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PHYSICO-CHEMICAL TRANSFORMATIONS OF SULPHATED COMPOUNDS DURING THE LEACHING OF HIGHLY SULPHATED CEMENTED WASTES

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ABSTRACT

Cementation of sulphated evaporator concentrates leads to highly sulphated low level wastes, (ca. 25% w/w sodium sulphate solution as mix water), which exhibit the presence of "U-phase," a sodium-bearing calcium monosulphoaluminate-like phase. During the leaching of simulated highly sulphated OPC/BFS cements, cured at room temperature and containing U-phase, sodium sulphate, and ettringite, physico-chemical transformations have been pointed out (transformation of U-phase into ettringite). Samples having the same chemical composition, but cured at high temperature (maximal temperature during curing: 120°C), do not contain ettringite initially, but secondary ettringite is formed during leaching. XRD spectra point out the existence of precipitation fronts (or of phase formation fronts) varying linearly versus the square root of time. The analysis of leaching solutions has provided complementary data used in a code, the aim of which is to assess cement degradation, based on coupling between transport by diffusion and chemical reactions (DIFFUZON code). The U-phase-ettringite transformation is confirmed. © *1997 Elsevier Science Ltd*

Introduction

The presence of sulphated compounds in cements often leads to the presence of well known ettringite. In the case of very concentrated sodium sulphate solutions used as mixing water, the presence of other sulphated phases, such as U-phase (4 CaO, 0.9 Al_2O_3, 1.1 SO_3, 0.5 Na_2O, 16 H_2O) (1), can be pointed out. As this phase is stable in high alkali concentrated pore solutions (2), leaching of cement samples containing U-phase may lead to destabilisation of this phase, and conversion into other phases.

Three degradation mechanisms had been envisaged, all of them being expansive (3–5): 1)

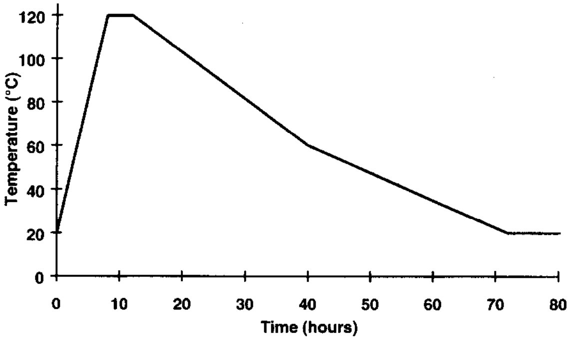

FIG. 1.
Thermal treatment of HTC samples during curing.

a complementary formation of U-phase, by hydration of anhydrous compounds during soaking; 2) a transformation of thenardite (anhydrous sodium sulphate) into mirabilite (hydrated sodium sulphate); and 3) a transformation of U-phase into ettringite.

The aim of this study is to point out the physico-chemical transformations of sulphated compounds present in simulated wastes containing large quantities of sodium and sulphate ions during leaching in deionised water using several complementary techniques.

Materials and Methods

The cements used in this study were a mixture of OPC and BFS (30/70 wt). Mixing water was a solution of 25% w/w Na_2SO_4, and its temperature was 50°C. Ratios of Waste/Cement and Water/Cement were respectively 0.586 and 0.440.

Two types of curing conditions were used: curing during 28 days at room temperature, i.e. without thermal treatment, in order to simulate the external part of the cemented waste drums (called "RTC" samples), and curing during 28 days including an autoclave treatment (no water was evaporated during the curing), in order to simulate the core of the waste drums, according to Figure 1 (called "HTC" samples).

TABLE 1
Chemical composition of the main compounds encountered in the samples

	C	A	s	N	H	S	pointed out in samples	abbreviation
U-phase	4	0.9	1.1	0.5	16	0	RTC, HTC	U
ettringite	6	1	3	0	32	0	RTC only*	AFt
portlandite	1	0	0	0	1	0	RTC, HTC	CH
thenardite	0	0	0	1	1	0	RTC, HTC	Ns
Si-katoïte	3	1	0	0	4	1	HTC only	Kat
CSH	**	0	0	0	**	**	RTC, HTC	CSH

*Abbreviations: C, CaO; A, Al_2O_3; s, SO_3; N, Na_2O; H, H_2O; S, SiO_2; including degraded HTC samples.

