Hazardous industrial waste stabilization using inorganic phosphates: Investigation of possible mechanisms*

Themistoklis A. Ioannidis and Anastasios I. Zouboulis‡

Department of Chemistry, Division of Chemical Technology, P.O. Box 116, Aristotle University, GR 54 124, Thessaloniki, Greece

Abstract: The present study focuses on the use of phosphate-containing compounds, such as apatites, as stabilization additives for solid industrial wastes. The examined highly toxic waste contained mainly lead, iron, and bromides. Phosphates (synthetic or natural), when used as additives, were found to diminish the release of lead from the stabilized waste below the respective legislative concentration limits, following the application of DIN 38414 standard leaching method and within the range of pH values 7.5–10.5. The respective synthetic compounds of lead, PbO and Pb(OH)Br, existing also in the solid waste, were additionally studied during simulation experiments, in order to examine the possible mechanisms of waste stabilization, by using the same additives (phosphates). The obtained results showed the possibility of another parallel mechanism, different from that proposed in the literature, which is the sorption of aqueous lead ions onto the apatite surface. It was suggested that lead can be also transformed into the less soluble solid phases through the interaction (surface crystallization) of exposed lead surface with the aqueous environment. The formation of new crystals onto the surface of lead phase was sufficiently fast, especially in the case of natural phosphate mineral additive, most probably due to the presence of calcite, which supplies part of its carbonate content for the formation of respective lead carbonate solid phases.

Keywords: Waste stabilization; DIN 38414 leaching method; inorganic phosphates; Pb(OH)Br; crystal formation; mechanisms.

INTRODUCTION

The use of inorganic phosphates has received increased attention, regarding several research and development (application) issues, especially during the last decades. The main reason is that the major mineral phases (apatites), as well as those substituted with carbonates, are also present in bones and teeth in the form of hydroxyapatite and fluorapatite, respectively [1,2]. Nriagu had studied the conditions of apatite phase transitions in the environment [3–6]. Owing to the improved stability of these solid phases, their use has been also suggested for several environmental technology applications, such as soil remediation/stabilization [7–9], or water/wastewater treatment [10]. The initial apatite structure allows many substitutions, regarding both cations and anions. Several ions that can be incorporated (or replaced) into the apatite structure have been previously published [9–13].

In this study, the possibility of using inorganic phosphates as additives for the effective stabilization of hazardous industrial wastes, containing as major constituents lead, iron, and bromides, is shortly presented. The originality of the present work is mainly based on the performance of experiments using similar (although synthetic) compounds of lead, as those found in the actual industrial waste, in order to provide information regarding the morphologies of respective solid phases' formation, the interactions that might occur between the lead content and the phosphate additives and the possible mechanisms that may take place. The studied synthetic solid pollutants were PbO and Pb(OH)Br. Pb(OH)Br was especially found to be the main lead-containing phase of examined industrial solid waste. The other compound (PbO) can be also found in several other industrial solid wastes as the end-product of incineration processes, whereas both compounds (or mixtures of them, including also the thermal derivatives of the latter) can be found in street dusts and in soils near heavy traffic roads worldwide. In this case, photochemical reactions will occur, when lead bromide and its derivatives come in contact with the daylight, leading to the formation of PbO or $Pb(OH)_2$ [14]. The results obtained by these (simulation) experiments were compared with those performed by using the actual solid industrial waste, and useful conclusions regarding the respective mechanisms were depicted.

MATERIALS AND METHODS

The detailed characterization of studied waste is presented in Table 1. The examined inorganic phosphate additives were either synthetic (Merck 2196) or natural. According to the respective XRD data (not presented) the synthetic additive consisted mainly of $Ca_{9.8}Na_{0.058}(PO_4)_{5.6}(HPO_4)_{0.4}(OH)_2 \cdot 0.8H_2O$. The natural mineral phosphate was obtained from the Kosmiras area (Epirus, Greece); it contained 40.0 % francolite $[Ca_{9.25}Na_{0.35}Mg_{0.14}(PO_4)_{4.74}(CO_3)_{1.26}F_{2.50}]$ and 52.9 % calcite $(CaCO_3)$. Additional data about these additives can be found elsewhere [15,16].

Appropriate mixtures between the examined waste and the specific additives were prepared in order to examine a variety of conditions, such as waste stabilization and simulation of contaminated soil stabilization. Water was used for the formation of semi-aqueous pastes. The samples were dried, and the application of DIN 38414 standard leaching test method was applied [17]. The experimental compositions of mixtures are presented in Table 2. The low concentrations of lead in the leachates of stabilized waste were measured by the use of atomic absorption, combined with graphite furnace (Perkin Elmer 5100 ZL). The background modifier was an aqueous solution of $NH_4H_2PO_4$ (50 μg) and $Mg(NO_3)_2$ (3 μg). Total phosphorus was determined by the classical colorimetric method [18].

Table 1 Chemical characterization and the respective solid phases of studied hazardous industrial waste.

Element	(%) w/w	Deviation (± w/w %)	Solid phase	(%) w/w
Pb	29.58	2.11[1]	Pb- and Br-containing phases:	34–38
Fe	33.01	1.27[2]	mainly Pb(OH)Br and, in small	
Br	10.08	1.71[3]	amounts, its thermal derivatives	
Si	2.77	0.44		
Al	1.83	0.74	Other lead phases:	<5
Na	1.27	0.15	PbO, PbS, $PbSO_4$, $PbO \cdot PbSO_4$,	
Ca	0.54	0.02	and small amount as mixed	
S	0.53	0.06	oxides with iron	
Mg	0.41	0.04		
Bi	0.34	0.01	Iron oxides:	44–48
Mn	0.24	0.02	mainly Fe_2O_3,	
K	0.19	0.01	approximately 40 %	
Ti	0.10	–	crystalline and amorphous.	
Cr	0.05	–	In small amounts, Fe_3O_4	
Sb	0.07	–	and α-FeOOH	
Co	0.05	–		
As	<0.02*	–	Other:	10–15
Tl	0.04	–	Mainly silicates and	
V	0.04	–	aluminosilicates	
P	0.03			
Cu	0.03			
Zn	0.02	–		

Total carbon: <1 % w/w	Inorganic carbon: 0.2 (TIC)
	Organic carbon <0.75 (TOC)

H_2O: 4 % w/w

[1] and [2]Pb and Fe: Average deviation of 7 samples (AAS).
[3]Br: Average deviation of 3 samples (UV–vis).
The other values were obtained by XRF measurements (average of at least 2 samples).
*In one sample: As 0.4 % w/w.
The maximum deviation of these measurements, regarding the concentration of minor elements (i.e., those existing in concentrations less than 0.5 % w/w) was less than 0.04 % w/w for all samples.

