



# XPS studies of alite hydration products in the presence of hexavalent chromium reducers

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## Abstract

The X-Ray photoelectron spectrometry was applied to elucidate an impact of iron(II), tin(II) and manganese(II) sulphates on cement hydration. Iron(II) sulphate, most commonly added as a reducer of Cr(VI) to Cr(III) on cement grinding, was taken as a reference. The tin(II) and manganese(II) sulphates could be potentially used as reducers of Cr(VI) too. However, the tin(II) sulphate has very strong retarding action on cement setting. In order to find out the relevant mechanisms, the main component of Portland cement – alite (solid solution of tricalcium silicate) was used as a model material. The hydrated alite samples were subjected to the X-ray photoelectron studies to identify the surface products responsible for retarding effects. These products appeared to be quite different in the presence of particular sulphate admixtures. The formation of a Ca-Sn containing compound has been proved directly.

**Keywords:** Reducers of Cr(VI), Iron(II), Tin(II), Manganese(II) sulphate, Cement, XPS

## METODA SPEKTROSKOPII FOTOELEKTRONÓW W BADANIACH HYDRATACJI ALITU Z DOMIESZKAMI REDUKTORÓW CHROMU SZEŚCIOWARTOŚCIOWEGO

W pracy badano wpływ siarczanów żelaza(II), manganu i cyny stosowanych w roli reduktorów Cr(VI) na proces wiązania i twardnienia cementu. W celu wyjaśnienia obserwowanych zjawisk przeprowadzono badania z udziałem alitu traktowanego jako uproszczony model cementu. Postęp hydratacji śledzono metodą mikrokalorymetryczną i stwierdzono silnie opóźniające działanie siarczanu cyny. W celu określenia w sposób bezpośredni przyczyny zahamowania hydratacji przeprowadzono badania metodą spektroskopii fotoelektronów, która daje możliwość detekcji produktów utworzonych na powierzchni hydratyzującego materiału; produkty te są różne w przypadku poszczególnych siarczanów. W ten sposób potwierdzono bezpośrednio obecność związku cyny i wapnia w warstwie powierzchniowej, stanowiącej barierę hamującą proces hydratacji w stadium początkowym.

**Słowa kluczowe:** reduktory Cr(VI), żelazo(II), cyna(II), siarczan manganu(II), cement, s XPS

## 1. Introduction

According to the European Community Directive [1], the reduction of Cr(VI) to Cr(III) in cement is required in order to limit the chromium(VI) content below 2 ppm in the leachate from cement. In practice, this is done by the addition of approximately 0.3% to 0.7% iron(II) sulphate [2–6] being available and economical. However, the iron sulphate reveals lower effectiveness as compared to other reducers [2, 3], and it is usually added as an excess. Because  $\text{FeSO}_4$  is highly hygroscopic, it reveals very often the inhomogeneous distribution, and brown stains can appear on the surface of concrete elements, while the other admixtures, for example antimony or manganese(II) sulphates, have no colouring effect, as it appeared in our previous studies [7].

The problem of reducers of Cr(VI) is discussed mainly from the point of view of effectiveness, economy and handling methods [2, 6]. However, the reducers have an impact on the properties of hydrating cement paste, despite of their low content. The setting and hardening process can be al-

tered due to the presence of heavy metals and sulphate ions because of the interaction with hydrating cement minerals. The phenomena occurring during the hydration process (dissolution of cement constituents, hydrolysis, precipitation of nearly amorphous products and crystallization of the other ones) in the presence of the excess of reducer, when added to guarantee the complete reduction, as it is in industrial practice, or when the reducer is not homogeneously distributed and hygroscopic ( $\text{FeSO}_4$ ), are similar to the process which occurs when the solidification of hazardous wastes (with heavy metal compounds) or external sulphate attack takes place. Therefore they can be discussed based on the relevant reports [e.g. 8–10]. Additions of more or less amphoteric salts are expected to hydrolyze and form, in highly basic environment of cement paste, some new basic salts of Ca or the hydroxides [e.g. 8, 11]. This was investigated in sixties of XX c. for example by Hill et al. in case of tin compounds [11].