**Variable composition. An approximate composition could be $C_{1.5}SH_{2.3}$.

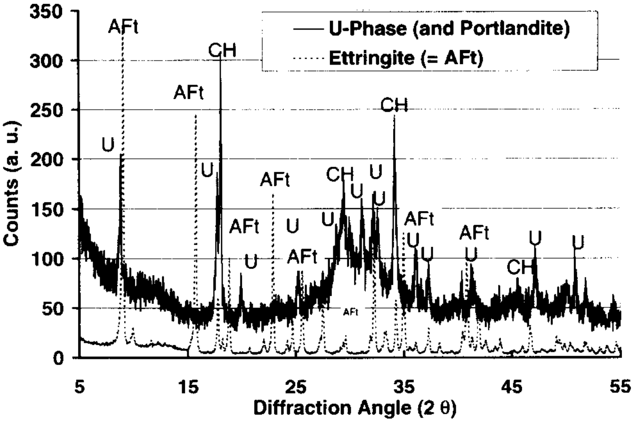

FIG. 2.
XRD diagrams (Cu-Kα) of U-phase (containing some portlandite) and ettringite.

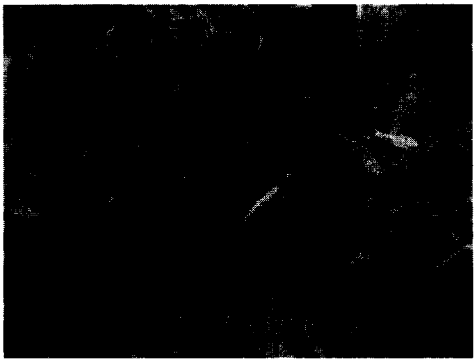

FIG. 3.
U-phase. Magnification 5000×.

FIG. 4.
Ettringite. Magnification 1500×.

TABLE 2
Main XRD peaks of considered compounds

Compound	U-Phase	Ettringite	Portlandite	Sodium Sulphate	Katoite (HTC Samples only)	Quartz (internal standard)
Chosen peak (Å)	10.0	5.61	4.92	3.18	4.38	3.34

After curing, the samples were kept in deionised water (pH = 7, T = 20°C) for predetermined soaking times (2, 4, 8, 16, 24, 36, and 48 weeks), then analyzed. According to the experimental method, samples were prisms 4 cm × 4 cm × 16 cm or cylinders ϕ 3.3 cm - H 6 cm.

In some cases, the samples were only powders after manual scraping.

XRD measurements were carried out on a Siemens D500 diffractometer (Cu - Kα radiation under 40 kV/25 mA; 5 s/0.02°) using powder samples. An internal standard (quartz) was used in almost all tests. Minimal thickness of the samples was ca. 600 μm with the wire saw (ca. 100 μm for manual scraping). Precision depended on crystallization and concentrations. XRD analyses were carried out between 5 and 55° (i.e., <1.7 to >10 Angström, allowing the main peaks of major components to be pointed out).

SEM pictures were taken with a JEOL 820 device with microanalysis (secondary electrons for surfaces of cracking or back-scattered electrons for polished sections). The samples were coated with gold after vacuum cryo-sublimation. The shape of the various minerals was not modified; however, some microcracks might appear. Acceleration tension was 15 kV. SEM observations were carried out along depth (transversal section) on samples 4 × 4 cm cut in the middle of the prism. Magnification was up to 5000× (details under 0.1 μm were visible).

The extraction of pore solution was conducted on CEA prototype equipment with a 3000 kN press.

The leaching device has been described in reference (6). The leachant (volume ca. 1.5 L) was maintained at a constant pH by adding nitric acid (0.1 M). However, in order to limit the influence of nitrate ions on the samples, the leachant was renewed when a small volume of nitric acid had been introduced into the leachant (volume <20 mL). The leachant was then analyzed.

