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SYNTHESIS OF THE U PHASE ($4CaO . 0.9Al_2O_3 . 1.1SO_3 . 0.5Na_2O . 16H_2O$)

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ABSTRACT

A mineral called "U phase" was recently identified in cement-based systems at high alkali concentration. This sodium-substituted AFm phase with chemical composition $4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.16H_2O$ can induce deleterious effects through its secondary formation and its transformation into ettringite. In order to go further in its properties, this paper reports some methods of the pure U phase synthesis. Ten compositions were chosen and tested. It was found that the reaction between Na_2SO_4 (0.5mole) + $Ca(OH)_2$ (0.5mole) and a fresh sodium aluminate solution (dissolution of 0.41~0.82 mole metallic aluminum fine powder in 1 liter 1N NaOH solution) may be considered as the most efficient way for synthesizing the U phase.

Introduction

In 1967, Dosch and zur Strassen (1) reported the existence of the U phase in their study of the chemical system $4CaO-Al_2O_3-SO_3-Na_2O-H_2O$ in a vast range of alkaline concentration. It was presumed that it possessed a hexagonal or pseudo-hexagonal structure like AF_m (a = 5.75Å) and its approximate composition was established to be as $4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.16H_2O$. These authors supposed that the U phase could be formed in dry cement systems, although they thought that high concentrations in alumina and sulfate were necessary for the U phase formation.

In the study of Shayan, Quick and Lancucki (2) on the steam-cured concretes containing or not densified silica fume and various alkali levels, the U phase was systematically detected, especially at high alkali concentration, not only in the OPC cement concretes but also in the concretes containing silica fume.

Recently, the formation of the U phase in cement-based systems containing high amount of Na_2SO_4 was evoked (3-6). Its deleterious effects on the samples immersed in water were observed and two degradation mechanisms were identified: (i) the secondary formation of the U phase, (ii) the transformation of the U phase into ettringite.

Considering the temperature effect in mass concretes and possible high alkali concentrations in the cement used, it appears that the U phase can also be formed. Its formation could result in concrete deterioration.

However, the U phase has seldom been studied. In order to investigate more deeply the physico-chemical properties of the U phase and their influence on the durability of concrete, it was necessary to establish an efficient process for the synthesis of the pure U phase. For this purpose, Dosch and zur Strassen (1) proposed two synthesis procedures using soda solution, aluminum, lime and gypsum. We tried these two procedures, but they didn't give very satisfactory results. Moreover, it is also important to know whether the U phase can be formed or synthesized with Na_2SO_4, in the absence of gypsum. This paper examines ten compositions chosen for the U phase synthesis. The mineralogical evolution was monitored systematically by means of X-ray diffraction (XRD) for all mixtures. The examination of the pure U phase by a scanning electron microscope (SEM) associated with an energy-dispersive analyser (EDS) was also performed.

Experimental

The two synthesis procedures proposed by Dosch and zur Strassen are as follows (1):

- Procedure 1: dissolve first one mole metallic aluminum in one liter 1N NaOH solution, free of CO_2. Treat immediately the fresh sodium aluminate solution with gypsum and calcium oxide, the proportions corresponding to the stoichiometry of the $CaO.Al_2O_3.CaSO_4.Na_2O$ system. Filter the solid precipitated from the solution after at least one day of the continuous stirring.
- Procedure 2: Put at one time all solid constituents in the sodium hydroxide solution of the procedure 1. The reaction progresses more slowly following the dissolution of the aluminum.

Table 1 gives the ten different compositions; each one was calculated on the base of one liter 1N NaOH solution. They were chosen according to the following criteria:

- N° 1: verify the first procedure proposed by Dosch and zur Strassen, i.e. use NaOH, Al, $Ca(OH)_2$ and $CaSO_4.2H_2O$ as the initial constituents. Their proportions correspond to the stoichiometry $CaO.Al_2O_3.CaSO_4.Na_2O$,
- N° 2: use the same initial constituents NaOH, Al, $Ca(OH)_2$ and $CaSO_4.2H_2O$, but their proportions correspond exactly to the stoichiometry of the U phase $4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.16H_2O$,
- N° 3: use NaOH, Al, $Ca(OH)_2$ and $Al_2(SO_4)_3$ as the initial constituents; their proportions correspond to the stoichiometry of the U phase (SO_3 is slightly in excess,
- N° 4: use NaOH, Al, $Ca(OH)_2$, $CaSO_4.2H_2O$ and C_3A as the initial constituents; their proportions correspond also exactly to the stoichiometry of the U phase,