Table 2 Initial compositions and coding for the formation of aqueous admixtures (pastes) between the industrial solid waste and the respective additive.

Code	Waste (g)	Additive (g)	Water used for the preparation of paste ("process water") (g)
		Synthetic phosphates	
SW1	2	0.48	1.8
SW2	2	0.99	1.55
SW3	2	0.27	0.85
		Natural mineral phosphates	
FW1	2	1.46	0.75
FW2	2	2.56	1.4
FW3	2	0.97	0.8

	Simulation of lead-contaminated soil			
	Waste (g)	SiO_2* (g)	Synthetic phosphates	
SWS1	0.5	9.5	0.12	2.7
SWS2	1	9	0.24	2.9
SWS3	5	5	1.20	3.2
			Natural mineral phosphates	
FWS1	0.5	9.5	0.37	2.7
FWS2	1	9	0.73	2.5
FWS3	5	5	3.66	2.8

	Simulation of lead-contaminated soil, using PbO as the contaminant			
	PbO (g)	SiO_2* (g)	Synthetic phosphates	
SO1	0.5	9.5	0.38	2
SO2	1	9	0.75	2.5
SO3	5	5	3.76	5.5
			Natural mineral phosphates	
FO1	0.5	9.5	1.15	2.3
FO2	1	9	2.29	2.5
FO3	5	5	11.47	3.8

*Addition of clean sand, containing over 99.5 % w/w SiO_2.

Additionally, experiments were also performed, applying higher dilutions of solid mixture (waste and additive) by using deionized water. For this reason, microquantities of the examined additives (phosphates) were mixed with the respective synthetic compounds of lead, i.e., with (yellow) PbO (Johnson Matthey GmbH, Alfa) or with Pb(OH)Br, which was synthesized according to the experimental conditions found in the literature [19–21]; the relevant procedure, producing a polycrystalline material, was appropriately adopted [22]. The respective compositions/samples, regarding the "high-dilution" experiments, are presented in Table 3. These samples, after interacting with water for 24 h in the horizontal thermostated shaking bath (200 rpm and 30 °C), were filtrated and the obtained solid residues were examined by the use of FT-IR (Perkin–Elmer Spectrum One model) and scanning electron microscopy (SEM) (JEOL JSM-840 model).

Table 3 Initial compositions of the admixtures (contaminant and additive) and coding for the "high-dilution" experiments; the initial molecular quantity of lead (96.5 μmol), as well as of synthetic phosphate addition (20 mg), was the same in all experiments.

Code	PbO (mg)	Pb(OH)Br (mg)	H_2O (g)	L/S (w/w)
SHD1	20	–	50	1250
SHD2	20	–	250	6250
SHD3	–	27.6	20	420
SHD4	–	27.6	250	5250
FHD1	20	–	50	1250
FHD2	20	–	250	6250
FHD3	–	27.6	20	420
FHD4	–	27.6	250	5250

RESULTS AND DISCUSSION

Lead release from the stabilized solid industrial waste after the application of standard leaching method (DIN 38414)

The obtained results showed a significant decrease of lead concentrations in the leaching solutions, after the application of standard leaching method (DIN 38414), when both additives (synthetic and natural apatite) were applied for the stabilization of examined hazardous solid industrial waste, in comparison with the initial (raw) waste. The respective lead concentrations were found either within the limits of DIN method (0.4–2 mg/l) [23], or below them (Fig. 1). The presence of silicates in the form of clean sand, used for the simulation of contaminated soils, resulted in lower concentrations of lead in the respective leachates. This can be attributed to the further improvement of lead sorption onto the surface of silicates, owing to the introduction of new surface groups in the system, hence increasing the availability of surface sites for sorption, as it has recently been discussed in the literature [24]. It was also proved that the sorption of lead onto the surface of the silicates will increase as the ionic strength decreases, whereas the formation of mononuclear and polynuclear complexes of lead should be also expected onto the solid surface.
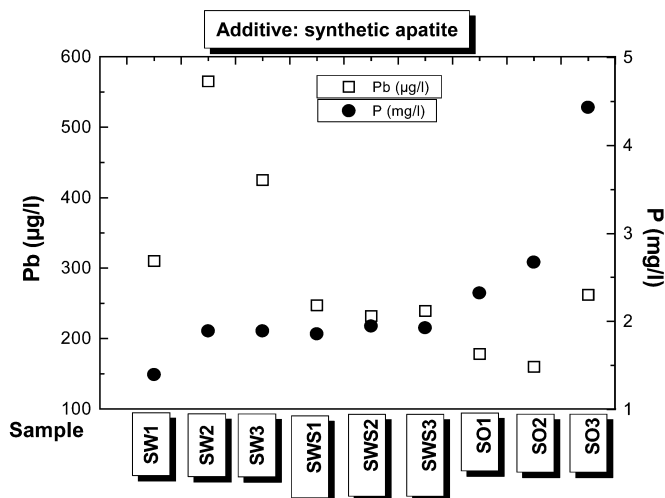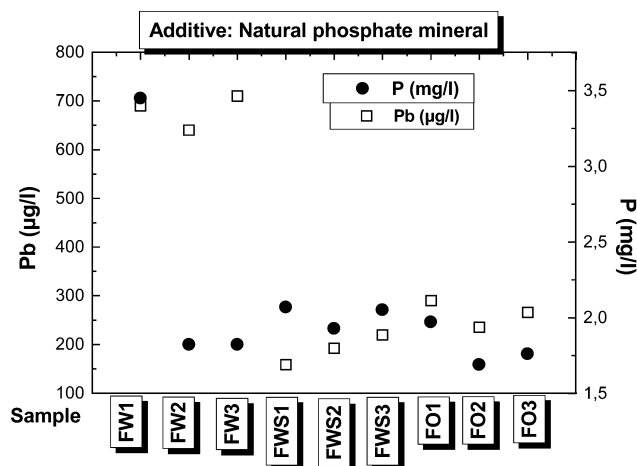
Fig. 1 Lead and phosphate (total) concentrations measured in the leaching solutions after the application of DIN 38414 standard leaching test method, when (a) the synthetic phosphate, or (b) the natural mineral phosphate was applied as stabilization additive of the examined hazardous solid industrial waste.

