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Interaction of Pb with hydrating alite paste XPS studies of surface products

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A study into the effect of Pb-bearing compounds on hydration of cement has been carried out, using simplified cement models, including models for alite and gypsum. The kinetics of hydration of these compounds was evaluated by the calorimetry method. The microstructure has been characterized, and X-ray photoelectron spectroscopy was used to analyze thin layers of products formed on the surface of hydrating grains. Depending on the composition of the initial mixture and Pb-bearing compounds various effects were observed. When pure PbO was used as the additive, the reaction of alite with water was significantly accelerated but when the additive consisted of a mixture of PbO and gypsum, the alite/water reaction was retarded, as in the case of cement. As was found by the XPS studies, a part of Pb^{2+} ions enters the reaction with sulfate ions and the barrier of $PbSO_4$ which is poorly soluble is thus formed. Furthermore, lead introduced to the hydrated alite suspension is strongly bound by C–S–H, as can be derived from high binding energies of core electrons on Pb 4f orbitals.

Key words: alite; calorimetry; hydration; lead; XPS

1. Introduction

The interaction of cement paste/concrete mixtures with compounds containing heavy metals has been investigated for a long time [1–5]. Detailed studies focused on the immobilization (stabilization) of these materials in cement matrices [2–5]. Such interactions typically occur in waste products from the industrial manufacture of cement/concrete, for example with fly ash of various origins. Lead(II) oxide (PbO) is the most commonly occurring heavy metal impurity but other compounds such as sulfates, chlorides and nitrates also occur. As is well known, the latter compounds show better solubility in water than PbO.

Heavy metal compounds affect strongly the setting, hardening as well as the durability of cement paste/hardened material. As was reported over 30 years ago, small amounts of solid PbO or ZnO added to cement paste retard strongly the hydration process [1]. This effect has been attributed to the formation of an impermeable layer

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of products – heavy metal hydroxides or other compounds produced as a result of C_3S hydration in the presence of these oxides. Calorimetric studies revealed a prolonged, dormant period with a "gap" of many hours between the first and the second heat evolution peaks [1]. The author [1] was of the opinion that full explanation of this serious retarding effect was not possible.

The retarding effect of Pb or other heavy metal compounds (salts) on hydration of cement was also proved in some later works [6, 7]. The hindering of the hydration process, depending on the additive content, was confirmed by calorimetric measurements. These results were compatible with delayed setting and hardening of cement mortars. However, for PbO content not exceeding 1–2 wt. % of cement, the data showed good conformity with the standard manufacturing requirements; the later strength results were even higher. There were no significant changes in water uptake or stability of volume.

The effect of heavy metals has been widely studied from the point of view of their immobilization in hardened cement matrix [2–4]. The researchers focused on studying the stabilization mechanism and leaching of heavy metals from various cement based materials. A very high degree of Pb immobilization was reported, as well as the formation of a highly disordered hydration product – calcium silicate hydrate (so-called C–S–H), in the presence of heavy metal compounds was found [3, 8–10].

It seems that the effect of PbO on cement/concrete hardening is principally attributed to the hydration of alite – the main constituent of cement but there are also some other aspects. The studies presented in this paper started on cements and were subsequently continued using alite samples. This is now common practice in research work [11]. Additionally, in previous works a close similarity was detected between the synthetic C–S–H phases and the cement pastes, used as immobilizing materials for heavy metals [8, 9].

2. Experimental

Synthetic alite was produced by repeated heating of analytically pure calcium carbonate and a silica gel mixture at 1450 °C. A small quantity of magnesium and aluminum hydroxides was added to facilitate the synthesis and to make the alite composition similar to those occurring in cements (MgO and Al_2O_3 contents – 0.3 and 0.5 wt. % of alite). 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^2/g. The calcium sulfate dihydrate was also used as a component of the hydrating mixtures. In the experiments, the PbO additive was used (as it is the one most frequently occurring in wastes) or $Pb(NO_3)_2$ (easily soluble). PbO and $Pb(NO_3)_2$ were taken as materials of analytical purity.

Differential calorimetry was applied, similarly as in the case of cements, as a basic method of evaluating the hydration progress. The rate of heat evolution was monitored with a BMR type nonisothermal nonadiabatic calorimeter (constructed in the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw) on 5 g alite samples mixed with water: the water-to-alite ratio was 0.5. The external (reference) temperature was 25 °C.

The experiments for the estimation of the composition of liquid phase were carried out on the suspension with excess water ($w/s = 10$). The suspensions were shaken and, after a time, filtered using a vacuum pump. The samples were collected after 10 min (i.e., at the beginning of the process when the dissolution occurs), 1 h (during the latent period, when the nuclei of products are formed), 10 h (when the formation of early hydrates is advanced, if there is no hindrance effect from admixtures) and 24 h (the formation of hydrates is generally completed if not seriously hindered).

