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THE U PHASE FORMATION IN CEMENT-BASED SYSTEMS CONTAINING HIGH AMOUNTS OF Na_2SO_4

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ABSTRACT

Simulated cemented low level wastes containing high amounts of Na_2SO_4 (10 ~ 15%) were examined with respect to the mineralogy of the solid phases, chemical composition of the interstitial aqueous phase and immersion behaviour in water. All results reveal the formation of a mineral called U phase, first observed by Dosch and zur Strassen in 1967, and its deleterious effects on the samples immersed in water. It appears that this phase can form only at very high alkaline concentration, not compatible with traditional cement paste. Two possible degradation mechanisms associated with the U phase are proposed which are to be elucidated in further works.

Introduction

The low level liquid wastes (LLW) produced by nuclear industry are often partly evaporated in order to reduce their apparent volume. This process leads to concentrated solutions characterised by high concentrations of different salts such as sodium borate, nitrate or sulfate. In some cases, the concentration of sodium sulfate may reach 200 to 250 g/l. Large quantities of these wastes are solidified in cement matrix. As some of the components have the ability to produce waste-binder interactions, it is necessary to investigate the behaviour of this kind of cemented wastes.

Considering that the solidification of simulated wastes leads to high amounts of Na_2SO_4 (10 ~ 15%), this paper presents a preliminary study of the simulated samples. The mineralogical analysis of the solid phases, and chemical composition of the aqueous phase reveal the formation of the U phase. From experimental evidence, two possible degradation mechanisms associated with the U phase are proposed.

Experimental Procedure and Results

Mineralogy of the Solid Phases. Corresponding to one of the methods used in cementing the waste solutions, the following composition was chosen for this preliminary study: the hydraulic

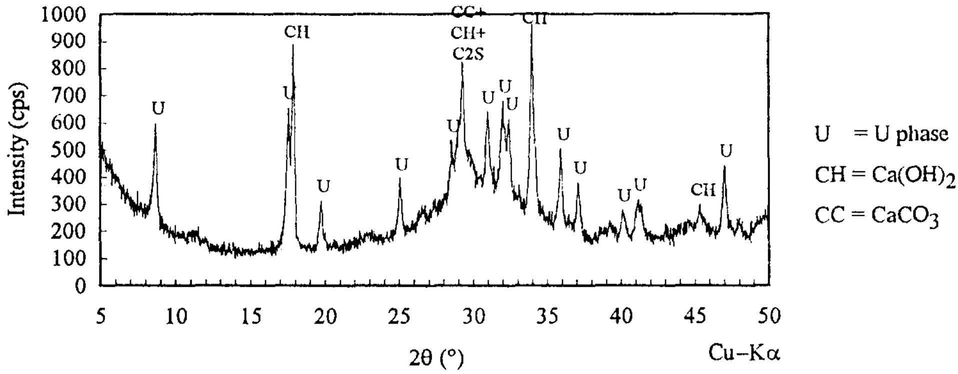


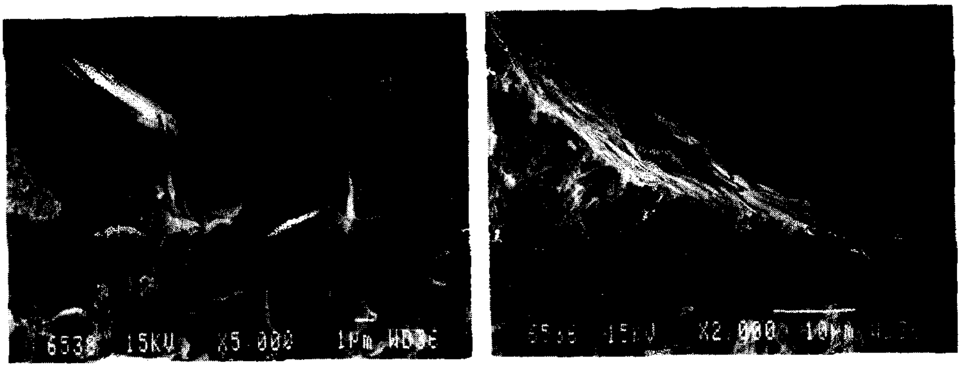
FIG. 1.
XRD pattern of the studied system after three months.

material composed of French OPC cement (CPA55R) and blast furnace slag, in proportion of 42 : 58, in weight, the simulated solution contained 25% Na_2SO_4 wt. and the mixing ratio of solution/solid was 0.58 wt. The samples were prepared according to the French norm NF EN196-3. Since in cementing concentrated liquid wastes, indrum mixing is the most frequently used process, the sealed adiabatic curing was therefore applied.