The molecular ratio between lead and phosphorous (Pb/P) in the leaching solutions was found to be rather low (below 0.01), i.e., much less than the theoretical value of 1.67, which is supposed to imply the formation of insoluble pyromorphite, $Pb_5(PO_4)OH$. These results can be attributed to sorption re-actions [25], which are considered the main cause for the stabilization of lead for both examined cases, i.e., with the addition of phosphates, as well as in the phosphates and silicates mixture. It is worth not-ing that during a previous study, when using natural mineral phosphate, the formation of hydroxy-cerussite, $Pb_3(CO_3)_2(OH)_2$, was recorded [15]. Nevertheless, the available information regarding the formation of new crystals could not be considered adequate, owing to the complexity of examined ad-mixture. However, in specific places of stabilized products, new needle-like crystal phases were identi-fied, containing different molecular ratios between Pb/P, which varied within a wide range of values, as

found by energy-dispersive spectrometry (EDS) measurements. Particle–particle interactions due to the applied homogenization procedure (manually) may be also possible in the microscale, making the interpretation of obtained results rather unclear. Solid particles containing lead phosphate and bromides were found to contain also calcium and iron (data not shown), indicating that phase transitions (if they occurred) were rather in the primary stage. The same remark can be made for the needle-like crystals. As a result, it can be assumed that when lead is released from the industrial waste (or from the respective synthetic lead compounds), it can be either sorbed onto the surface of coexisting silicates, or onto the surface of phosphates, whereas the presence of aqueous phosphates and carbonates will be the reason for the precipitation of newly formed insoluble lead-containing solid phases, which would present the morphology of needle-like crystals.

Certain (indicative) measurements of leaching solutions' conductivity revealed that the total amount of major ions, which may contribute to the respective values (i.e., mainly Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-), was higher for the case of natural mineral phosphate additive; more specifically, the range of values was approximately 150–250 µS/cm higher. This finding was more profound during the conductivity and pH measurements of samples containing PbO as the solid contaminant. In these measurements, the pH values of 9.7 ± 0.2 and the conductivity values of 70 ± 10 µS/cm were recorded for the case of synthetic phosphate additive, whereas the respective values for the natural mineral phosphate additive were higher, i.e., 10.3 ± 0.2 for the pH and 320 ± 40 µS/cm for the conductivity, respectively. These differences can be attributed to the possible simultaneous release of alkali and alkaline earth metals in the case of natural mineral phosphate additive. It must be noted however, that unlike other relevant studies, background electrolyte was not used in this case, which directly implies that the ionic strength (initial and final) would be as low as possible; as a result, the pH measurements were expected to be rather sensitive. When the synthetic contaminant PbO was used as a simulation pollutant, the respective pH values of leaching solutions were found to be higher, as compared to those found with the industrial waste; in the latter case (i.e., in the real waste), bromide release and its acidic hydrolysis was the reason for the observed lower pH values.

The results found in this study suggest that when calcite and aqueous phosphates are simultaneously present, as in the case of natural mineral phosphate additive, there would be a phase transformation toward the apatite phase (Fig. 2 and [26]). However, this theoretical approach will not necessarily prevent the formation of possible other (intermediate) solid phases. In that case, the solubility of newly formed solid phases would be expected particularly low, making the long-term assessment of waste disposal environmentally safe, concerning the overall phase transformations and stabilization of created lead phases.
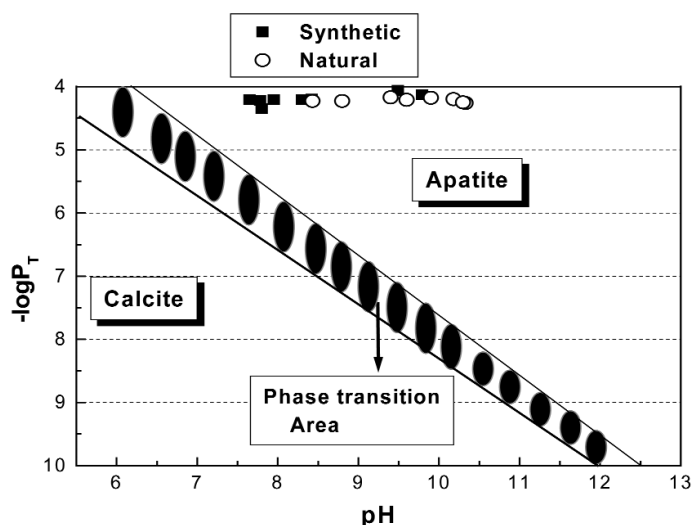
Fig. 2 Indicative diagram of the possible phase transition between calcite and apatite solid phases (and vice versa) in conjunction with the obtained experimental measurements. The borders' area, regarding the phase-transition area, was obtained from the literature [26].

"High-dilution" experiments

In order to elucidate further the transformations and the phase modifications occurring on the surface of solids, further experiments were performed, using microquantities of the additives and of the (synthetic) contaminants, PbO and Pb(OH)Br, termed hereafter as "high-dilution" experiments (Table 3), according to the aforementioned procedure. The FT-IR spectra of residues obtained after the performance of "high-dilution" experiments (Fig. 3), revealed that the observed peaks were similar with those of the examined additive (synthetic phosphate or natural mineral phosphate), regarding the respective wave number values. However, certain differences were observed, concerning the relative intensity of these peaks, which is expected to be lower for the case of mixtures, owing to the lower content of additives.