This contribution is a part of a project aimed in the optimization of the Cr(VI) reducers use. The explanation of the occurrence of the brown patches on the surface of decora-

tive concrete elements was the practical goal [7]. These patches resulted from the precipitation of iron compounds (hydroxides), being the consequence of inhomogeneity of iron sulphate agent distribution. In this study, the investigations focused on the determination of the surface products formed on cement grains in the presence of Fe(II), Mn(II) and Sn(II) sulphates during the hydration process of cement and some model mixtures.

The heat evolution measurements, that give the direct view on the hydration kinetics, were taken as a starting point, as it is commonly accepted in cement chemistry [e.g. 7]. Subsequently the other properties of hydrating pastes were characterized.

In order to explain the retarding action of tin(II) sulphate directly, the experiments were carried out using the synthetic alite – tricalcium silicate, being the main constituent of cement, responsible for the hydration/setting/hardening process. Finally, the specially prepared alite specimens, hydrated in water suspensions with admixtures of reducers of Cr(VI), were subjected to the X-Ray photoelectron (XPS) studies to get the information about the mechanism of alite – sulphate interaction. The XPS method has not been applied frequently in the chemistry of cements. The data appertaining to the alite hydration of short duration, based upon the XPS studies, were firstly reported by Ménérier et al. [12] and Regourd [13]. One of the authors of the present work applied this method to investigate the products formed in alite paste hydrated with microsilica addition [14]. Similarly, the XPS study related to the effect of Pb-bearing compounds on the hydration of cement has been carried out using simplified cement models [15]. X-ray photoelectron spectroscopy was then used to analyze thin layers of products formed on the surface of hydrating grains. A report dealing with hydrating systems based, among the other data, on the XPS studies of hydrated material in volume, appeared quite recently [16].

The XPS method gives a possibility to identify the surface products, which can form an impermeable layer on cement grains and bring about the retarding effect; these products appear to be quite different from those found in paste volume, detectable by XRD measurements. However, the special sample preparation is necessary [12, 15].

## 2. Experimental

### 2.1. Materials

Synthetic alite was produced by repeated heating of a mixture of analytically pure calcium carbonate and silica gel at 1450 °C. A small quantity of magnesium and aluminium hydroxides was added to facilitate the synthesis and to make the alite composition similar to those occurring in cements (MgO and Al<sub>2</sub>O<sub>3</sub> content of 0.3 wt. % and 0.5 wt. % of alite, respectively). The phase composition of final products was controlled by XRD. The sinter was subsequently ground in a laboratory ball mill to a Blaine specific surface of 3000 ± 50 cm<sup>2</sup>/g. The pastes produced from 20 g alite samples processed with 1% solutions of commercially available iron, manganese and tin sulphate at water to solid ratio 0.5 were produced for the calorimetric measurements. In

such a way alite pastes were hydrated with 0.5% admixture added by mass of alite

Special preparation of hydrating material consisted in the separation of coarse alite grains (> 80 μm), their 24 h hydration in excess water or water solution of reducer, added to produce 1% admixture content by mass of alite. Water to alite ratio (w/c) was 10. The alite grains surrounded by the products precipitated on their surface were very carefully washed with acetone on the 60 μm sieve to remove the liquid residue and smaller particles from the suspension.

The following samples were studied by XPS:

- anhydrous, synthetic alite (A),
- hydrated alite (AH),
- alite hydrated with an admixture of 1% FeSO<sub>4</sub> by mass of alite (AHFe),
- alite hydrated with an admixture of 1% MnSO<sub>4</sub> by mass of alite (AHMn),
- alite hydrated with an admixture of 1% SnSO<sub>4</sub> by mass of alite (AHSn).