Calcium, lead(II) and sulfate ion concentrations in the filtrate were determined by the ICP method. SEM and EDS studies (scanning electron microscope JEOL 5200 with the LINK ISIS equipment) were performed on the pieces of hydrated samples (soaked in acetone and dried). XRD studies were carried out on the powdered samples (ground and washed with acetone, before being finally dried).

In order to extract some information about the chemical composition of the products formed on the surface of the hydrating alite grains, the samples were specially prepared and 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. 3×10^{-8} mbar; X-ray source characteristics: Al K_α, 200 W (10 kV, 20 mA), calibration on the C 1s peak position assuming 284.6 eV as a C–H peak position). These energies provide information concerning the chemical environment of analyzed atoms – the composition of the surface layer of molecular thickness. This method has not been applied frequently in the chemistry of cements. The data appertaining to alite hydration of short duration, based upon the XPS studies, were firstly reported by Ménétrier et al. [12]. One of the authors of the present work applied this method to investigate the products formed in alite paste hydrated with microsilica addition [13]. The analysis of the spectra related to alite hydrated in a Pb-containing environment was done using different databases with respect to Pb compounds; some measurements on the reference samples were also done. Special preparation of hydrating material consisted in the separation of coarse alite grains (>80 μm), their 24 h hydration in excess water (at water to alite ratio 10) and very careful washing with acetone on the 60 μm sieve, to remove smaller particles from the suspension.

3. Results and discussion

The sets of calorimetric curves are shown in Figs. 1–3. As is evident from the microcalorimetric curves, for PbO additive, the reaction of alite with water is accelerated (Fig. 1), while for lead nitrate the acceleration stage is retarded at higher concentrations but afterwards the process is more intense (Fig. 2).

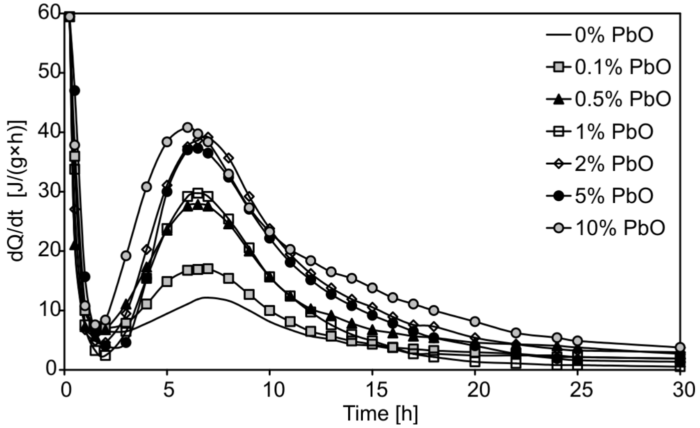

Fig. 1. Heat evolution during hydration of alite with PbO in water

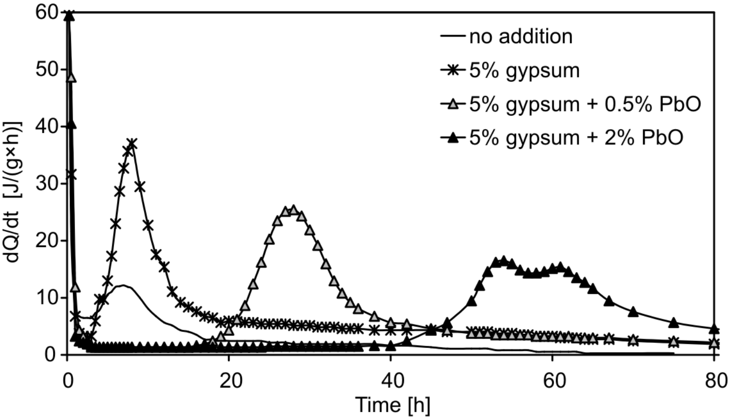

Fig. 2. Heat evolution during hydration of alite + gypsum +PbO

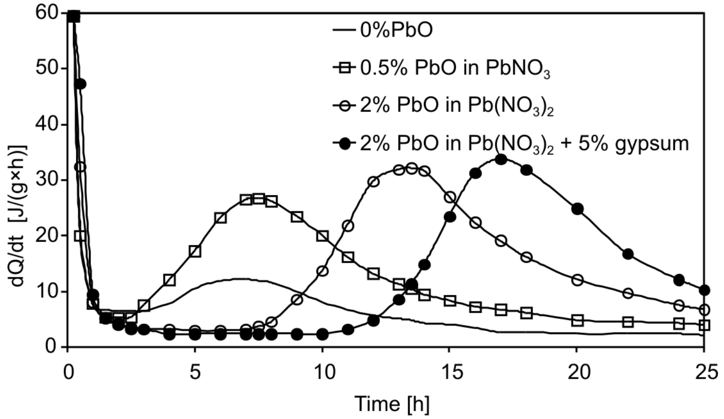

Fig. 3. Heat evolution during hydration of alite and alite + gypsum in $Pb(NO_3)_2$ solution

