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**CEMENT HYDRATION IN THE PRESENCE OF MUNICIPAL  
SOLID WASTE INCINERATION FLY ASH.**

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**Résumé :** Cette étude s'intègre dans un programme de recherche visant à développer une méthodologie permettant d'évaluer les caractéristiques utiles, l'impact environnemental et la durabilité des bétons contenant des déchets. Cette méthodologie a été développée à partir de l'étude de mortiers contenant un déchet "d'expérimentation" : les cendres volantes d'Usines d'Incineration d'Ordures Ménagères (cendres volantes d'UIOM). Dans cet article, nous décrivons le travail expérimental mené afin d'étudier l'hydratation de pâtes de ciment Portland en présence de cendres volantes d'UIOM. Les caractéristiques physiques et chimiques des cendres volantes d'UIOM ont tout d'abord été étudiées. Des analyses chimiques, des diffractions des rayons X (DRX), et des observations au microscope électronique à balayage ont été réalisées. Les produits d'hydratation formés dans une pâte de ciment en présence de cendres volantes d'UIOM ont également été étudiés. Des DRX ont été réalisées sur des pâtes de ciment avec et sans cendres volantes d'UIOM. Une comparaison des diffractogrammes nous a permis d'identifier les principaux hydrates formés, dus à la présence de cendres volantes d'UIOM. Enfin, des essais de calorimétrie basse température (DSC) ont été réalisés sur des pâtes de ciment avec et sans cendres volantes d'UIOM pour déterminer l'influence de ces dernières sur la microstructure des pâtes de ciment.

## **1. INTRODUCTION**

Incorporating wastes into concrete on an appropriately selective basis could help to solve some of the problems encountered in waste management. Some industrial by-products (fly ash and slag for example) have been used in the manufacture of cement and concrete for many years. However, before waste can be used on a large scale in concrete, the properties of the resulting concrete need to be studied in order to ensure that the new material is suitable for use in construction.

The main aim of this research is to develop an approach for assessing the performance characteristics, environmental impact and durability of concretes containing wastes [1]. In this paper we describe the study bearing on the environmental impact of these materials. This approach is based on a study of mortars containing an "experimental" waste, Municipal Solid Waste Incineration Fly Ash (MSWIFA). These wastes are very heterogeneous and contain large quantities of heavy metals and soluble salts which could give rise to problems when incorporated in concrete.

The leaching of toxic materials from concretes containing wastes may present health and environmental risks. The quantities released over a period of time must therefore be determined in assessing the environmental impact of these concretes. To predict the quantities of toxic materials released in actual conditions of use over the long term, models of leaching from waste-containing concrete need to be developed. To achieve this, one must understand the influence of waste on cement hydration, the mechanisms by which pollutants pass into solution, and the evolution of the material microstructure during leaching. The objective of this study is to apply the CEMHYD3D model developed by Bentz and Garboczi [2,3] to cement pastes containing MSWIFA in order to simulate the hydration of this material and the evolution of its microstructure during leaching. In

this article, we describe the experimental study undertaken in order to determine the model input data.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 MSWIFA characterization

#### 2.1.1 Sampling and mixing of the MSWIFA

The MSWIFA samples were obtained from the Municipal Solid Waste Incineration Plant in Lagny, near Paris, France, which operates with a wet scrubber. Approximately 300 kg of MSWIFA were sampled during 4 days of normal plant operation in June of 1996. Samples (four) were kept in separate sealed drums. Before carrying out any tests, an identical quantity of each sample was taken and then passed through a 630  $\mu\text{m}$  sieve (around 5% in mass was retained) and carefully homogenized.

#### 2.1.2 Physico-chemical and mineralogical characterization of the MSWIFA

The granulometry of the MSWIFA was determined using laser granulometry.

The oxide contents were determined using X-ray fluorescence spectrometry. The chloride content was measured by precipitating it as silver chloride and using a potentiometric method. The sulphate content was obtained gravimetrically by precipitating it as barium sulphate. The heavy metal content was determined by dissolution in hydrofluoric and perchloric acids followed by atomic emission spectrometry.

X-ray diffraction tests were also carried out (with the  $K\alpha$  line of copper) in order to determine the mineralogical composition of the MSWIFA.

Scanning electron microscope (SEM) observations were performed using polished samples prepared by mixing MSWIFA with a low viscosity epoxy resin. Backscattered electron images and X-ray images were collected for two different fields of observation (FA1 and FA2). Eight elements (Ca, Si, Al, Fe, Na, K, S, and Cl) were studied.