Every soaking tank was equipped with a circulation pump and ion exchange resins

TABLE 3
Evolution of phase composition along depth after 48 weeks soaking
(RTC samples)

AFt	→	↗	↗	↗	↘	↘	
U	→	↘	↘	↘	↘		
CH	→	↘	↘				
Ns	→	↘					
depth > (μm)	core	~7000	~3300	~1300	~600	~300	0

↗: increasing from core towards external layer; ↘: decreasing from core towards external layer; →: no significant variation.

TABLE 4
Evolution of phase composition along depth after 48 weeks soaking (HTC samples)

AFt				↗	↗	↗	↘	
U	→	→	→	→	↘			
CH	→	↘						
Ns	0							
depth > (μm)	core	>8000	~8000	~4000	~1600	~1400	~600	0

↗: increasing from core towards external layer; ↘: decreasing from core towards external layer; →: no significant variation.

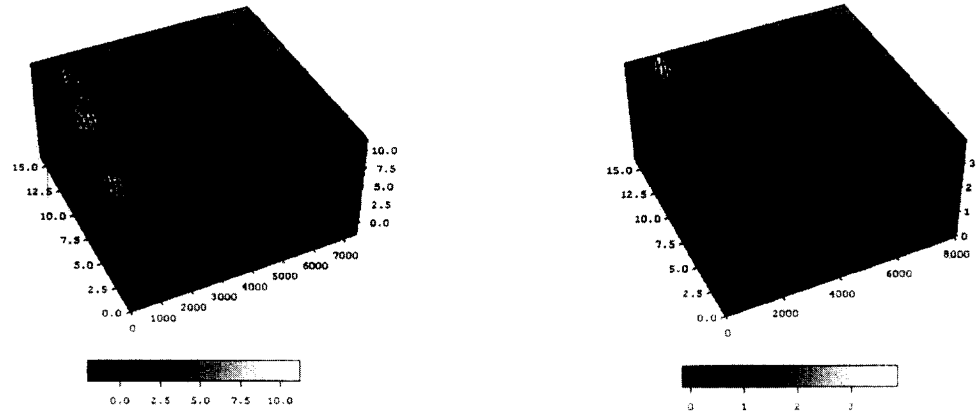

FIG. 5.
Ettringite (left side, RTC samples; right side, HTC samples; left axis, square root of time in days; right axis, depth in μm; vertical axis, mass fraction in %).

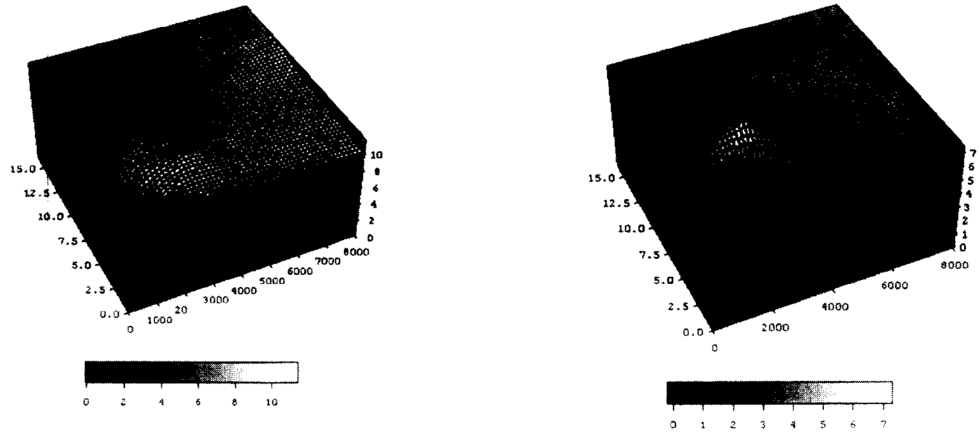

FIG. 6.
U-Phase (left side, RTC samples; right side, HTC samples; left axis, square root of time in days; right axis, depth in μm; vertical axis, mass fraction in %).