### 2.2. Methods

The heat of hardening was measured by using a non-isothermal-non-adiabatic microcalorimeter of our own laboratory construction which utilised commercially available elements, and equipped with computer controlled registration and data refinement. A starting temperature was 25 °C. The example calorimetric results are presented as  $dQ/dt = f(t)$  plots in Fig. 1.

The samples were subjected to very sensitive X-Ray photoelectron studies (XPS) with an XPS spectrometer produced by VSW. The method is based on measuring the energy of photoelectrons – core electrons emitted from the internal atomic orbitals as a result of soft X-ray radiation in high vacuum, ca.  $3 \times 10^{-8}$  mbar. These energies provide information concerning the chemical environment of analyzed atoms. The composition of surface layer of molecular thickness can be thus determined. X-ray source characteristics: Al K $\alpha$ , 200 W (10 kV, 20 mA), calibration on the C 1s peak position assuming 284.6 eV as a C–H peak position). The examples of XPS spectra are shown in Figs 2 and 3.

The treatment of XPS data was done with of a software described in Ref. 17. The binding energies of core electrons were measured on the following atomic orbitals: C 1s, O 1s, Ca 2p, Si 2p, Fe 2p, Mn 2p, S 2p, Sn 3d; the results are listed in Table 1. Subsequently the binding energies and their relative distribution were attributed to the particular compounds based on the data occurring in database and on the previous results [15, 17]. The concentration of surface hydration products was evaluated from the relative energy distribution values and presented as a scheme in Fig. 4.

## 2.3. Results and discussion

### 2.3.1. Heat evolution

The early hydration followed by calorimetry is almost not hindered by the presence of Fe and Mn sulphates during the first few hours of early hydration in the case of alite (Fig. 1). In the presence of manganese and iron sulphates,

the induction period is short and not specially profound. It means that these admixtures affect the intense hydrolysis of cement and simultaneously the precipitation of products; they do not slow down the hydration process as a whole. It should be underlined that the sulphate ions originated from the admixtures seem to accelerate the alite hydration (see

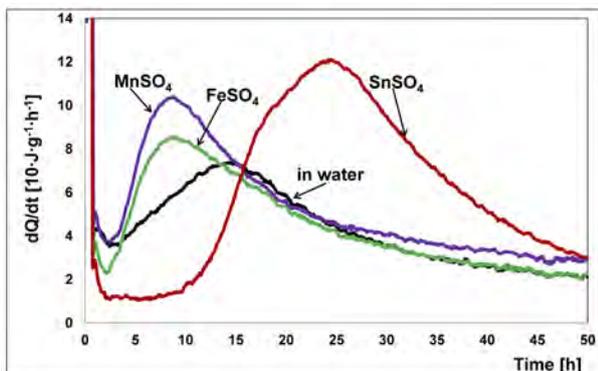


Fig. 1. Heat of hardening curves for alite pastes hydrated with 0.5%  $\text{SnSO}_4$ ,  $\text{FeSO}_4$  and  $\text{MnSO}_4$  admixtures (by mass of alite;  $w/c = 0.5$ ).

Rys. 1. Krzywe szybkości wydzielania ciepła twardnienia dla zaczynów alitowych hydratyzowanych z domieszką 0,5%  $\text{SnSO}_4$ ,  $\text{FeSO}_4$  i  $\text{MnSO}_4$  w przeliczeniu na masę alitu ( $w/c = 0,5$ ).

Fig. 1). On the other hand, at the presence of tin sulphate, a serious retarding action is evident and the significant elongation of induction period, up to over 10 h, is observed. After this period of time, the hindering effect of tin sulphate seems to be compensated by the renewed hydration (see the area of main peak reflecting the and  $Q = f(t)$ ). In case of Fe and Mn sulphates, the total heat evolved after approximately 8–10 h is almost equal to the value for the reference paste processed with water. These results match very well with those previously and recently reported [7, 17].