The synthetic phosphate additive, when compared with the respective admixtures containing also synthetic contaminants (i.e., apatite and PbO or Pb(OH)Br), presented broader and stronger peaks around 1650 cm^{-1}, as well as in the 660–680 cm^{-1} range, indicating that a certain amount of crystallized water was removed or altered [27]. The intensity of functional group PO_4^{3-} around 1035 and 1090 cm^{-1} (v_3) [2] presented certain variations, becoming sharper, whereas the intensity of the latter peak became lower, indicating that the new phases, which include the O–P bond in their structure, were more stable. The wave number of 1030 cm^{-1} peak presented a small shift toward lower values. The peak in 962 cm^{-1}, which was attributed also to $v1$ vibration of PO_4^{3-}, was unchanged, whereas the peak in 878 cm^{-1} became broader for the case of admixtures. Furthermore, the v_4 (PO_4^{3-}) peaks in 630, 602, and 564 cm^{-1} became sharper and relatively smaller for the case of admixtures. Major differences were observed in the area of double peak (1415 and 1447 cm^{-1}), where the vibration of HPO_4^{2-} functional group is expected [28]. The peaks became broader for the admixtures, whereas clear differences in the relative intensities were recorded. The peak in the 1411–1415 cm^{-1} range was sufficiently increased, and a small shift toward lower wave numbers was recorded. The peak in 473 cm^{-1} was also attributed to the v_2 vibration of functional group PO_4^{3-}. The sharp peak in 3571 and 632 cm^{-1} was assigned to the OH (stretch and liberation), as well as the broad peak in 3468 cm^{-1} [29]. The 600–640 cm^{-1} triple peak, which became lower for the case of the admixtures, was attributed to O–P–O bonds [30]. These data can be considered indications that the newly formed solid phases contain the functional group of
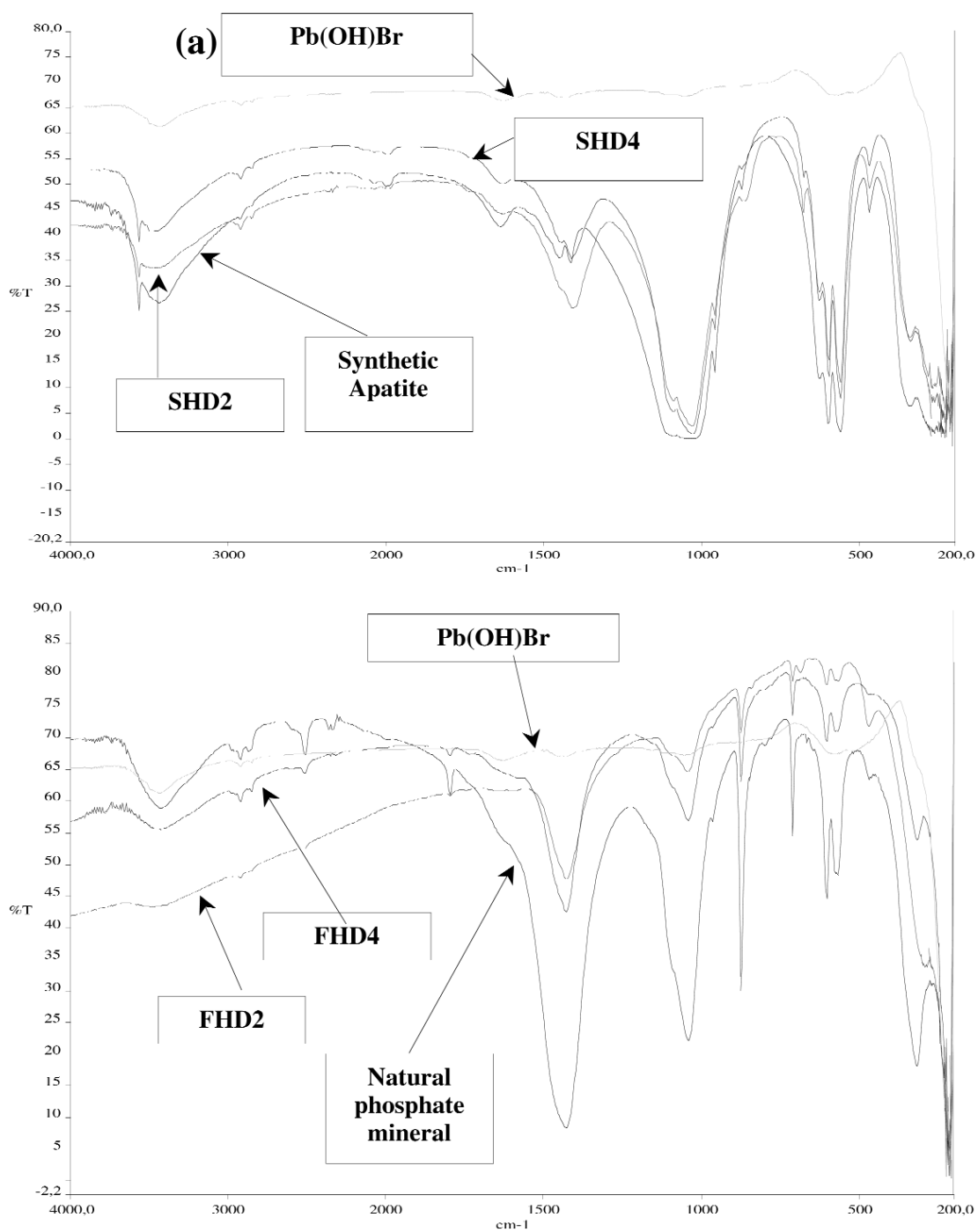
Fig. 3 FT-IR spectra of the solid residues obtained after the "high-dilution" experiments, using as stabilization additives: (a) synthetic apatite, and (b) natural mineral phosphate. All these samples were preheated at 105 °C.

HPO_4^{2-} in their structure, as well as that of PO_4^{3-}; also, the formation of bonds Pb–O–P with both aforementioned functional groups was highly possible.