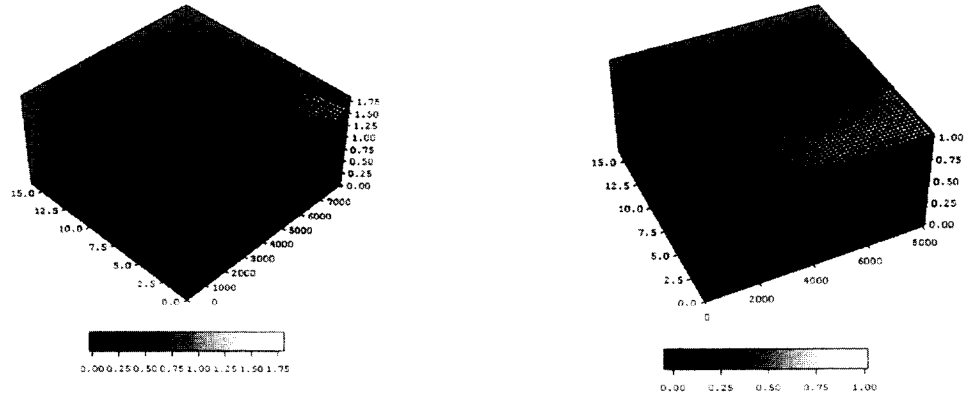

FIG. 7.
Portlandite (left side, RTC samples; right side, HTC samples; left axis, square root of time in days; right axis, depth in μm; vertical axis, mass fraction in %).

(mixture of anionic and cationic resins) and contained ca. 40 L water (deionised continuously). The period of renewal was ca. 2 hours.

Results and Discussion

The chemical compositions of the main compounds pointed out in the samples are summarized in Table 1.

Ettringite is found in the samples cured at low temperature, but disappears in the samples cured at hot temperature (maximal stability temperature of ettringite is ca. 90°C (7)). A compound identified as silicated katoïte C_3ASH_4 (8) has been pointed out in HTC samples. This compound is very stable and is found even in degraded layers, indicating a very low solubility. The absence of ettringite is not astonishing due to the application of the rule of phases. But as ettringite is pointed out in degraded layers (see later in the text), this can only occur if another compound disappears (local equilibrium hypothesis). We point out the incompatibility of ettringite and portlandite in our experimental conditions.

Differentiation between Ettringite and U-phase

U-phase is an AFm-like phase, containing sodium hydroxide (9). It can easily be differentiated from ettringite by its XRD spectrum, especially by the line at 5.6Å, which is not present

TABLE 5
Composition of pore solution (RTC samples before and after 48 weeks leaching results in mmol/L

Element	OH^-	SO_4^{2-}	Na^+	Ca (total)
Initial	680	1140	2850	1.7
After 48 weeks soaking	63	538	1140	7

TABLE 6
Leached fractions of main components after
48 weeks leaching (Cylinders ϕ 3.3 cm - H 6 cm)

After 48 weeks	RTC leached fractions	HTC leached fractions
Na^+	49%	47%
Ca^{2+}	10%	8%
SO_4^{2-}	20%	23%

in U-phase diagrams. Figure 2 gives the XRD spectrum of U-phase (containing some portlandite) and pure ettringite.

SEM photographs of U-phase and ettringite are different. Figure 3 shows the characteristic plates of U-phase, and Figure 4 shows the characteristic needles of ettringite.

Samples Degraded by Leaching

For a detailed examination of phase modifications, the chosen peaks are given in Table 2.

A clear evolution of phase composition has been determined (RTC and HC samples).

Tables 3 (RTC samples) and 4 (HTC samples) show the phase evolution along depth after 48 weeks soaking.

Figures 5–7 give the evolution of the composition of ettringite, U-phase, and portlandite along depth vs. square root of soaking time.

For samples cured at room temperature, the phase evolution from core towards outside is as follows (in the order of vanishing): sound core/sodium sulphate/portlandite/U-phase/ettringite/amorphous layer.

For samples cured at hot temperature, the phase evolution from core towards outside is as follows (in the order of emergence or vanishing): sound core/vanishing of sodium sulphate/vanishing of portlandite/emergence of ettringite/vanishing of U-phase/vanishing of ettringite/amorphous layer.

In both cases, the vanishing (or emergence) of the various phases follows roughly a law in square root of time.

Pore Solution Composition

The results for RTC samples are summarized in Table 5:

The initial pore solution is likely in equilibrium with portlandite, sodium sulphate, U-phase, and ettringite. Taking into account a solubility product of ettringite from literature (Ks (ettringite) = 2.8×10^{-44} (10)), a value of the solubility product of U-phase could be estimated (using concentrations instead of activities): a constant value of 6×10^{-33} to 4×10^{-32} is obtained for Ks of U-phase (pKs = 31.4 to 32.2), in good agreement with previous values (pKs ≈ 28 (11)).