However, gypsum and PbO introduced simultaneously cause retardation of alite reaction with water, as well as some reduction of the height and modification of the shape of the main heat evolution peak (Fig. 3). This retarding effect is clearly lower in the lead nitrate solution (shorter induction period, Figs. 2 and 3). XRD studies did not reveal any new phases apart from C–S–H and gypsum.

Table 1. Binding energies (E_b) of core electrons and relative distribution of energies (*ED*) among particular bands/elements on the surface of hydrate alite grains from XPS measurements

Sample		O 1s			Si 2p		Ca 2p		Pb 4f		S 2p
Alite	E_b [eV]	533.2	531.6		102.0		351.9	348.5			
	ED [%]	55.2	17.6		4.3		6.4	16.4			
Alite hydrated	E_b [eV]	532.3	530.9		102.2	99.5	347.7	345.5			
	ED [%]	44.2	34.3		6.1	1.4	11.7	2.2			
Alite +gypsum hydrated	E_b [eV]	532.7	531.4		102.6	100.6	348.0	347.2			170.2
	ED [%]	62.6	23.9		4.4	0.9	18.1	4.6			5.1
Alite hydrated + PbO	E_b [eV]	531.5	530.9		102.7		348.2		140.1	138.5	
	ED [%]	73.2	5.9		8.1		11.5		0.9	0.4	
Alite + gypsum + PbO hydrated	E_b [eV]	533.0	531.5		103.5		348.9	347.3	140.4		168.0
	ED [%]	51.4	24.5		8.5		9.6	1.7	1.5		1.9
Alite hydrated in $Pb(NO_3)$	E_b [eV]	532.5	530.0		102.8		348.3		140.0	138.8	
	ED [%]	70.6	6.2		8.1		13.7		0.9	0.5	
Alite +gypsum hydrated in $Pb(NO_3)$	E_b [eV]	532.7	531.4	529.7	103.0		348.4	346.5	140.2	138.6	168.5
	ED [%]	55.4	10.7	8.0	8.8		9.3	3.2	1.1	0.7	2.8

The treatment of the data produced as the results of XPS measurements was done with the aid of the XPSPEAK 4.1 program. The binding energies of core electron bonds on the atomic orbitals O 1s, Ca 2p, Pb 4f, S 2p were measured (Table 1) and subsequently compared to the database for XPS. As this database appeared to be insufficient for interpretation of XPS results for our disordered materials, the spectra recorded were identified and attributed to particular compounds based on other data occurring in the database and on the previous results. [13]. Some results were presented as a scheme of distribution of binding energies attributed to the core electrons on the O 1s and Ca 2p orbitals among the particular compounds occurring on the surface of hydrate alite grains (see Fig. 14)

The effect of PbO on the heat evolution during the reaction of alite with water differs from that observed in case of cement. PbO has no retarding influence on the neat alite paste (see Fig. 1). What is more – the substantial acceleration of alite hydration in the presence of PbO takes place, as is proved by an increase in the main heat evolution peak. Therefore one can conclude that the PbO hampering effect in cement paste, first reported many years ago [1], most probably should be attributed to the presence of components of cement other than silicates. In order to verify this assumption, 5% of gypsum was added to alite + PbO and the hindering effect similar to that observed for cement paste (see Fig. 3) appeared. The induction period increased with the amount of the additive. However, the hindering effect was less visible as the additive was introduced in the form of lead nitrate solution (Fig. 2). When gypsum is not present in the mixture, the effect of lead in the form of soluble $Pb(NO_3)_2$ on alite hydration differs from that at PbO admixture (see Figs. 1 and 2). The calorimetric curve for the $Pb(NO_3)_2$ concentration, corresponding to 0.5% PbO, is almost identical, while at higher $Pb(NO_3)_2$ concentration, the prolonged induction period is followed by the accelerated reaction with a high *dQ*/*dt* peak. Obviously, one cannot exclude the nucleation effect of small PbO particles, however there are other factors involved.

The concentrations in the liquid phase shed some light on the process; however one should remember about the higher water-to-solid ratio, compared with the paste. From the solubility point of view there is no problem, because the solubility of the initial material and the hydration products is very low (calcium hydroxide and gypsum, considered as being highly soluble hydrated materials, exhibit solubility at the level of 1–2 g/dm^3). The excess of water and continuous agitation of the suspension may facilitate the dissolution and abrasion of an unstable gel-like product deposited on the hydrating grains. However, the results reflect the phenomena occurring in the hydrating systems and match well with the calorimetric data. Calcium concentrations in the alite suspensions with PbO after 10 min, 1 h 10 h and 24 h show no significant differences (Fig. 4).