The FT-IR peaks for the case of natural mineral phosphate belong mainly to the phases of calcite and francolite. More specifically, the broad peak in 1430 cm^{-1}, the sharp peak in 875 cm^{-1}, the sharp peak in 713 cm^{-1}, as well as the broad band in the 3430 cm^{-1} belong (partly) to the phase of calcite [2,31]. The peak in 875 cm^{-1} became relatively weaker for the case of admixtures. This observation in conjunction with the small shift in the 1430 cm^{-1} peak for the case of the admixtures, as well as with the appearance of peak in 694 cm^{-1}, can be received as indications of phase transformations and the formation of bonds Pb–O–C. The double peak (partly overlapped in 1040 and 1080 cm^{-1}), as well as the peaks in 605 and 567 cm^{-1} (double) and in 471 cm^{-1}, can be attributed to the functional group of PO_4^{3-}. This peak presented weakened intensity and became broader for the admixtures, indicating the formation of solid phases that contain bonds of P–O type, partly substituted by other ions (such as lead). The relative vibrations revealed also that the peaks attributed to the vibrations of C–O bond were increased. Therefore, it can be assumed that the newly formed solid phases obtained by these experiments can be attributed to phases, which also contain carbonates in their structure. The samples SHD1, SHD3, FHD1, and FHD3 presented similar spectral patterns with the samples SHD2, SHD4, FHD2, and FHD4, respectively, and they are not further discussed.

The relevant SEM micrographs (Figs. 4–6) show that formation of crystalline lead phases occurred. In all these samples and irrelevantly of the initial form of lead solids (i.e., PbO or Pb(OH)Br), or from the applied additive (i.e., synthetic phosphate or natural mineral phosphate), needle-like as well as plane-like crystals were formed onto the lead solid phase, simultaneously with the formation of crystals observed onto the apatite surface.

As shown in Fig. 4a, particle–particle interactions can be observed. In most of these particles, Pb, P, as well as Ca were present, as found by the respective EDS measurements. A rather peculiar morphology was recorded in Fig. 4b, where plane-shaped particles were formed (rose-like). White needle-like crystals similar to those observed during other relevant studies [7] also appeared, although in the relevant literature studies, lead was added as aqueous solution, whereas the apatite was examined as sorbent material; crystals formed in the surface of phosphate solids, and the proposed mechanisms were the initial dissolution of apatite, leading to the release of calcium and phosphate, which was followed by the surface precipitation and sorption of lead [25], resulting to the formation of pyromorphite, $Pb_5(PO_4)OH$, crystals.

The SEM micrographs of the present study adequately reveal that there is a strong possibility for a different mechanism, which can take place during the applied experimental procedure, which involves the agitation of solids. In this case, the formation of crystals was also observed onto the surface of lead solids, whereas the crystals were larger, indicating that the newly formed phases would be less soluble. This observation suggests that the hydrated surface sites of lead solids may also be available for sorption and for eventual surface precipitation, acting as substrates for crystal growth. The later notice was more profound for the case of natural mineral phosphate additive, probably due to the higher solubility of calcite content.
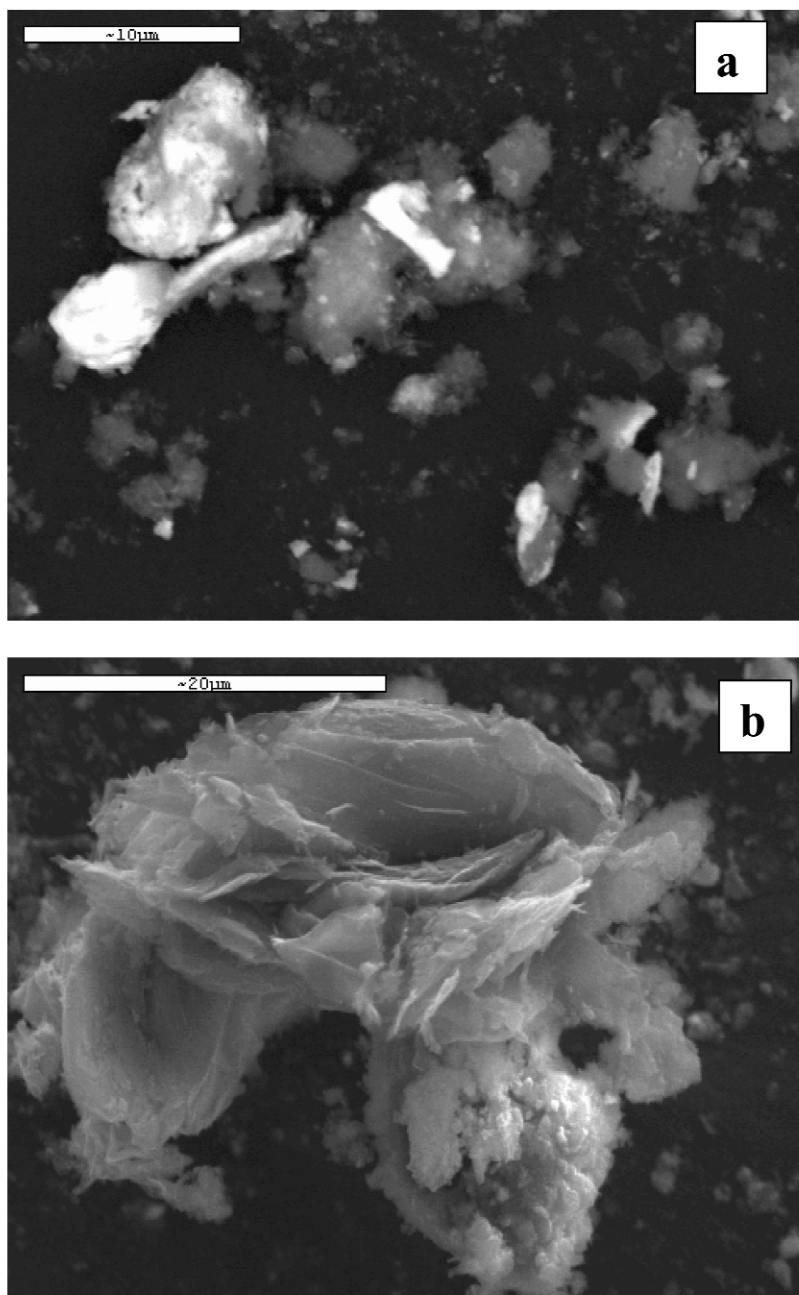
Fig. 4 SEM micrographs of the residue from the sample SHD2 (mixture of synthetic phosphates (apatite) with PbO), after the "high dilution" experiment; (a) particle–particle interaction, (b) appearance of plane-shaped particles (rose-like). The bars represent 10 or 20 μm length for Figs. 4a and 4b, respectively.