### 2.3.2. XPS studies of surface product

From the scheme in Fig. 4 one can conclude that:

- The surface of initial alite sample is enriched with siliceous component.
- The surface of hydrated alite grain is covered with calcium hydroxide and hydrated calcium silicate (the amount of oxygen in these both products is almost the same).
- On the surface of alite grain hydrated in the presence of iron sulphate used as a reducer of Cr(VI) the calcium hydroxide, calcium silicate hydrate and iron hydroxide(s) are detectable; the amount of different forms of hydrated iron oxide seems to be quite significant.

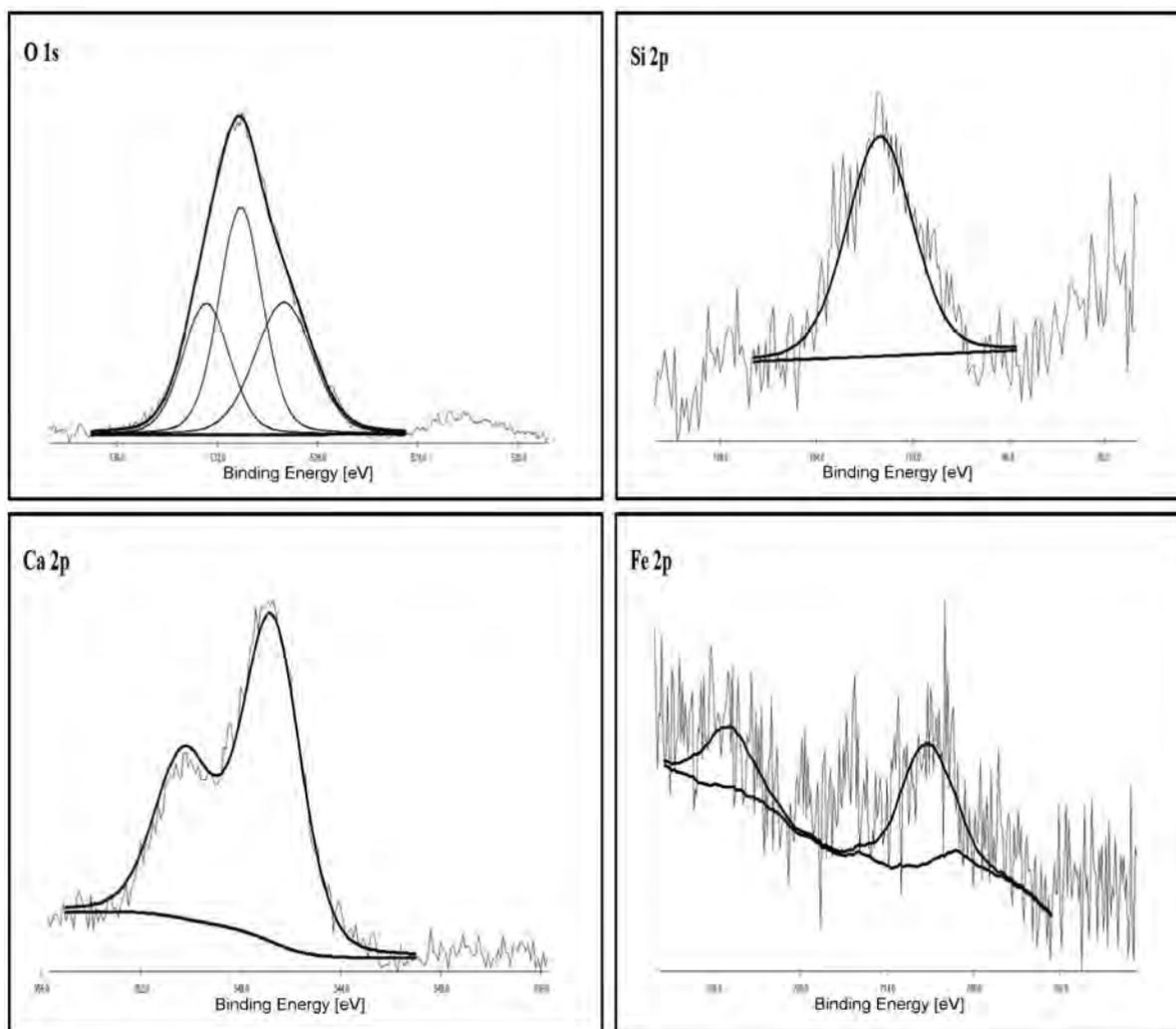


Fig. 2. XPS spectra of alite grain surface; hydration in  $\text{FeSO}_4$  solution (1% admixture by mass of alite).