No pore solution could be extracted from HTC samples.

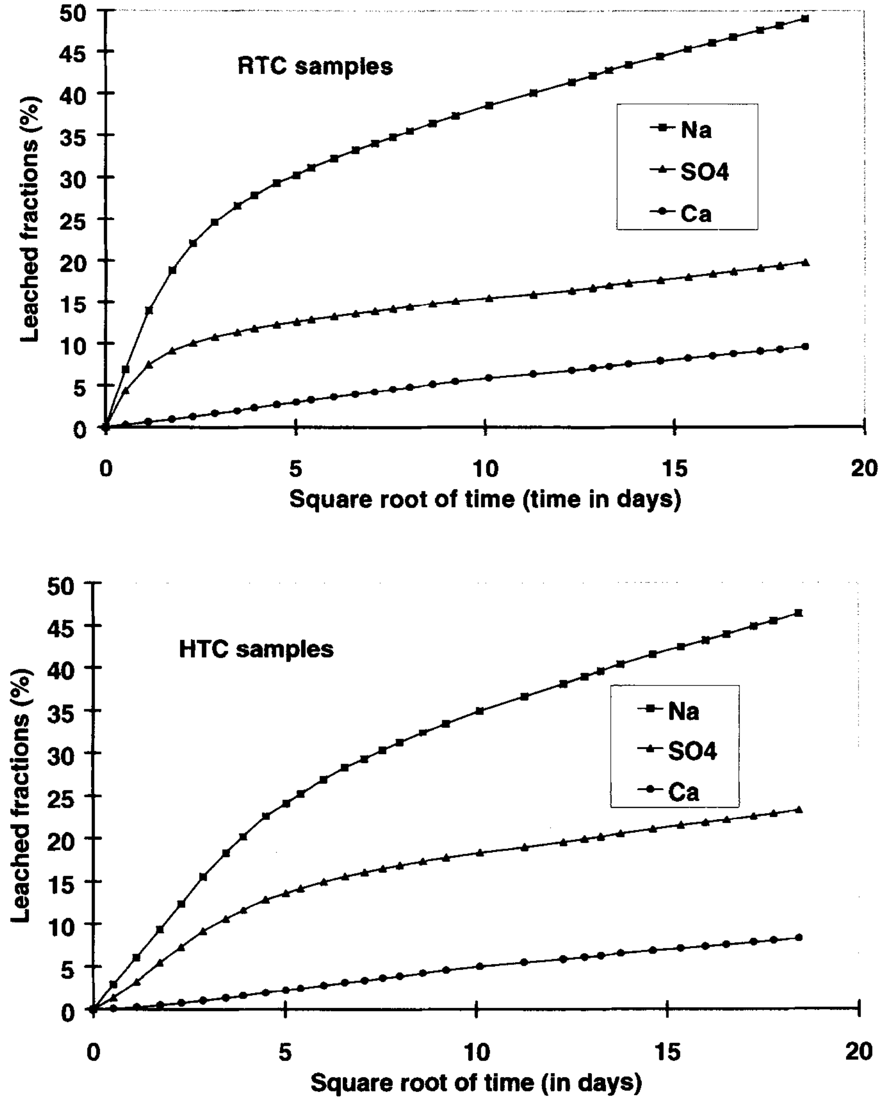

FIG. 8.

Leached fractions of sodium, sulphate ion and calcium (top, RTC samples; bottom, HTC samples).

Leaching Tests

Leaching of the main components of pore water (sodium, calcium, sulphate, and hydroxyl ions) was followed up for one year. Calcium shows a release proportional to the square root of time; sodium and sulphate exhibit a slowing down of release after a few days. In both cases (RTC and HTC), leached fractions of sodium and sulphate are important (Table 6).