To study the dissolution of the different phases, MSWIFA was washed with distilled water. Two samples of 40 g of MSWIFA were immersed in 800 mL of distilled water, and stirred using a magnetic stirrer, one for 1 day and the other for 7 days. After filtration, the solid residue was dried at 105 °C and the mass of the soluble fraction extracted by washing was determined. Polished samples were then prepared using the dry residue from one day's washing, and a backscattered electron image and X-ray images were collected using the SEM (WFA1). The same elements were studied as for the raw MSWIFA.

### 2.2 Tests carried out on cement paste

#### 2.2.1 Determining the products of hydration due to the presence of MSWIFA

In order to determine the products of hydration formed in the cement paste in the presence of MSWIFA, X-ray diffraction tests were carried out on different cement pastes. Two types of portland cement meeting NF P15-301 AFNOR standard specifications were used: a cement (C1) with low  $C_3A$  content (4.2%) (CPA-CEM1 52.5 PMES HTS from the Le Teil plant of the Lafarge company<sup>1</sup>), and a cement (C2) with high  $C_3A$  content (11.6%) (CPA-CEM1 52.5 from the Cormeilles plant of the Lafarge company<sup>1</sup>). Pastes with a water/cement ratio of 0.5 and MSWIFA/cement ratio of 0 and 0.2 by mass were prepared for each cement. Table 1 gives the compositions of the cement pastes.

Table 1: compositions of the cement pastes used in the X-ray diffraction tests.

<sup>1</sup> Names of companies and products are given to fully specify the conditions. They do not imply that they are necessarily the best for the purpose.

Samples	Cement (g)	Water (g)	MSWIFA (g)
P0-C1	1000 (C1)	500	0
P20-C1	1000 (C1)	500	200
P0-C2	1000 (C2)	500	0
P20-C2	1000 (C2)	500	200

The pastes were then cast into metal molds measuring 70 mm x 70 mm x 400 mm and then kept in sealed bags until removed from the mold. After removal, they were cured for 28 days in sealed bags. Then, the cores of the samples were cut and crushed.

### 2.2.2 Study of the pore structure of C-S-H formed in the presence of MSWIFA

To study the pore structure of the C-S-H formed in cement pastes in the presence of MSWIFA, Differential Scanning Calorimetry (DSC) tests were carried out. Pure cement pastes (P-C1) and pastes containing MSWIFA (P-FA, 20 % MSWIFA as a replacement of the cement) were prepared. The different components were mixed manually in plastic bags and poured into sealed PVC bottles. Table 2 gives the compositions of the cement pastes.

Table 2: compositions of the cement pastes used for the DSC tests.

Cement pastes	Cement C1 (g)	Distilled water (g)	MSWIFA (g)
P-C1	1000	400	0
P-FA	800	400	200

The DSC tests were performed on the pastes at 8, 14, 28, and 60 days. DSC measures the heat released by a sample as it undergoes chemical and physical changes while being heated or cooled at a constant rate. These tests were performed in a range of +5 °C to -60 °C by cooling at a rate of 0.5 °C per minute. During these tests, the heat flux peaks were assumed to correspond to solidification of the water in the cement paste pores. The positions and shapes of the peaks are essentially influenced by two parameters: the composition of the pore solution in the cement pastes and the size of the pores. In order to separate the influences of these two parameters, the pore solutions of the cement paste samples P-C1 and P-FA at 46 days age were replaced with distilled water. The test specimens were successively immersed in ethanol for 3 days, in ethylene glycol for 3 days and, lastly, in distilled water for 4 days. The cement pastes then underwent DSC tests with a temperature range from +5 °C to -70 °C at a rate of -0.5 °C per minute.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of the MSWIFA

Figure 1 shows the granulometry curves obtained for the MSWIFA and for cement C1. The MSWIFA is in the form of a powder which is coarser than the cement. The majority of MSWIFA particles have a dimension between 50 and 500 µm.

Table 3 shows the results of the chemical analyses of the MSWIFA. The most abundant oxides are (in decreasing order of importance) SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub>. Alkalies (K<sub>2</sub>O and Na<sub>2</sub>O), chlorides, and sulfates are also present in fairly large quantities (3 percent or more). The heavy metals analyzed represent approximately 2 % of the total mass of the MSWIFA.