- N° 5: test the transformation of C_3A into the U phase, with other constituents NaOH, $Ca(OH)_2$ and $CaSO_4.2H_2O$,
- N° 6: test the transformation of C_3A into the U phase, with other constituents NaOH, $Ca(OH)_2$ and Na_2SO_4,
- N° 7: use NaOH, Al, $Ca(OH)_2$ and Na_2SO_4 as the initial constituents; their proportions correspond to the stoichiometry of the U phase except NaOH which is in excess,
- N° 8a, N° 8b and N° 8c: modify the composition of the configuration N° 7 in order to obtain the U phase as pure as possible.

The synthesis procedure used in our study is described as follows:

- prepare the 1N NaOH solution. Sieve separately the solid constituents at 100μm except the metallic aluminum already in fine powder and weigh exactly all solid constituents,
- if necessary, homogenize the solid constituents by sieving them together at 100 μm except the metallic aluminum,
- dissolve progressively but as quickly as possible the metallic aluminum in the NaOH solution to avoid the carbonation. Special attention should be paid to the violent reaction with the high release of heat and hydrogen gas,
- stir continuously the fresh solution about three minutes until the complete dissolution of the metallic aluminum,
- introduce individually the remaining solid constituents or together at one time the solid mixture if they were prehomogenized, in the fresh sodium aluminate solution. For the former choice, the introduction order of sulfate → calcium aluminate → calcium oxide should be respected for avoiding the formation of hydrated calcium aluminates.

The slurries were stirred continuously for 14 days and then followed by 14 days aging. They were monitored regularly (2 hours, 1, 2, 7, 14, 28 days) by means of X-ray diffraction (Cu-Kα).

To prepare the sample for XRD analyses, the slurries were first filtered. The precipitates were then dispersed in ethanol and refiltered, this being repeated three times. The resulting products

TABLE 1

Composition of the Mixtures for the U Phase Synthesis (in mole)

No	NaOH	Al	$Ca(OH)_2$	$CaSO_4.2H_2O$	Na_2SO_4	C_3A	$Al_2(SO_4)_3$
1	1 liter (1 N)	1.00	0.50	0.50			
2		1.80	2.90	1.10			
3		1.00	4.00				0.40
4		1.00	1.60	1.20		0.40	
5			0.50	0.50		0.50	
6			0.50		0.50	0.50	
7		1.00	2.22		0.61		
8a		1.00	0.50		0.50		
8b		0.82	0.50		0.50		
8c		0.41	0.50		0.50		

were redispersed in ethanol by ultrasonic vibration. Then the slurries were removed, deposited on a flat sample support and slightly stricken as a homogeneous thin layer. Measurements could be taken just after the evaporation of ethanol; this needed about one minute.

The sample used for SEM observation was similarly prepared. The final product was dried in the atmosphere for some minutes as white powder. Then it was directly deposited on a plate of glass. No special treatment was carried out on samples.

Results and Discussion

The chemical reactions began immediately after the introduction of the solid constituents in the fresh sodium aluminate solution obtained by dissolving metallic aluminum powder in the soda solution. The mineralogical composition and solid content could change in the slurries within the first week, but after two weeks no significant evolution was observed.

The final products were usually obtained at the end of 28 days by alternative filtering and dispersion in ethanol for several times. The XRD analyses were performed for all final products, but the SEM observation and the EDS analysis were carried out only on the pure U phase.

The XRD analysis of the final products at 28 days are shown in Fig. 1. It can be observed that the U phase was formed in large quantities in all cases. The impurities were usually ettringite, monosulfoaluminate, calcium hydroxide, aluminum hydroxide and calcium aluminate carbonate, but their relative quantity in the precipitates could be different.

For the experiments N°s 1~4 where gypsum was used, the impurities in the final product were essentially the residual calcium hydroxide and ettringite as intermediate reaction compound. In fact, the evolution of the precipitates in the slurries followed by XRD showed that ettringite was the first product formed as soon as the reactions began and it increased during the first several hours even when the U phase abundantly precipitated. At longer term, ettringite was transformed progressively into the U phase, but its trace was always observed. The existence of ettringite, together with gibbsite and calcium hydroxide, although in small quantities, makes the first synthesis procedure proposed by Dosch and zur Strassen not very satisfactory.