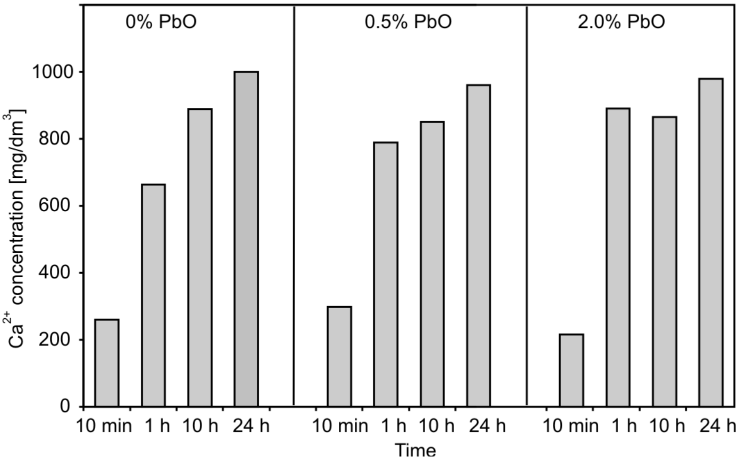

Fig. 4. Concentration of Ca^{2+} ions in the liquid phase during hydration of alite + PbO in water suspension (*w*/*c* = 10). Concentration of Ca^{2+} ions is not specially affected by the presence of PbO in the suspension. The saturation level with respect to calcium hydroxide is not attained

Upon addition of gypsum, the calcium concentration decreases when PbO is present in the suspension (Fig. 5). On the other hand, the lead ions in alite suspensions, which are effectively bound when introduced as 0.5% PbO, at 2% PbO, reveal higher concentrations. The maximum Pb ion concentration (fig. 6, after 10h) corresponds to ca. 30% of total PbO present in the suspension (70% is in the solid phase). This should be attributed to the effect of PbO transformation into the anionic complex [2], being the consequence of the amphoteric character of lead. It seems also reasonable that after a superficial incorporation (or adsorption) of Pb into C–S–H the "excess" Pb ions remain in the alkaline liquid phase. In the gypsum-containing suspensions, the concentrations of Pb ions are negligible for 0.5% PbO addition. However for 2% PbO, the lead concentration increases but is much lower than in the absence of sulfate ions (see different scales in Figs. 6 and 7).

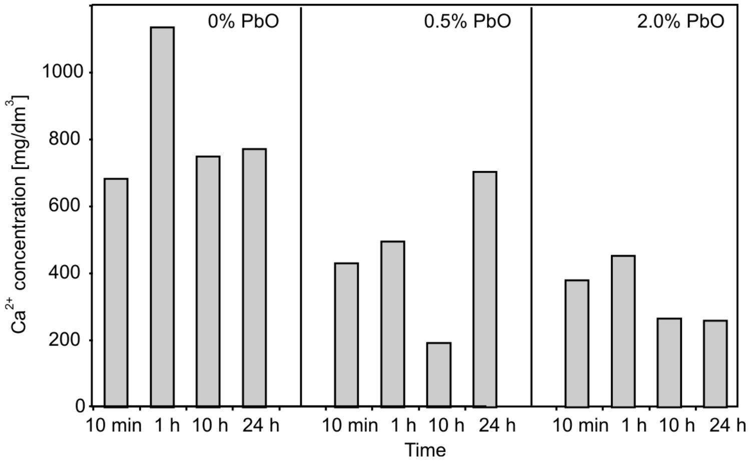

Fig. 5. Concentration of Ca^{2+} ions in the liquid phase during hydration of alite + gypsum + PbO in water suspension (*w*/*c* = 10). In the presence of gypsum and PbO, the concentration of Ca^{2+} ions is much lower than without gypsum. One should remember that the concentration of ions after a few hours corresponds to some intermediary situation between dissolution and precipitation from the liquid