The main crystalline compounds of the MSWIFA detected by X-ray diffraction are shown in Table 4. These compounds are quartz, sylvite, halite, anhydrite, calcite, and lime. Those results are in good agreement with other studies [4,5]. The respective quantities of the identified compounds were estimated based on the height of the corresponding X-ray diffraction peaks. The symbol "X"

given in the Quantity column of table 4 represent the relative height of the main peak of the components. "?" indicates that there is a doubt about the presence of the compound.

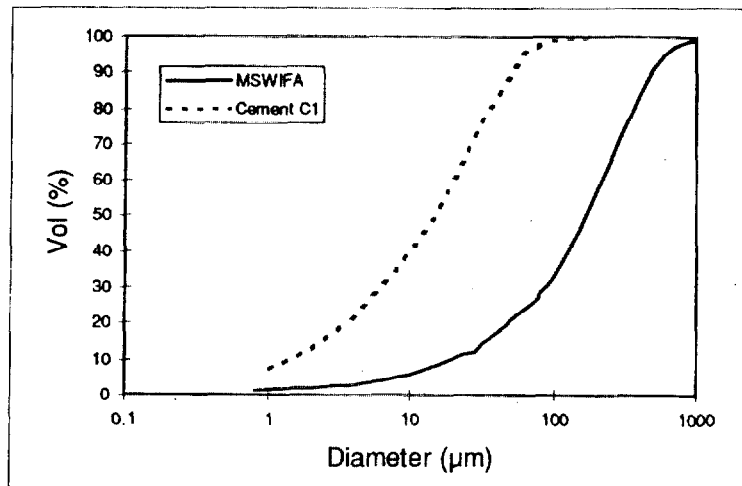


Figure 1: granulometric curves for the MSWIFA and cement C1.

Table 3: chemical composition of the MSWIFA. (LOI: loss on ignition)

Compound	Content (% mass)	Compound	Content (% mass)	Heavy metals	Content (mg/kg)	Heavy metals	Content (mg/kg)
LOI (975°C)	13.00	TiO <sub>2</sub>	0.84	Zn	11000	Ni	50
SiO <sub>2</sub>	27.23	P <sub>2</sub> O <sub>5</sub>	0.34	Pb	4000	Se	50
CaO	16.42	Mn <sub>2</sub> O <sub>3</sub>	0.05	Cu	670	Te	46
Al <sub>2</sub> O <sub>3</sub>	11.72	SrO	0.01	Mn	600	V	32
Na <sub>2</sub> O	5.86	Ba	0.22	Cr	450	Mo	25
K <sub>2</sub> O	5.80	Cl	7.20	Cd	270	As	21
MgO	2.52	SO <sub>3</sub>	3.00	Sn	180	Co	21
Fe <sub>2</sub> O <sub>3</sub>	1.80			Sb	110	Tl	<5

Table 4: main compounds detected by X-ray diffraction in the MSWIFA.

Compound	Formula	Quantity
Quartz	SiO <sub>2</sub>	X X X X X
Calcite	CaCO <sub>3</sub>	X
Sylvite	KCl	X X X
Halite	NaCl	X X X
Lime	CaO	X
Anhydrite	CaSO <sub>4</sub>	X X
Hemihydrate	CaSO <sub>4</sub> ·0.5H <sub>2</sub> O	?

The observations made using the scanning electron microscope showed that the MSWIFA particles have very varied shapes: full or hollow spherical particles, long or flat particles, very porous particles, etc. No predominant shape can be distinguished, as opposed to coal fly ash which is usually composed of particles which are practically all spherical.

For each image collected using the X-ray SEM, the intensity of the response obtained for the element analyzed was compared to a threshold intensity beyond which this element was considered

