratios (in weight) were applied to the $C_3A+C_3S+Na_2SO_4$ mixtures: $C_3S/C_3A = 1.000$ (>0.814), $C_3A/Na_2SO_4= 1.667$ (>1.556) and $H_2O/Na_2SO_4= 1.500$ (<2.144) (values inside the brackets are those of table 1), which correspond to $38.5\%C_3S + 38.5\%C_3A + 23.0\%Na_2SO_4$.

Taking into account the high basicity in the cement-stabilised wastes (3) and the U phase stability (4), two alkali solutions were used as immersion solutions: 3M NaOH and 3M NaOH saturated with Na_2SO_4.

The specimens with ϕ30mm x h30mm dimensions were prepared at 20°C. Na_2SO_4 was dissolved in the mixing water. The samples were demoulded after three days and then immersed in the solutions in a specially designed device, which measures continuously the linear dimensional variation. The samples were analysed by XRD (Cu-Kα radiation under 40kV/25mA, 3s/0.01°) both at the beginning and at the end of the tests.

Results and Discussion

The expansion tests were conducted for about four months till the dimensional variation became stable. The data are plotted in Fig.1 as a function of time in two different media: 3M NaOH solution and 3M NaOH solution saturated with Na_2SO_4.

In order to compare with the experimental results, the linear expansion was estimated by volume balance from the reactions [1] and [2]. The molar volumes (cm^3/mole) were taken (3): v_U=370.96, v_{Na2SO4}=53.00, v_{C3A}=90.07, v_{C3S}=72.95, $v_{Ca(OH)2}$=33.22, v_{NaOH}=18.78, and the volume variation for the formation of one mole U phase can be calculated in the two cases as:

(i): $\Delta V = ((v_U*3.0 + v_{NaOH}*3.6) - (v_{Ca(OH)2}*3.9 + v_{C3A}*2.7 + v_{Na2SO4}*3.3))/3 = 210.58$
(ii): $\Delta V = ((v_U*3.0 + v_{NaOH}*3.6) - (v_{Ca(OH)2}*3.9 + v_{C3A}*2.7))/3 = 269.25$

The linear expansions estimated from the volume variation and the total volume are also presented in Fig.1, denoted by broken lines n°2 and n°4.

It is observed that the specimens underwent an enormous swelling in both solutions: the expansion reached $4x10^4$ µm/m at the age of 20 days, this leads to a large cracking or even complete collapse of the specimens. In fact, this expansion phenomenon should be explained by the further formation of the U phase, because in the studied system, the conditions are compatible with the U phase formation and only this formation can occur beside the C_3S hydration.

It is interesting to remark that the calculated expansion amplitude is very close to that obtained experimentally, especially for the sample immersed in the 3M NaOH solution (n°1 and n°2). The fact that the measured expansion amplitude is higher for the sample in the 3M NaOH