In Fig. 5a, a particle of natural mineral phosphate is highlighted (marked with a parallelogram), revealing that certain changes in morphology were occurred, but not clearly enough, as those taken place onto the surface of PbO (marked with a circle). In Fig. 5b, certain similarities, regarding the surface morphology of solids, with other relevant studies were observed. The most interesting remark appears to be that similar crystal forms can be formed, although different initial experimental conditions
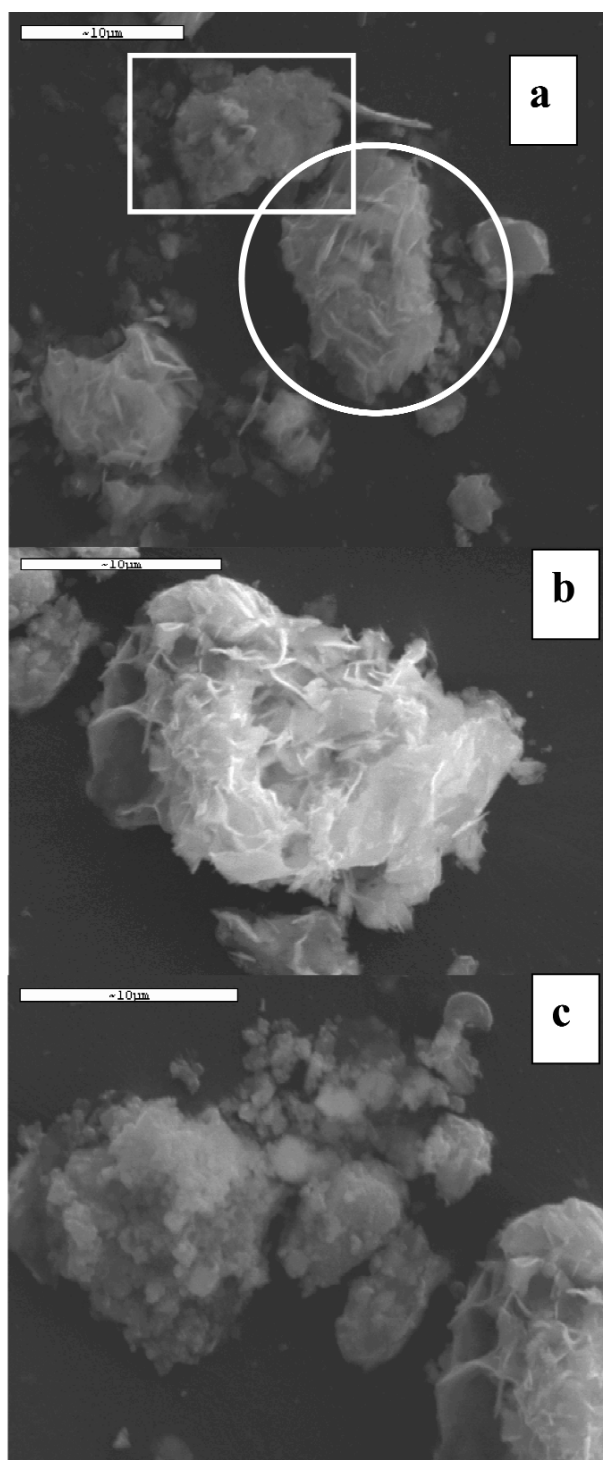
Fig. 5 SEM micrographs (a, b, and c) of the residue from the sample FHD1 (mixture of natural mineral phosphate with PbO), after the "high-dilution" experiment: (a) natural mineral phosphate (parallelogram) and PbO contaminant (circle), (b) PbO after surface precipitation/crystallization, and (c) natural mineral phosphate and PbO. The bar represents a 10 µm length.
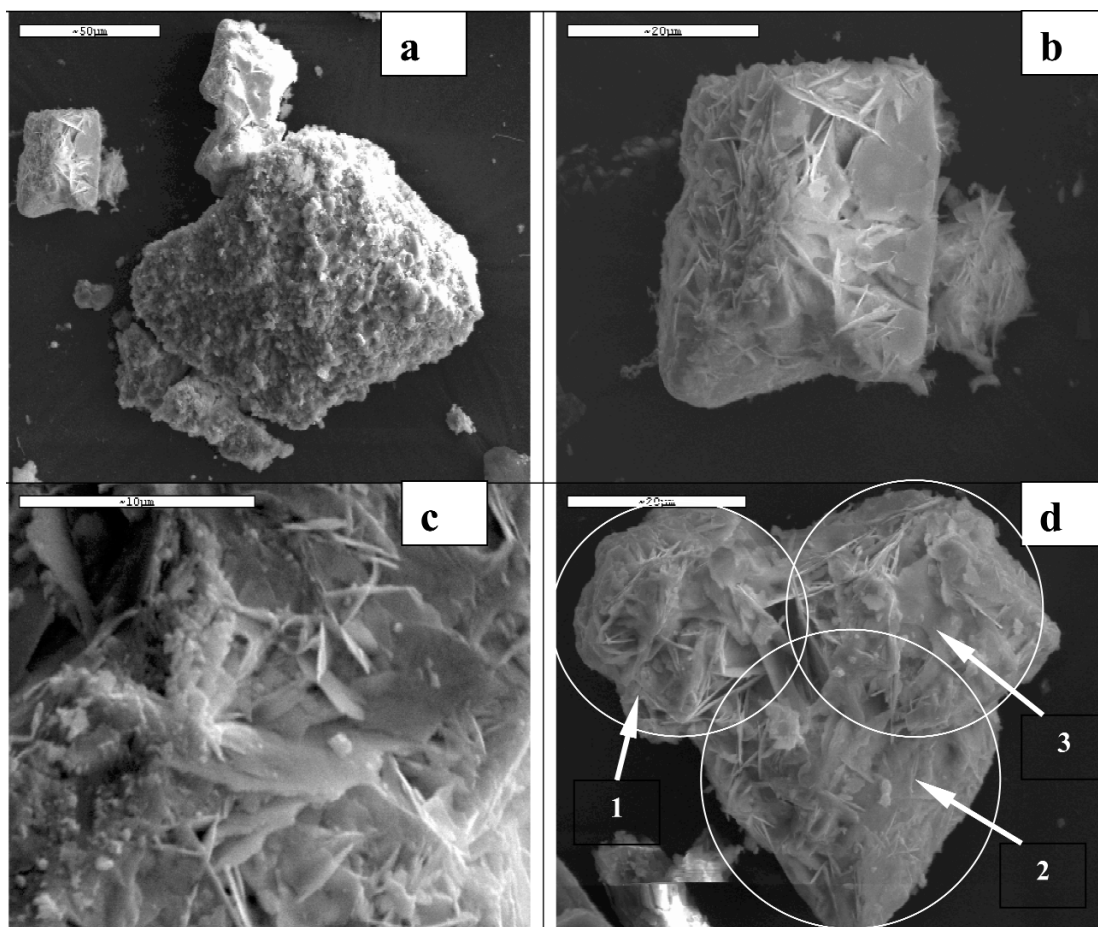
Fig. 6 SEM micrographs of residue from the sample FHD3 (mixture of natural phosphates with Pb(OH)Br) after the "high-dilution" experiment. The bars represent a 50, 20, 10, and 20 μm length for Figs. 6a–6d, respectively: (a) the central particle is the natural mineral phosphate additive; back in the left, a crystal of Pb(OH)Br can be noticed, (b) the previous crystal of Pb(OH)Br in higher magnification, (c) closer view of well-crystallized area of Pb(OH)Br, and (d) simultaneous crystallization/deposition among at least three different crystals, which are inter-connected by the newly formed phases.