Rys. 2. Widma XPS powierzchni ziaren alitu hydratyzującego w roztworze  $\text{FeSO}_4$  (domieszka wprowadzona w ilości 1% masy alitu).

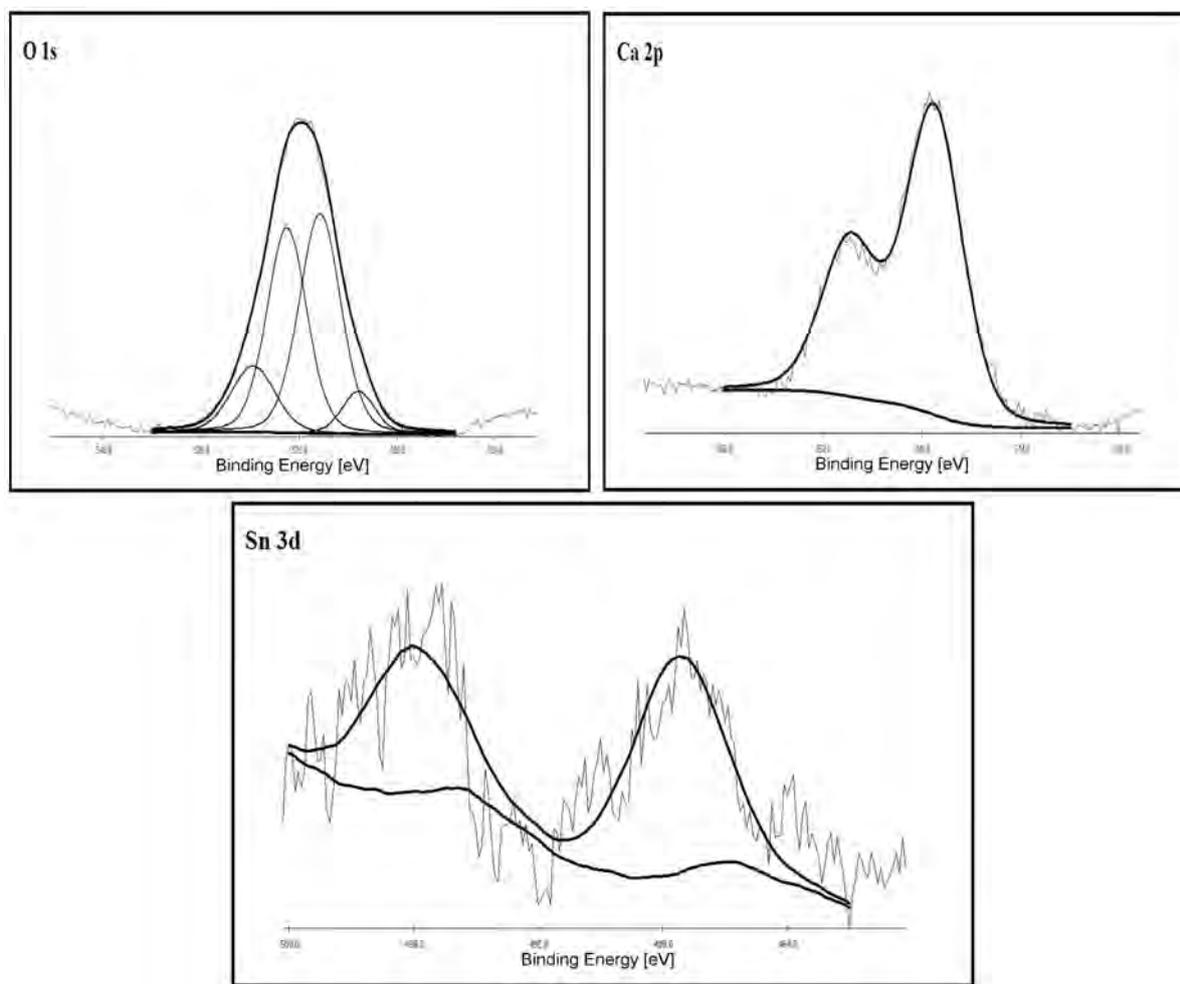


Fig. 3. XPS spectra of alite grain surface; hydration in  $\text{SnSO}_4$  solution (1% admixture by mass of alite).

Rys. 3. Widma XPS powierzchni ziaren alitu hydratyzującego w roztworze  $\text{SnSO}_4$  (domieszka wprowadzona w ilości 1% masy alitu).