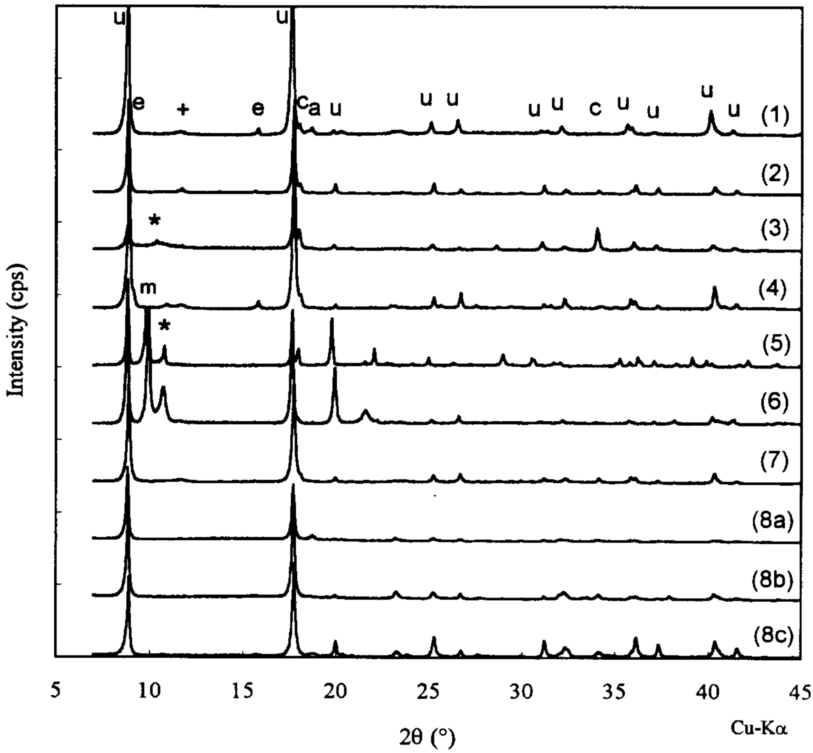
Similarly to the experiments N°s 1~4, ettringite was the first product formed in N° 5 and it increased even when the U phase formation took place. Later on, ettringite disappeared, but the monosulfoaluminate was considerably formed with intermediate compounds as α-tetracalcium aluminate 13-hydrate C_4AH_{13} incorporating some CO_3^{2-} ions. It is to be noted that the remaining $Ca(OH)_2$ was always quite high.

For the experiment N° 6, the U phase formation was observed as soon as the chemical reactions began and continued for about one week, but for longer time, the conversion of the U phase into AFm took place. The compound α-tetracalcium aluminate 13-hydrate C_4AH_{13} incorporating some essential CO_3^{2-} was also detected. The results of experiments N° 5 and N° 6 indicated that the U phase could be formed in the hydrated cement especially with high content of sulfate, although the synthesis conditions were very different from those of the normal hydrated cement. In addition, these results indirectly meant that the conversion could take place between the U phase, the monosulfoaluminate and ettringite.

For experiments N° 7 and N° 8 where sodium sulfate was used, analyses of precipitates at different ages indicated that the U phase was always the main product, sometimes with gibbsite in very small quantity, but ettringite was never present. Ettringite formation was probably avoided due to the high alkalinity driven by addition of sodium sulfate. The calcium hydroxide progressively disappeared following the formation of the U phase, and it was observed only in negligible quantity in the final products. It was further found that the purity of the synthesized U phase could be systematically improved by using sodium sulfate instead of gypsum.

It is to be noted that some carbonates were often detected in the precipitates. They were in most cases tetracalcium aluminate carbonate 12-hydrate $C_3A.CaCO_3.12H_2O$ and α-tetracalcium aluminate 13-hydrate (C_4AH_{13}) with some CO_3^{2-} ions. Sometimes the trace of sodium carbosulfate $Na_6CO_3(SO_4)_2$ was also observed. In fact, the carbonation of precipitates was always possible during the preparation of sodium aluminate solution which released considerable heat, or even during the XRD measurement. It was also possible that these carbonates were due to impurities in original compounds. For avoiding impurities caused by carbonation, it is better to prepare the synthesis slurries and take the XRD measurement under CO_2 free atmosphere.