Sodium and sulphate are supposed to be entirely in the hydrated phase, calcium partially (a part of BFS remains unhydrated after 48 weeks soaking). Calcium is supposed to be totally

TABLE 7
Leaching fluxes of main species
(steady state)

RTC Samples ($mol{\cdot}day^{-1/2}{\cdot}dm^{-2}$)		HTC Samples ($mol{\cdot}day^{-1/2}{\cdot}dm^{-2}$)	
Na^+	2.4	Na^+	2.5
Ca^{2+}	3.4	Ca^{2+}	2.8
SO_4^{2-}	0.5	SO_4^{2-}	0.5
OH^-	8.2	OH^-	7.1

available for migration. As BFS is not totally hydrated, the given values are likely underestimated.

The leaching curves are summarized in Figure 8.

The leaching fluxes are summarized in Table 7.

Modelling—Use of the DIFFUZON Code

The comparison of experimental results seem to point out the transformation of U-phase into ettringite. The DIFFUZON code (6) has been used. This code is based on the coupling between transport by diffusion and chemical reactions.

The degraded part of cement paste is divided into a set of zones having a constant mineralogy. For classical cement pastes, this fact is confirmed by experimental results and represents a consequence of the "local equilibrium principle." For the sulphated cements

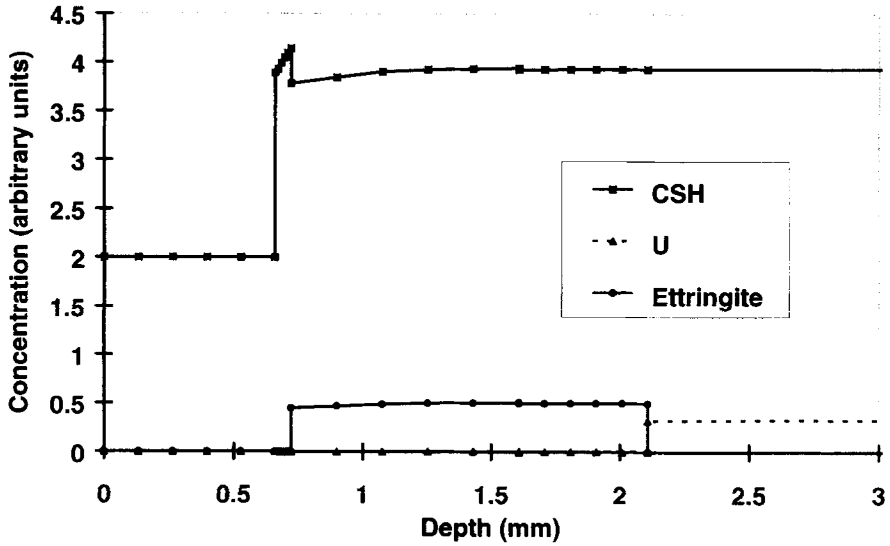

FIG. 9.
Simulation using the DIFFUZON code (6), pointing out the possible conversion of U-phase into ettringite (simulating HTC samples). U-phase vanishes when ettringite precipitates.

studied here, the same assumptions of constant mineralogy can be made concerning the main compounds (U-phase, ettringite, portlandite, sodium sulphate). Concerning C-S-H, similar assumptions are taken, i.e., possible precipitation of C-S-H having C/S ratios of 1.05, 1.15, 1.30, 1.45, and 1.65, although the corresponding compounds have not been clearly identified.

The code points out the possible coexistence of U-phase and ettringite, and confirms the phase evolution (U-phase front/ettringite front/amorphous layer, at least for RTC samples) already described. It confirms thus the possible U-phase-ettringite transformation, as pointed out in Figure 9.

Conclusions

Three degradation mechanisms for sulphated cemented wastes were envisaged in order to explain the degradation of samples.

The first mechanism (complementary formation of U-phase by hydration of anhydrous compounds during soaking) has never been pointed out experimentally: no increase of U-phase concentration is pointed out in the synthesis tables.

The second mechanism (transformation of thenardite (anhydrous sodium sulphate) into mirabilite (hydrated sodium sulphate)) has not been identified during leaching experiments.

The third mechanism (U-phase-ettringite transformation) has been clearly pointed out by XRD (an increase of ettringite concentration and a simultaneously decrease of U-phase concentration) and confirmed by modeling by the use of the DIFFUZON code.

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