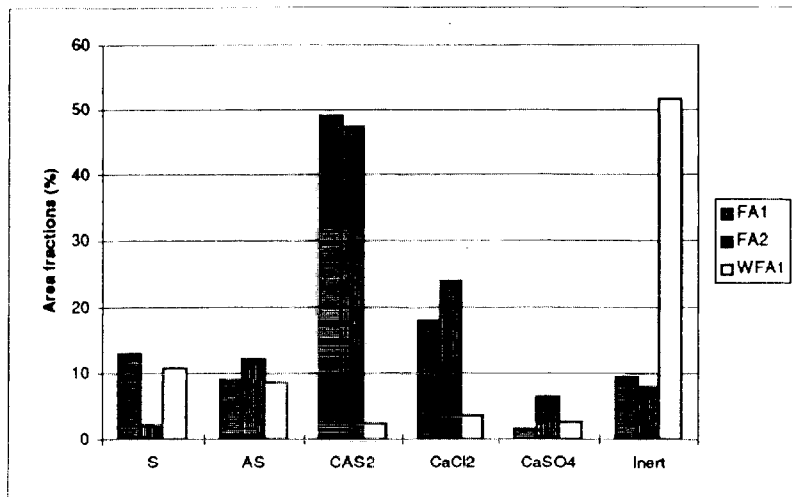


Figure 2: area fractions of the MSWIFA phases before and after washing.

### 3.2 Determination of the products of hydration

Table 5 shows the main hydrates determined by the X-ray diffraction tests in the MSWIFA-free cement pastes (P0-C1 and P0-C2) and cement pastes with 20 % MSWIFA (P20-C1 and P20-C2). The results obtained for the two cements C1 and C2 were very similar. The addition of MSWIFA into the cement pastes leads to an input of quartz and calcite (already present in MSWIFA). The main crystalline hydrates formed due to the addition of MSWIFA are ettringite, Friedel's salt, and thenardite. The formation of ettringite or Friedel's salt in cement pastes containing MSWIFA has been reported in other studies [5,6].

Table 5: main hydrates and other compounds identified in cement pastes. (ND: not detected)

Compound	Formula	P0-C1	P0-C2	P20-C1	P20-C2
Quartz	SiO <sub>2</sub>	ND	ND	X	X
Calcite	CaCO <sub>3</sub>	?	?	X X	X X
Portlandite	Ca(OH) <sub>2</sub>	X X X X X	X X X X X	X X X X	X X X X
Monosulfoaluminate	C <sub>3</sub> A.CS.H <sub>12</sub>	?	?	ND	ND
Ettringite	C <sub>3</sub> A.3CS.H <sub>32</sub>	X	X	X	X X
Friedel's salt	C <sub>3</sub> A.CaCl <sub>2</sub> .H <sub>10</sub>	ND	ND	X	X X
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	ND	ND	X X	X X

### 3.3 Influence of MSWIFA on cement hydration

The DSC results obtained at 8, 14, 28, and 60 days do not show significant differences. Figure 3 shows the DSC results obtained for the cement paste P-C1 and for the cement paste P-FA containing 20 % MSWIFA (replacement of the cement) on a mass basis at 28 days. We observe a shift in the peak attributed to freezing of water in C-S-H towards lower temperatures for the paste P-FA.

Figure 4 shows the DSC curves for the pastes P-C1 and P-FA after the successive immersions in ethanol, ethylene glycol, and distilled water. The main effect of these successive immersions was believed to be replacement of pore solution by distilled water in the cement pastes. After these immersions, the two cement pastes had pore solutions of similar chemical composition (assuming that the dissolution of the hydrates is slow enough). As can be observed in Figure 4, the DSC curves for the two cement pastes are practically identical. In particular, the peak temperature corresponding to the C-S-H is the same. It is reasonable to deduce from this result that the pore

structures of these two cement pastes (with and without MSWIFA) are similar. Therefore, the differences observed between the DSC curves of the P-C1 and P-FA after 28 days of hydration should be due to a difference in the chemical compositions of the pore solutions. A large concentration of alkali in the pore solution of the paste P-FA could explain the larger freezing point depression.

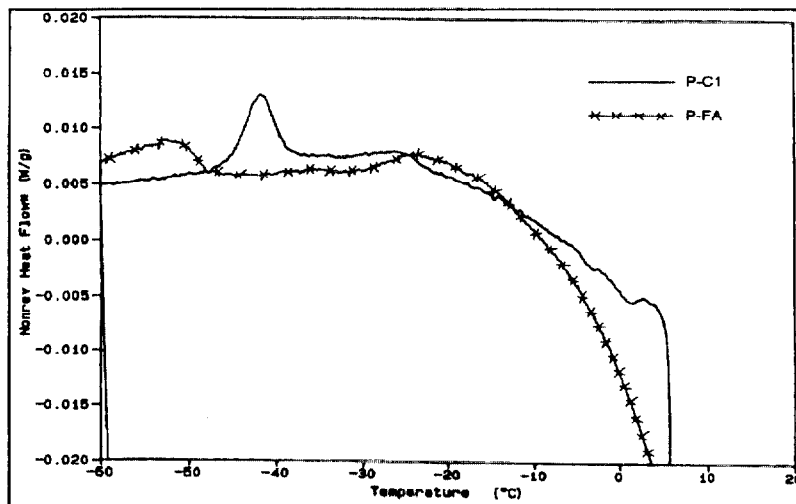


Figure 3: DSC curves obtained for P-C1 and P-FA at 28 days.