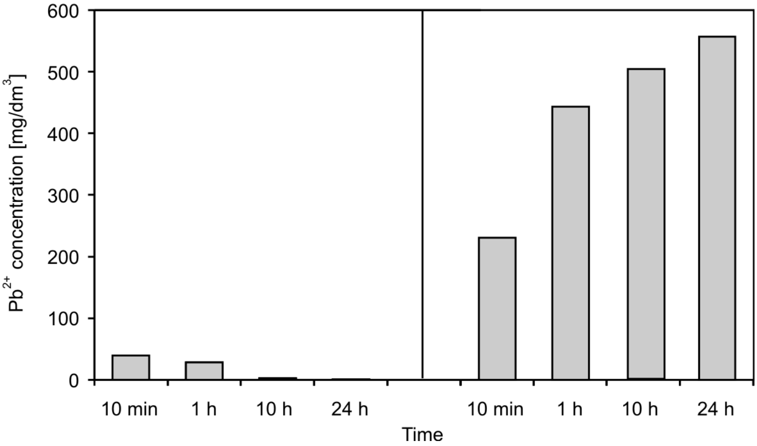

Fig. 6. Concentration of Pb^{2+} ions in the liquid phase during hydration of suspension of alite + PbO in water (*w*/*c* = 10). For a low PbO content, the there are hardly any Pb cations in the liquid phase (PbO consumption in the alkaline liquid – dissolution and precipitation). For a higher PbO content, the dissolution of PbO in alkaline suspension, followed by precipitation of Pb containing compounds takes place but there is always an excess of not precipitated Pb^{2+} ions

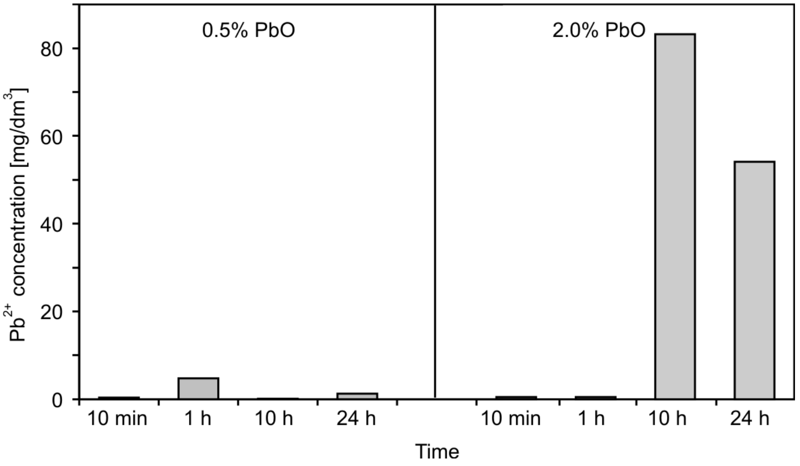

Fig. 7. Concentration of Pb^{2+} ions in the liquid phase during hydration of suspension of alite + PbO + gypsum in water suspension (*w*/*c* = 10) (note various scales in Figs. 6 and 7!). The concentration of Pb^{2+} ions is very low even for higher initial PbO content. The higher Pb contents for 2% PbO obtained after 10 h and 24 h reflect the instability of hydrating suspension and a competition between dissolution and precipitation of newly formed phases

The sulfate ion concentrations decrease systematically. The ions react with Ca and Pb ions and they also enter the C–S–H structure (SEM – EDS results), however their concentrations are higher after a time corresponding still to the induction period on the heat evolution curve for alite + gypsum + 2% PbO mixture.

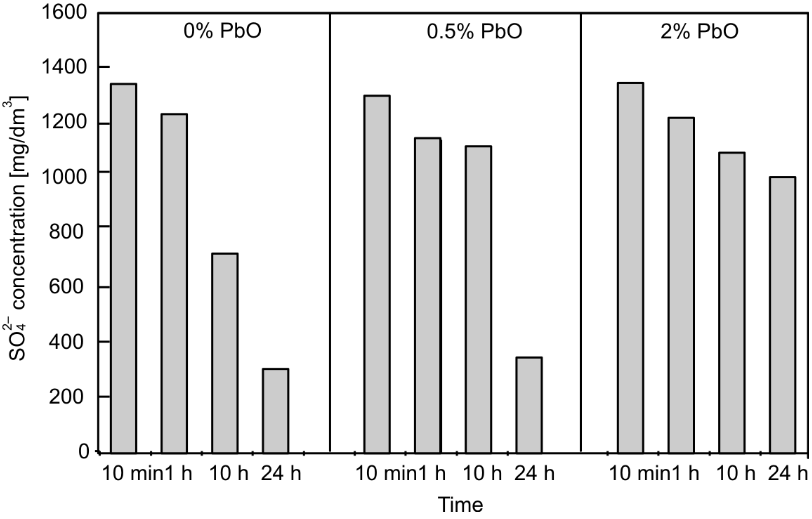

Fig. 8. Concentration of SO_4^{2-} ions in the liquid phase during hydration of suspension of alite + gypsum + PbO in water suspension (*w*/*s* = 10). Rather high concentration of sulfate ions at the beginning of the hydration further decreases upon time. It seems to be related to the calcium sulfate than to lead sulfate solubility