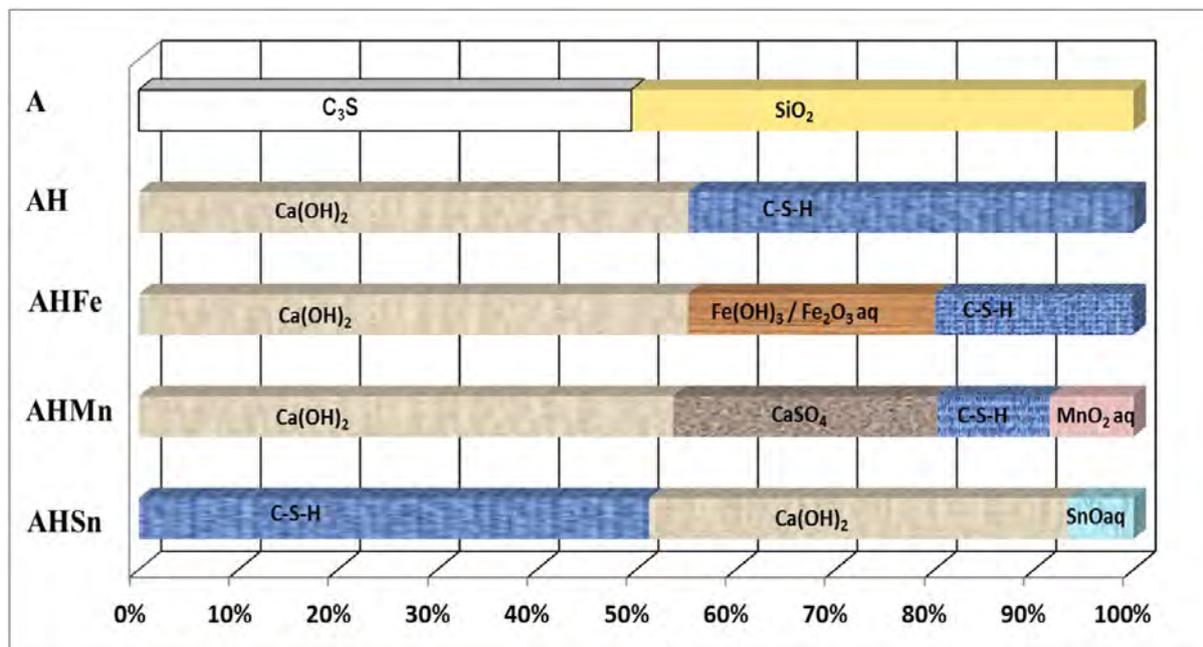


Fig. 4. Distribution of binding energies of core electrons on O 1s orbitals among particular compounds on the surface of hydrated alite grains from XPS measurements (A – alite, AH – alite hydrated, AHFe, AHMn, AHSn – alite hydrated in Fe, Mn and Sn sulphate solution, respectively).