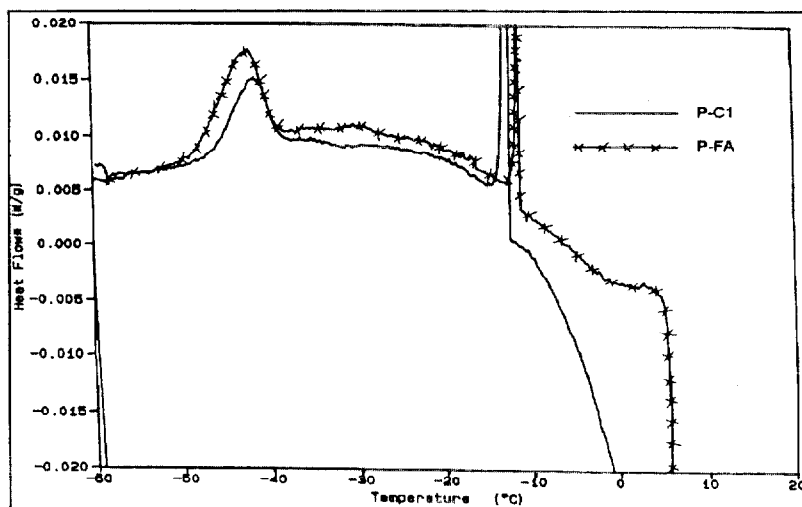


Figure 4: DSC curves obtained for the pastes P-C1 and P-FA after successive immersions.

### 3.4 Incorporation of MSWIFA into the CEMHYD3D hydration model

Using the results presented in section 3.1, MSWIFA has been incorporated into the CEMHYD3D model. MSWIFA is represented using digitized spheres. In the model we assume that the chlorides are present as  $\text{CaCl}_2$ . The six phases S, AS,  $\text{CAS}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ , and "inert phase" are randomly distributed amongst the MSWIFA particles, so that all particles are assumed to be monophasic (the input phase volume fractions are then not exactly maintained).

From the results presented in section 3.2, additional reactions have been introduced into the model. Friedel's salt is formed from the collision of "diffusing  $\text{CaCl}_2$ " and "diffusing  $\text{C}_4\text{AF}$ " or "diffusing

C<sub>3</sub>A". Formation of ettringite from CaSO<sub>4</sub> is taken into account by converting "diffusing anhydrite" into gypsum, the formation of ettringite being then as in the original model.

Finally, in order to take into account pozzolanic properties of MSWIFA, the formation of stratlingite has been introduced into the model. Indeed, stratlingite has been observed by Kessler et al. [6] in pastes of C<sub>3</sub>S containing MSWIFA. In the model, stratlingite is formed from the collision of "diffusing AS" and "diffusing CH", or of "diffusing CAS<sub>2</sub>" and "diffusing C<sub>4</sub>AF" or "diffusing C<sub>3</sub>A".

The incorporation of MSWIFA into the model is described in more detail in reference [7].

#### 4. CONCLUSION

The physico-chemical characteristics of a municipal solid waste incineration fly ash (MSWIFA) were studied. The comparison of results obtained using three independent techniques led to the identification of six phases in the MSWIFA: S, AS, CAS<sub>2</sub>, chlorides, CaSO<sub>4</sub>, and an "inert phase". New hydration products formed in the cement pastes containing MSWIFA were identified by X-ray diffractometry. In particular, formation of Friedel's salt, ettringite, and thenardite was observed. Information on the pore structures of a pure cement paste and a cement paste containing MSWIFA was obtained using DSC. The differences observed between these two cement pastes due to freezing of pore solutions are attributed to a higher concentration of salts in the pore solution of the cement paste containing MSWIFA. This suggests that the pore structure of the C-S-H in these two cement pastes was not changed by incorporating the MSWIFA. MSWIFA was incorporated into the CEMHYD3D hydration model. Leaching simulation is currently in progress. This simulation will help us understand the leaching behavior of waste-containing concrete.

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