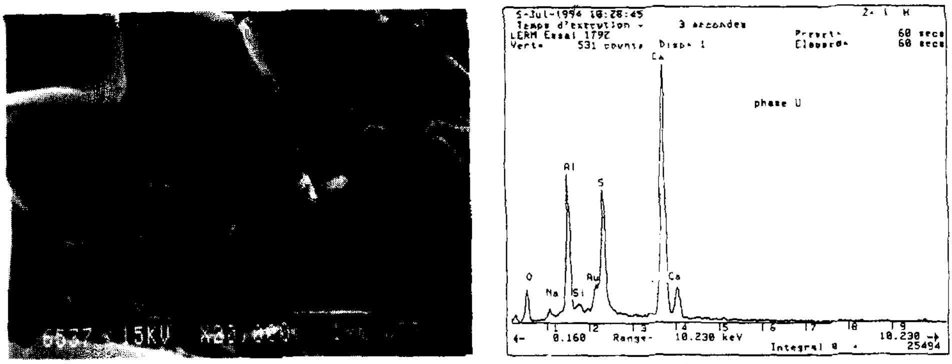
The mineralogical XRD analysis using the radiation Cu-Kα and 0.02°/3s were carried out after three months. A typical pattern is shown in Fig. 1. The identification of the peaks started by searching for typical phases in the sulfate-cement system such as ettringite, monosulfoaluminate and sulfates, and then proceeded by searching for usual hydrates like silicates, portlandite and carbonate, and anhydrous cement phases. However, there remained many diffraction lines, some even with very strong intensity, which can not be interpreted. The inter-reticular distances of these peaks are (Å): 10.00, 5.00, 4.46, 3.53, 3.33, 2.88, 2.77, 2.76 . . . .

In order to identify these peaks, literature searching was made with special attention paid to sulfates incorporated hydrates which may be influenced by alkalis. A mineral called U phase which was first observed by Dosch and zur Strassen in 1967 (1) was noticed. In their study of the chemical system $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}Na_2O\text{-}H_2O$ in a very vast range of concentrations, these authors found that a new phase was formed. The plausible composition of this phase was established as $4CaO \cdot 0.9Al_2O_3 \cdot 1.1SO_3 \cdot 0.5Na_2O \cdot 16H_2O$, belonging to the group of hexagonal or pseudo-hexagonal layered structures like AFm, but differing from the latter in the fact that it contained sodium between the layers and possessed a higher interlayer distance. Comparing the XRD pattern of the studied system with that obtained by these authors, we found immediately that all the non-identified lines could be attributed to the U phase, even the relative intensities corresponded exactly to those of the U phase.

The samples were also examined on fracture surfaces using the JEOL-820 SEM system equipped with an EDS analyzer. All observations showed the presence of abundant hexagonal platelets, both in the matrix (Fig. 2a), and more clearly in bubbles (Fig. 2b and 2c). The EDS analysis (Fig. 2d) indicated that these platelets had a similar composition with that of AFm, except that they contained sodium in a weak concentration. These results correlated consistently with the XRD analysis and the proposition of the structure of the U phase by Dosch and zur Strassen (1).



a. U phase in the matrix b. U phase in a bubble



c. Detailed observation of the U phase d. EDS analyse of the U phase

FIG. 2.
SEM observations and EDS analysis of the U phase.

Several tests on cemented wastes with other compositions were also carried out and all results revealed the presence of the U phase. For example, using French cement CLK45 (19% clinker and 81% BFS), the samples were prepared with a solution 20% Na_2SO_4 /solid ratio of 0.5 and with sealed adiabatic curing. At the age of seven days, in the XRD pattern, the U phase was clearly detected (Fig. 4a). Chemical analysis of the aqueous phase and expansion tests were also realized to obtain more information on these samples. The results are given beneath.

Composition of the Interstitial Solution. Considering the chemical equilibrium between the solid phases and the interstitial solution, it is preferable to take chemical analysis of the interstitial solution. The tests were conducted on the above-mentioned CLK45 samples. The interstitial solution was directly extracted from the samples under high squeezing pressure (500MPa for about one hour). It can be considered that the solution obtained in this way is close to the original interstitial phase.

A precipitation phenomenon took place immediately in the solution after extraction. XRD analysis of the precipitated solid showed the coexistence of two sulfates: thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4 \cdot 10H_2O$). Because of the very high alkalinity (>1 mole/l), it was impossible to measure the pH value by usual methods. The complete chemical analysis of the obtained solution was not performed, but the SO_4^{2-} and Ca^{2+} concentrations were carried out

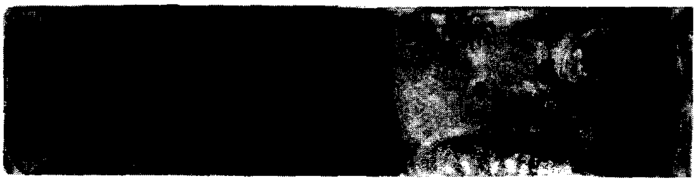


FIG. 3.
Surface deterioration of the sample CLK45 immersed in water for one year.

respectively by means of chromatography and EDTA. The concentration in SO_4^{2-} was found to be very high, around 1.72 ~ 1.99 mole/l, but no significant Ca^{2+} concentration was detected probably due to the very high alkalinity of the interstitial solution, in which $Ca(OH)_2$ is almost insoluble.