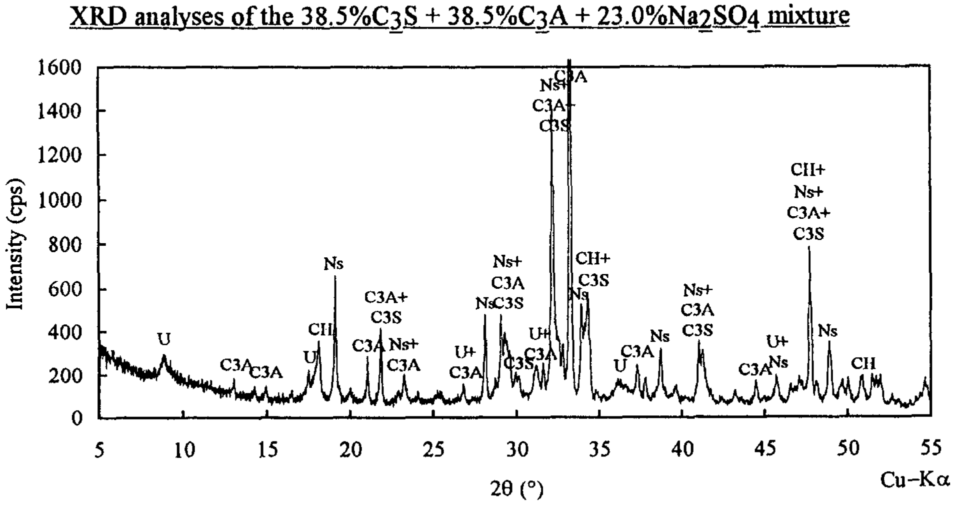

FIG. 2.
XRD pattern at the beginning of the test.

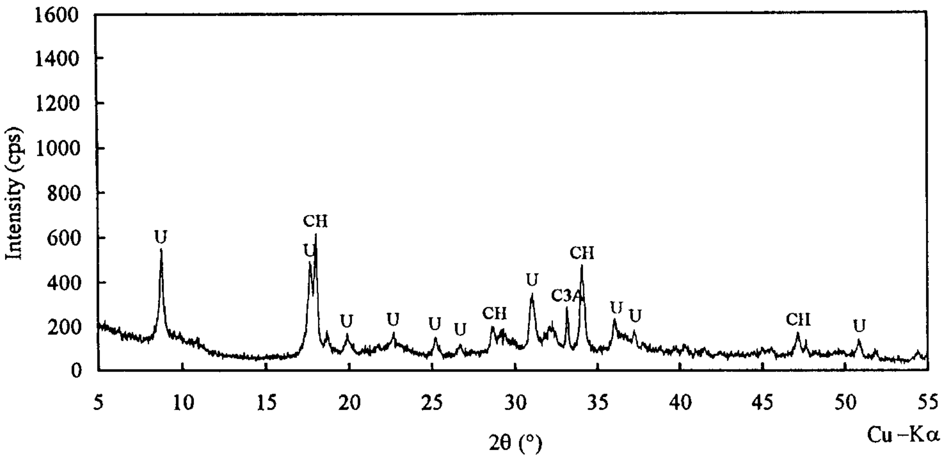

FIG. 3.
XRD pattern after four months—in 3M NaOH solution.

solution saturated with Na_2SO_4 (n°3 and n°4) may be attributed to the enormous cracking and deformation of the specimen.

It is further noted that the expansion began almost at the same time in both solutions, but each developed alone its own way (Fig.1). For the specimen in 3M NaOH solution (n°1), the expansion increased rapidly at the beginning and reached a stable level (4x10^4μm/m) after three months, while for the specimen in 3M NaOH solution saturated with Na_2SO_4 (n°3), the expansion curve had crossed the n°1 curve and continued to increase till 8x10^4μm/m.

The mineralogical analysis of the specimens by X-ray diffraction clearly show that in comparison with the standard sample (Fig.2), the amount of the U-phase changed considerably in function of the immersion conditions: the intensity of the first peak (d = 10 Å, 2θ = 8.84° Cu-Kα) increased strongly for the sample in 3M NaOH solution (Fig.3) and more strongly for that in 3 M NaOH solution saturated with Na_2SO_4(Fig.4), so that the secondary formation of the U phase was very evident.

Since experimental conditions have guaranteed the U phase stability and no trace of other deleterious phases formation was detected, the reaction process of the secondary U phase formation appears to be responsible for the observed expansion phenomenon.

The secondary formation of U phase can also be confirmed by the evolution of C_3A characteristic peaks. In fact, in the studied system, the U phase is the only hydrate which forms at the expense of C_3A, therefore the occurring of the U phase corresponds to the disappearance of C_3A. The evolution of C_3A can be clearly observed at the peak at d=2.70Å (2θ=33.15° Cu-Kα). The difference in the amount of the remaining C_3A between the samples in the two solutions can be explained by the fact that an external sulfate supply was available for the sample in 3M NaOH solution saturated with Na_2SO_4. The further formation of secondary U phase consumed more C_3A, even all the C_3A.