The retarding effect observed for the mixture of alite with gypsum, similar as in the case of portland cement paste, leads to the presumption that a part of Pb^{2+} ions enters the reaction with sulfate ions, and the barrier of poorly soluble $PbSO_4$ is thus formed. Sulfate ions in alite paste without any other additive cause acceleration of hydration. Gypsum dissolves relatively well, and it is present in the liquid phase, together with calcium ions (from gypsum and alite) being in an equilibrium (see Fig. 8). Subsequently an intense precipitation of calcium hydroxide and C–S–H takes place, as was confirmed by a very high heat evolution peak on the *dQ*/*dt* curve. One can presume that in the liquid phase of high concentration (water-to-solid ratio = 0.5) of complex composition in which, apart from calcium, silicate and sulfate ions, also lead ions appear, a new (pseudo)equilibrium can occur and the crystallization of $PbSO_4$ is possible; this phase can form a thin, impermeable membrane. The membrane collapses after a time. The crystallization of compounds more complex than simple sulfate cannot be excluded. High saturation of the liquid phase, numerous components, shortage of good analytical procedures of chemical composition determination give no possibility of obtaining a satisfactory set of data for verification of thermodynamic predictions indicating which phases might be potentially formed.

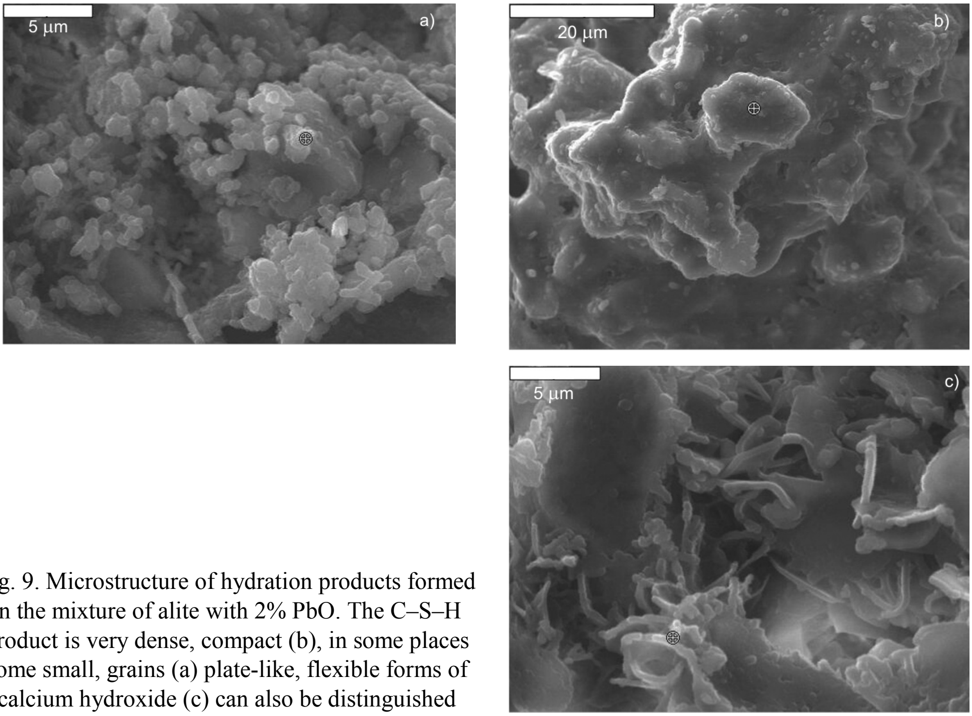

Fig. 9. Microstructure of hydration products formed in the mixture of alite with 2% PbO. The C–S–H product is very dense, compact (b), in some places some small, grains (a) plate-like, flexible forms of calcium hydroxide (c) can also be distinguished

A compact matrix of C–S–H phase, built up from very fine, well adherent particles, is the main component of alite pastes doped with Pb compounds (Figs. 9–13). In the areas of loose structure one can observe small, deformed portlandite platelets as well as C–S–H short rods. In many analytical points in C–S–H particles Pb is easily detectable (Fig. 10).