Rys. 4. Rozkład energii wiązania elektronów na orbitalu O 1s pomiędzy poszczególne związki na powierzchni hydratyzujących ziaren alitu i względne udziały wynikające z rozkładu energii na podstawie pomiarów metodą XPS (A – alit, AH – alit hydratyzowany, AHFe, AHMn, AHSn – alit hydratyzowany w roztworach siarczanów odpowiednio Fe, Mn i Sn).

Table 1. Binding energies ( $E_b$ ) of core electrons and relative distribution of energies ED (concentration) among particular bands/elements on the surface of hydrated alite grains from XPS measurements. Sample notation: A – alite, AH – alite hydrated, AHFe, AHMn, AHSn – alite hydrated in Fe, Mn and Sn sulphate solution, respectively.

Tabela 1. Energie wiązania elektronów w rdzeniach atomowych ( $E_b$ ) i względne udziały wynikające z rozkładu energii (ED) w poszczególnych pasmach/pierwiastkach na powierzchni alitu i alitu hydratyzowanego na podstawie pomiarów metodą spektroskopii fotoelektronów (XPS). Oznaczenia próbek: : A – alit, AH – alit hydratyzowany, AHFe, AHMn, AHSn – alit hydratyzowany w roztworach siarczanów odpowiednio Fe, Mn i Sn.

Sample	Binding energy, $E_b$	O 1s				Si 2p	Ca 2p	S 2p	Fe 2p	Mn 2p		Sn 3d
	Concentration, ED											
A	$E_b$ [eV]	529.5	531.0	532.1	533.4	101.0	346.8					
	ED [%]	11.4	28.8	14.0	4.0	7.9	33.9					
AH	$E_b$ [eV]	529.3	530.9	532.1	533.2	101.5	346.9					
	ED [%]	4.9	35.0	16.4	7.0	10.2	26.5					
AHFe	$E_b$ [eV]	529.3	531.1	532.4	-	101.4	346.8	-	711.4			
	ED [%]	21.7	28.1	17.5	-	10.0	21.5	-	1.3			
AHMn	$E_b$ [eV]	529.2	530.8	532.0	533.2	-	347.1	168.9		642.9	650.3	
	ED [%]	5.9	37.7	18.6	7.9	-	29.1	3.1		2.7	1.1	
AHSn	$E_b$ [eV]	529.6	531.1	532.5	533.9	-	347.5	-				487.5
	ED [%]	4.9	31.2	28.0	10.0	-	23.5	-				2.5

– On the surface of alite grain hydrated in the presence of Mn sulphate the gypsum deposit appears, apart from the calcium hydroxide; C-S-H and some amount of hydrated Mn oxide is detected.

– On the surface of alite grains hydrated with Sn sulphate, a half of oxygen atoms approximately occurs in calcium hydroxide and Sn hydrated oxide. Presumably there is a mixture of Ca-Sn hydrated compound covering the surface of alite grain.

### 3. Conclusions

The following concluding remarks can be drawn directly or indirectly from the results presented above:

– The role of particular sulphate admixtures with the following accompanying cations: Fe, Mn and Sn, as modifiers of hydration process, is different.

– The Fe(II) and Mn(II) sulphates, that are present in an amount of 0.5% by mass of alite in process water, do not retard generally the hydration at early age, as determined by heat evolution studies. The tin(II) sulphate acts as a retarder.

– As it could be proved by XPS studies of the product formed on alite grains in a layer of low (multimolecular) thickness, the most evident features are as follows: the iron hydroxide appears in the presence of Fe, the manganese

hydroxide is formed in the presence of Mn, the Sn is detected in the Sn-Ca hydroxide compound.

– The retarding action of tin sulphate can be attributed to the phenomena relating to the dissolution-precipitation of products occurring in the paste i.e. the formation of product (hydrated tin oxide mixed with calcium hydroxide) adherent to the surface, acting as an impermeable membrane around alite grains hindering the hydration process.

– The hindering action of Sn sulphate seems to be compensated by the renewed hydration after a long-lasting dormant period.

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