Regarding Na_2SO_4, its characteristic peaks are present at the beginning of the test (Fig.2) and at the end in NaOH solution saturated with Na_2SO_4 (Fig.4), but absent in the pattern for the sample in NaOH solution (Fig.3), so that the formation of the U phase is due to a supply of external water (Fig.3) and promoted by both external water and sulfate (Fig.4).

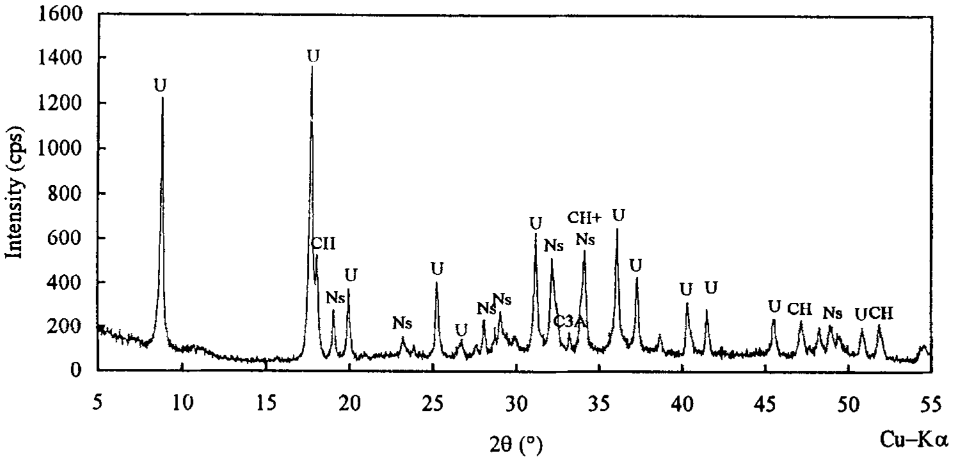

FIG. 4.
XRD pattern after about four months—in 3M NaOH solution saturated with Na_2SO_4.

Concerning the portlandite, the characteristic peaks are clearly observed in all cases. In fact, the amount of C_3A had been adjusted so that the C_3S hydration supplies enough portlandite for the formation of the U phase. In the case of 3M NaOH solution saturated with Na_2SO_4, the XRD peaks are slightly weaker due to the higher secondary formation of the U phase, which consumes more portlandite.

These results confirm the secondary formation of the expansive U phase. The more the U phase is formed, the more the expansion is induced.

Conclusions

With respect to the experimental results on the system C_3A+C_3S+Na_2SO_4 and according to the discussion, it can be concluded that:

- the secondary formation of the U phase can occur by external water supply and this reaction process can induce a large expansion.

-taking into account the compatibility of this system with all cement based systems containing high amount of alkalis and sulfates, such as the cement stabilised wastes containing Na_2SO_4 (10~15% or higher), this secondary formation of the U phase should be considered as deleterious.

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References

1. M. D. Cohen, Cem. Concr. Res., 13, 809, (1983).
2. P.K. Mehta, Cem. Concr. Res., 3, 1, (1973).
3. Guanshu Li, Ph. D. Thesis, Ecole Nationale des Ponts et Chaussées, Paris (1994).
4. W. Dosch, H. zur Strassen, Zement-Kalk-Gips, 20, No9, 392, (1967).
5. B. Cottin, Ann. Chim. Fr. 4, 139, (1979).
6. M. Regourd, in "Le béton hydraulique", Presse de l'Ecole Nationale des Ponts et Chaussées, 513, (1982).
7. G. L. Kalousek, ACI, 26, 233, (1954).
8. M. Regourd, J.H. Tomassin, P. Baillif, J.C. Touray, Cem. Concr. Res., 10, 223, (1980).
9. K. Fujii, W. Kondo, Journ. Chem. Soc., Dalton, 2, 645, (1981).