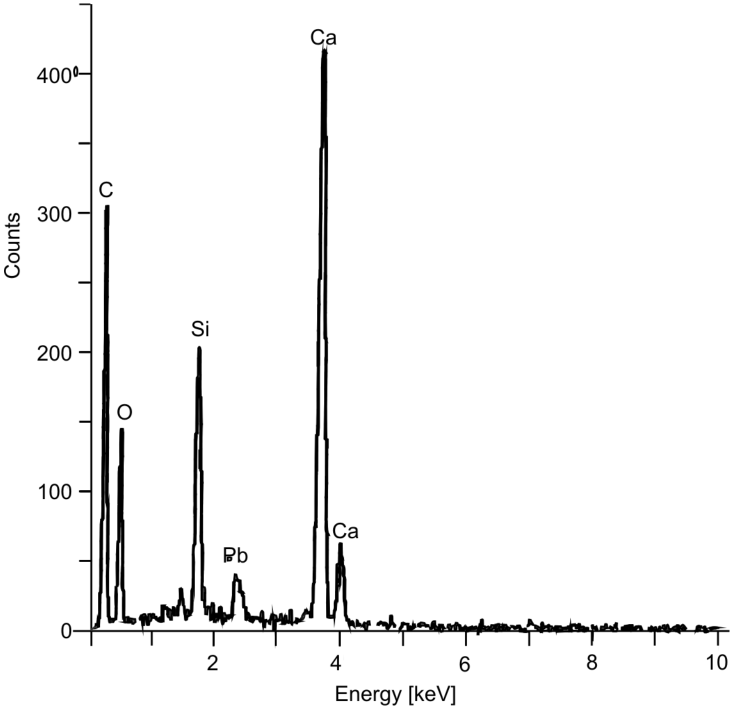

Fig. 10. EDS analysis in the spot shown in Fig. 9a. Pb is built up to the C–S–H

Because the attempt of detecting lead-containing phases by XRD failed (too low content or amorphous character), X-Ray electron spectroscopy was applied for the chemical analysis of the surfaces of hydrated grains. This method was adopted mainly to acquire additional information about the "binding state" of Pb with the alite hydrating surface. It was found that the binding energies of core electrons relating to the Pb 4f orbital (≥ 140 eV, in some cases splitting with some lower value) should be mainly attributed to the occurrence of lead in the form of $PbSO_4$; similar values are characteristic of Pb in complex organic compounds. It was also found that the binding energies of core electrons on the S 2p orbitals in the samples with Pb correspond to the sulfate ions bound in $PbSO_4$ (binding energies of core electrons 2p in sulfur atoms are lower in the case of gypsum; this has been also verified experimentally in this work). However, because there is a disproportion between the total energy values (surfaces of bands), showing the shortage of sulfate ions on the surfaces of hydrating alite grains to transform all the Pb ions into sulfate (in the samples with lead- and sulfate-bearing components), one can conclude that the part of Pb^{2+} is built in superficial parts of the C–S–H phase. In the samples with Pb compounds containing no sulfate, high energies of XPS spectra (≥ 140 eV) were also recorded.

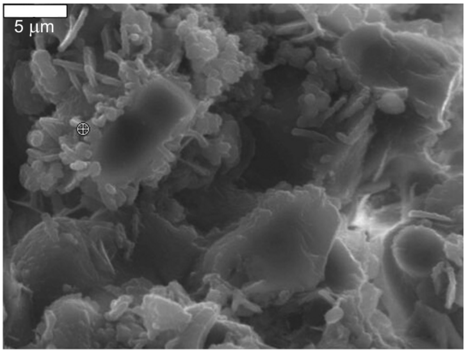

Fig. 11. SEM. Microstructure of hydration products formed in alite paste processed with $Pb(NO_3)_2$ solution (concentration corresponds to 2% PbO by mass of alite), similar to that produced with 2% PbO

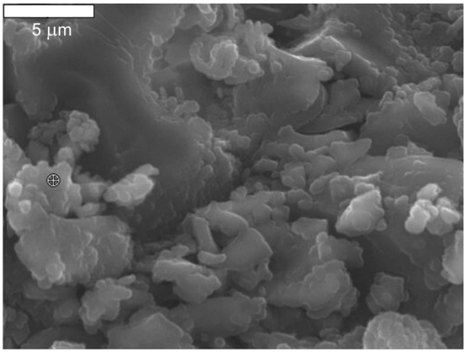

Fig. 12. SEM. Microstructure of hydration products formed in 95% alite + 5% gypsum mixture with 2% PbO. Massive, uniform C–S–H together with small, poorly separated grains

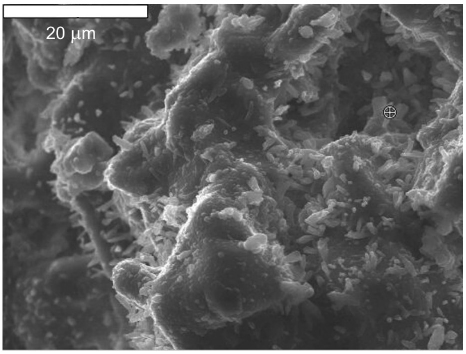

Fig. 13. Microstructure of products of hydration formed in the 95% alite + 5% gypsum mixture with 2% PbO (dense, compact, low porosity; similar as that in Fig. 9b)