According to the study on the chemical system of H_2O-NaOH-Na_2SO_4 (2), the thenardite and mirabilite equilibrium corresponds to ~ 1.85 mole/l of Na_2SO_4 and ~ 3.0 mole/l of NaOH. The coexistence of thenardite and mirabilite in the extracted solution suggests that the alkalinity is very high (3mole/l, pH>14) and the SO_4^{2-} concentration is around 1.85 mole/l, although the solution deviates possibly from its equilibrium state because of atmospheric influence.

Immersion Behaviour of the Samples. In order to examine the immersion behaviour, a set of immersion tests was carried out on the samples with different compositions (10 ~ 15% Na_2SO_4) under sealed adiabatic curing for seven days. Generally, these samples underwent obvious swelling which led to many cracks or even complete destruction. For example, the Fig. 3 showed the severe degradation of a CLK45 sample (4 × 4 × 16cm) in which many microcracks appeared.

The mineralogical analysis by XRD of these samples at the end of one year immersion was carried out (Fig. 4b) and compared to the initial composition (Fig. 4a). Large differences appear. It is first observed that the intensity of the peaks due to the U phase increases

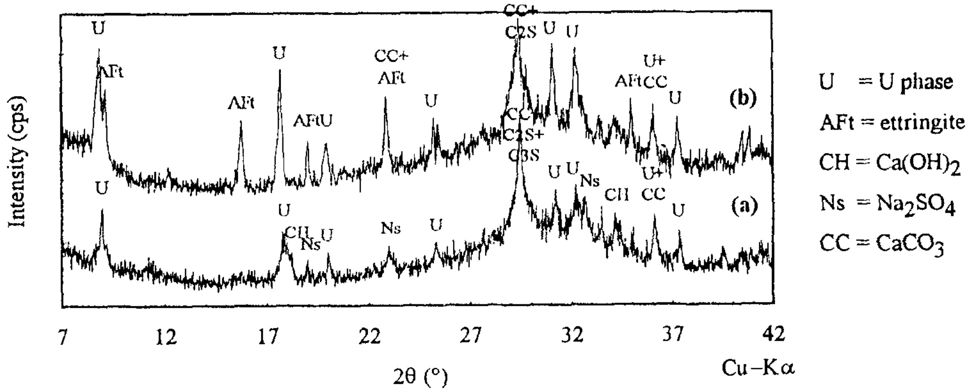


FIG. 4.
XRD patterns of the sample CLK45 before (a) and after (b) immersion. (U = U phase; AFt = ettringite; CH = $Ca(OH)_2$; Ns = Na_2SO_4; CC = $CaCO_3$).

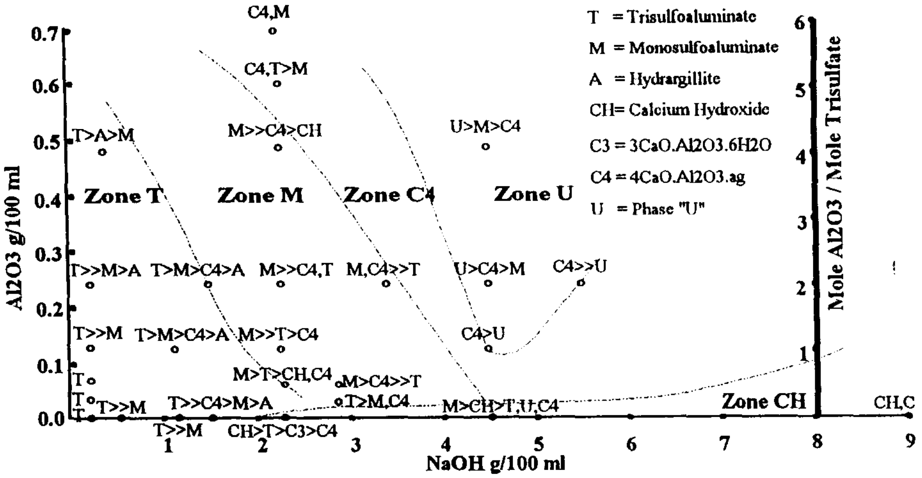


FIG. 5.

Formation of the U phase from ettringite at high alkaline concentration (1).

significantly compared to the initial mineralogy. This change indicates a secondary formation of the U phase after the immersion. It is further found that besides the secondary formation of the U phase, the ettringite was formed abundantly.