were applied. Plate-like crystals were also produced in a recent study, where a biomimetic process using apatite was applied, but without the presence of aqueous or solid lead [32]. The SEM micrographs presented in that study showed the formation of well-formed crystals onto the apatite surface; these new crystals contained molar ratio of Ca/P = 1.48. Considering also that carbonates were present in both studies, it can be assumed that crystals containing calcium and carbonates may also form. Similar plate-like crystals were found in the present study, suggesting that the morphology of new crystals can be quite similar, irrelevantly from the initial form of substrate. These observations can be also noticed in Fig. 5c.

On the contrary, the EDS analysis of apatite surface revealed that the deposited/formed lead phases were found either in needle-like crystals, or in irregular morphologies. As a result, it can be assumed that particle–particle interactions was the main reason for these observations, which means that the initial mixing of solids was responsible for these surface modifications, whereas water was actually acted as the binding agent. However, it is also possible that the coexisting colloidal particles (with di-

mensions less than 1 μm) may become nuclei centers for the subsequent crystal growth, or appropriate substrates for the surface precipitation of lead-containing phases.

In Fig. 6, where the synthetically produced compound Pb(OH)Br was used as the lead contaminant, the orientation of newly formed crystals was observed to be perpendicular to the surface of substrate. A closer view revealed that even the areas, which appeared as needle-like crystals, were rather plane-shaped. The characteristic precipitation/crystallization onto the surface of Pb(OH)Br can be clearly observed in Fig. 6b, where the background crystal of Pb(OH)Br maintained its initial morphology. In this micrograph, crystals that grew across the main body of the substrate, and not only onto the surface, can also be noticed. Moreover, in Figs. 6c and 6d, the extent of crystallization can be further and more clearly observed. Especially in Fig. 6d, some of the newly formed crystals seem to bind three (at least) distinct initial crystals, suggesting that crystallization would possibly proceed to different particles, which are in close distance to each other and will be connected by the newly formed crystals.

Further analysis of the newly formed crystals was performed by EDS, revealing that they present varying compositions, regarding the molar ratio of Pb/P, even for the case of needle-like crystals. The possible explanation for this observation is that the newly formed phases were either metastable, or that the examined crystals were intermediate ("primary") products, partly substituted, which were not thermodynamically stable and can be further transformed.
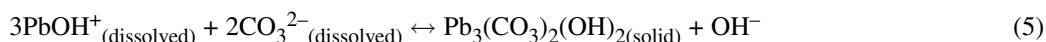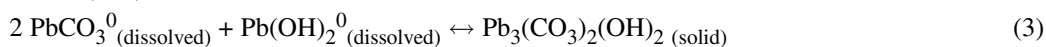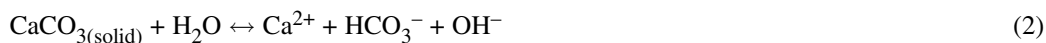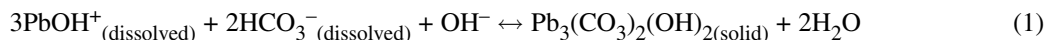
In the case of natural mineral phosphate, especially in the experiments where Pb(OH)Br was used, the crystals formed onto the Pb(OH)Br surface were not found to contain phosphates, although they contain mainly lead. Considering that carbon cannot be measured, owing to the initial procedure of the samples, taking place before taking the SEM micrographs (i.e., due to carbonation), these crystals might be carbonated lead compounds, such as hydroxy-ceroussite, a phase that is not thermodynamically stable, but has been observed during several relevant studies in the pH area 7–11 [15,33,34]. Moreover, although the calculations of Gibbs free energies may suggest the formation of bromopyromorphite, $Pb_5(PO_4)_3Br$, the respective EDS analysis of the formed crystals suggest that if this phase can be formed, it would be rather incorporated into other solid phases, before the total substitution of lead with calcium would take place.