XPS measurements provided other information regarding hydrating samples. XPS analysis of the surface of the alite sample exposed to water revealed the presence of C–S–H and calcium hydroxide in the layer that was only a few molecules thick. When alite is hydrated in the mixture with gypsum at excess water, a substantial part of C–S–H is replaced by a sulfate product – undoubtedly gypsum. With the addition of PbO to the hydrating suspension, there is no portlandite on the alite surface but the $PbO/Pb(OH)_2$ together with Pb incorporated to the C–S–H can be derived from distribution of oxygen. Addition of gypsum with PbO to the hydrating alite gives in turn C–S–H with strongly bound Pb (with energy $\geq$ 140 eV, as mentioned above). The formation of lead sulfate results from the presence of sulfate anion with binding energies of core electrons 2p in sulfur atoms attributed to sulfate anion in $PbSO_4$ (as discussed above). The composition of hydrated alite surface is modified also when the hydration takes place in the lead nitrate solution – Pb is then incorporated to the C–S–H phase, some amount of portlandite crystallizes. When gypsum is introduced to this mixture, one can find C–S–H modified by Pb, $PbSO_4$, as well as by some amount of $PbO/Pb(OH)_2$ and portlandite.

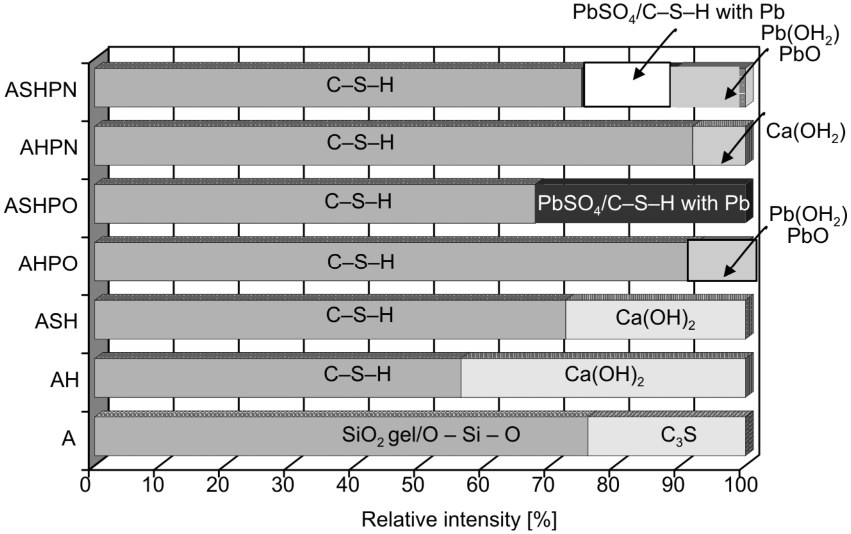

Fig. 14. Distribution of binding energies of core electrons on O 1s orbitals among particular compounds on the surface of hydrated alite grains, from XPS measurements (A – alite; H – hydration in water suspension, S – gypsum, PO – PbO, PN – $Pb(NO_3)_2$)

The spectrum of alite coarse grained surface in Pb^{2+} ions and gypsum containing suspension is complex. One should remember that alite was shaken with water (*w*/*s* = 10) and it could be the reason why only a part of $PbSO_4$ was precipitated on the surface of grains (this compound shows some solubility). It should be underlined that throughout all the measurements a strong bond is seen between Pb and a component of hydrated alite paste – mainly C–S–H. Therefore C–S–H in the experiments reported in the presented work acts as a Pb ion immobilizing environment. Recently in some reports the Ca–Pb–S–H formula appeared, as attributed to the C–S–H soaked with Pb ions; this combination has been fully described based on the microstructure and microprobe analysis [5].

4. Conclusions

PbO additive does not retard the hydration of alite as in cement paste. A significant acceleration of heat evolution and heat evolved value is observed with increasing PbO content. Upon the addition of gypsum to the alite paste, hydrated with PbO or $Pb(NO_3)_2$, the reaction becomes strongly retarded – a substantial elongation of the induction period takes place. In alite pastes hydrated with Pb-bearing compounds, there are no other phases, apart from alite and alite hydration products (C–S–H and portlandite), according to XRD analysis. The microstructure of alite pastes hydrated with Pb compounds shows the presence of compact, homogenous C–S–H (poorly distinguishable, highly adherent, small particles) with Pb bound to the surface. The portlandite crystals are imperfect, with declination from a hexagonal shape. Lead introduced to the hydrated alite suspension is presumably incorporated into the C–S–H phase, as it can be derived from the high binding energies of core electrons on Pb 4f orbitals. The sulfate ions in Pb^{2+} containing hydrated suspension are combined in $PbSO_4$.

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