In this study, the U phase was essentially identified by XRD analyses at the peaks d = 10.00 Å and d = 5.00 Å which correspond respectively to the planes (001) and (002). The other peaks



u = U phase e = ettringite m = monosulfoaluminate a = gibbsite c = $Ca(OH)_2$
+ = tetracalcium aluminate carbonate 12-hydrate $C_3A.CaCO_3.12H_2O$
* = α-tetracalcium aluminate 13-hydrate (C_4AH_{13}) with some CO_3^{2-} ions

FIG. 1.
XRD patterns of the precipitates at 28 days - U phase synthesis experiments N°s 1~8.

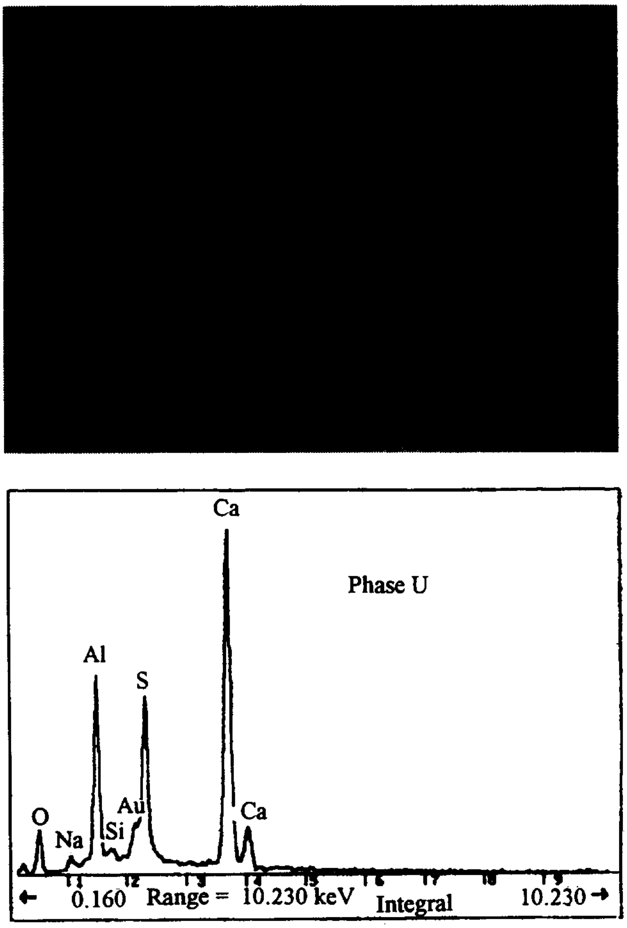


FIG. 2.
SEM observation and EDS spectrum of the pure synthesized U phase.

were often too weak due to the preferential orientation of crystals caused by the special preparation.

Comparing the relative quantities of impurities in the final products, it is found that the experiments N° 8b and N° 8c can be considered as the best methods for synthesizing the U phase. In fact, these procedures were already applied to the pure U phase for the study of the expansion mechanism by transformation of the U phase into ettringite (3).

SEM observations with EDS analysis on the pure synthesized U phase (Fig. 2) show that the U phase occurs in hexagonal plates isomorphous of the calcium monosulfoaluminate. Therefore it is difficult to distinguish the U phase from the monosulfoaluminate on SEM. The best way to identify the U phase is the XRD analysis.

The density of the U phase was also measured by means of multipycnometry. The value obtained at 20°C is 1.95g/cm^3 which is very close to that of the calcium monosulfoaluminate 1.99g/cm^3 (7).

Conclusions

The synthesis of the pure U phase is relatively difficult. The minor phases detected in the ten compositions tested in this study were essentially residual calcium hydroxide, ettringite and different carbonates.

To conclude, the most efficient method corresponds to the immediate reaction between Na_2SO_4 (0.5 mole) + $Ca(OH)_2$ (0.5 mole) and the fresh sodium aluminate solution resulting from the dissolution of metallic aluminum fine powder (0.41~0.82 mole) in NaOH solution (1 liter of 1 N).

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