Discussion

Formation Conditions of the U Phase. In traditional concrete, the only well-known calciumsulfo-aluminates are AFm and AFt. They have important influences, both favourable and unfavourable on the properties, performance and durability of concrete as it is known that AFt is responsible for the sulphate expansion (3–4). Because of the high alkalinity of the pore water in concrete, the stability of AFm and AFt in alkali solutions have been a subject of many studies (5–6), but the alkaline concentration in these studies is often limited under 1.0M and no new phases were observed other than those formed in the alkali-free system.

However, in the study by Dosch and zur Strassen (1), in which the range of alkaline concentrations was larger, a new mineral was observed. Fig. 5 gives the nature of the precipitated solid phases obtained by stirring a constant quantity 1.45g AFt in 100 ml NaOH solutions of different concentrations. Although these tests gave only an approximate view of the equilibrium phase diagram, since an evolution was still detected after the end of the tests at 28 days, it was shown that when the alkaline concentration was high, a new phase was formed in the relatively high alumina concentrations and was called as U phase probably because its region of existence resembles the character "U".

Seligmann and Greening (7) undertook a similar set of tests (stirring ettringite in NaOH solution) and the results confirmed the U phase formation. In addition, it was found that when the slurries made from one part of cement and as much as 8 parts of 8 percent sodium hydroxide solution were hydrated, the U phase was the only sulfate-containing phase formed in the solid.

The U phase was also observed by Way and Shayan (8) in their study of the effects of NaOH on the composition of the aqueous phase and the nature of the solid phases formed during the early hydration of cement. By hydrating the OPC cement in 0, 0.5, 1, 2 and 5M NaOH solutions with w/c = 1.0, the U phase was detected at 2 and 4.5M.

In some publications (9–13), the U phase was mentioned , but all of them quoted the work of Dosch and zur Strassen and no more experimental study was carried out.

Recently, the U phase formation in cement medium was finally confirmed in studying the cement-based systems composed of high aluminate cement or Portland cement and Na_2SO_4 in high proportions (14). It was found that this compound could form in cement in the presence of high alkali concentration although the studied systems are not compatible with the traditional cement pastes, and the U phase appeared as deleterious for the samples immersed in water.

It appears that the U phase formation can occur only at high alkaline concentration, in the presence of sulfates and alumina. This compound is unlikely to form in traditional cement paste because the particular formation conditions are generally not satisfied. On the contrary, for the studied systems containing high amounts of Na_2SO_4, the alkalinity of the interstitial solution reached 3M or higher. This highly alkaline media is compatible with the U phase formation which was revealed experimentally (XRD analysis and SEM observations). It is therefore concluded that the U phase can form in cement paste in the presence of high alkali content.

Possible Degradation Mechanisms Associated with the U Phase. As it is shown, the samples in which the U phase was formed exhibited severe degradation. It thus seemed necessary to investigate on the potential influence of the U phase on the immersion behaviour. From experimental evidence, it is reasonable to assume that the degradation may be produced in two ways:

(i) Secondary formation of the U phase. For certain deleterious phases such as ettringite and gypsum, the secondary formation in the presence of sulfate and external water supply can induce an expansion phenomenon by creating necessary space for accommodating the new solid phase (15–16). In the case of the U phase, its secondary formation in the immersed samples was clearly identified by XRD analysis. It is possible that this reaction, probably due to the mixing water deficit, accomplishes an expansion phenomenon which contributes to the degradation.

(ii) The transformation of the U phase into ettringite. The experiments of Dosch and zur Strassen (Fig. 5) show that when the alkaline concentration progressively decreases, the U phase is transformed finally into ettringite, with some intermediate compounds which are generally considered as not deleterious: $U \rightarrow C_4AH_{13} \rightarrow AFm \rightarrow AFt$. Taking into account the diffusion of the alkalis during the immersion which leads to the decrease of alkaline concentration and the presence of ettringite in the immersed samples which underwent severe degradation, it can be envisaged that the transformation of the U phase into ettringite is an expansion process.

To verify these two possible degradation mechanisms, it is advocated to undertake some further works with special experimental conditions in order to completely separate the influence of the two mechanisms proposed.

Conclusions

1. The mineral called U, a sodium-substituted AFm phase can occur only at very high alkaline concentration, in the presence of sulfate and alumina. It has never been observed

in traditional cement paste because of its particular formation conditions, but occurred in cemented low level wastes containing high amounts of Na_2SO_4 (10 ~ 15%).

2. It appears that the U phase has deleterious effects on the immersed samples. Two possible degradation mechanisms associated with the U phase are proposed and to be elucidated in further works: the secondary formation of the U phase under an external water supply and the transformation of the U phase into ettringite caused by the decrease of alkaline concentration.

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