Proposed mechanism

As proved by the aforementioned experimental results, new crystal phases were formed, which are likely to coexist during the stabilization process. The interpretation of results involves the simultaneous dissolution of the additive (solid phosphates, either synthetic or natural), as well as of the examined synthetic solid lead-containing phases (PbO or Pb(OH)Br), followed by the surface precipitation onto the lead phase, or onto the additive. These observations were more clearly observed in the case of synthetic lead compound experiments. The relevant examination of the industrial waste-additive system did not reveal similar crystallization in such an extent. The main reasons were that part of the dissolved lead was sorbed onto the surface of the additive, as well as onto the surface of silicates (in the case of contaminated soil simulation). Furthermore, the initial morphology of lead content in the industrial waste (i.e., its random distribution and mixing with other non-lead phases) cannot act as an appropriate substrate for surface crystallization. Additionally, the release of certain cations (such as other heavy metals) or other anions (such as sulfates) probably inhibited the extent of deposition/surface crystallization of new crystals.

The relevant aqueous chemistry data suggest that there are many ionic species coexisting in such systems, which include lead, phosphates, and carbonates (and all the respective hydrolysis products). However, the polynuclear species of lead, existing in low concentrations of lead [35], have been recently questioned, as newer studies suggest that in such low (aquatic) concentrations lead can be mainly found as mononuclear species [36]. Moreover, when lead coexists with carbonates in aqueous solution, recent data [24] suggested that the main aqueous complex recorded in pH 8.3, was $PbCO_3^0$ and that this aqueous complex will be transported to the calcite surface, prior to uptake. In combination with the reac-

tions proposed by other relevant studies [22,33], as well as with the hydration of calcite surface [37], the following reactions can be proposed, regarding the proposed formation of hydroxy-cerousite:

$$3PbOH^+_{(dissolved)} + 2HCO_3^-_{(dissolved)} + OH^- \leftrightarrow Pb_3(CO_3)_2(OH)_{2(solid)} + 2H_2O \quad (1)$$

$$CaCO_{3(solid)} + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^- \quad (2)$$

$$2\ PbCO_3^0_{(dissolved)} + Pb(OH)_2^0_{(dissolved)} \leftrightarrow Pb_3(CO_3)_2(OH)_{2\ (solid)} \quad (3)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (4)$$

$$3PbOH^+_{(dissolved)} + 2CO_3^{2-}_{(dissolved)} \leftrightarrow Pb_3(CO_3)_2(OH)_{2(solid)} + OH^- \quad (5)$$

Equations 1–3 are proposed mainly for the pH values 7.5–8.5, whereas eqs. 4 and 5 are expected also to contribute, but in higher pH values (8.5–11.5), where the second deprotonation stage of carbonic acid occurs.

CONCLUSIONS

Phosphates (synthetic apatite or natural mineral) proved to be promising additives, concerning the stabilization of industrial solid wastes, especially those containing lead. The concentrations of released lead from the stabilized products after the application of standard leaching test DIN 38414 were found to be in the range of μg/l (i.e., sufficiently lower than the permissible limit of specific leaching test method). The presence of silicates (added in the form of sand in order to simulate the contaminated soil) enhanced the sorption reactions of lead, whereas the stabilization results were adequate in the area of pH measurements around 7–10.5. The indications received from the experimental results suggest that the phase transition of initial calcite content to apatite may occur in the case of natural mineral phosphate, although the formation of intermediate solid phases can be also primarily expected.

The main reasons for the observed stabilization of lead, as well as for the newly formed crystals, appeared to be the following: particle–particle interactions with water acting as the binding agent for the case of micro- and sub-microscale, whereas the dissolution of phosphates in conjunction with the parallel dissolution of lead solid phase produced well-formed crystals, needle-like (in lesser extent) or plane-shaped onto either the surface of the additive, or onto the surface of lead solid phase.

When natural mineral phosphates were applied as additives, the formation of crystals onto the lead solid phases was more profound, especially for the case of Pb(OH)Br. The composition of these crystals was mainly lead carbonate-containing phases with the most probable being hydroxy-cerousite. Generally, the obtained results suggested that phosphates, used as stabilization additives, especially when applied in the hazardous waste landfills can be considered merit materials that will increase the environmental safety of disposed toxic industrial wastes.

ACKNOWLEDGMENTS

REFERENCES

1. J. C. Elliot. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Studies in Inorganic Chemistry*, p. 18, Elsevier, UK (1994).
2. G. Xu, I. A. Aksay, J. T. Groves. *J. Am. Chem. Soc.* **123**, 2196 (2001).
3. J. O. Nriagu. *Inorg. Chem.* **11**, 2499 (1972a).
4. J. O. Nriagu. *Geochim. Cosmochim. Acta* **36**, 459 (1972b).
5. J. O. Nriagu. *Geochim. Cosmochim. Acta* **37**, 1735 (1973).

6. J. O. Nriagu. *Geochim. Cosmochim. Acta* **38**, 887 (1974).
7. Q. Y. Ma, S. J. Traina, T. Logan, J. A. Ryan. *Environ. Sci. Technol.* **27**, 1803 (1993).
8. Q. Y. Ma, T. J. Logan, S. J Traina, J. A. Ryan. *Environ. Sci. Technol.* **28**, 408 (1994a).
9. Q. Y. Ma, S. J. Traina, T. J. Logan, J. A. Ryan. *Environ. Sci. Technol.* **28**, 1219 (1994b).
10. T. Suzuki, K. Ishigaki, M. Miyake. *J. Chem. Soc., Faraday Trans. 1* **80**, 3157 (1984).
11. F. Monteil-Rivera and M. Fedoroff. "Sorption of inorganic species on apatites from aqueous solutions", in *Encyclopedia of Colloids and Surface Science*, pp. 1–26, Marcel Dekker, New York (2002).
12. A. G. Leyva, J. Marrero, P. Smichowski, D. Cicerone. *Environ. Sci. Technol.* **35**, 3669 (2001).
13. J. Rakovan, R. J. Reeder, E. J. Elzinga, D. J. Cherniak, C. D. Tait, D. E. Morris. *Environ. Sci. Technol.* **36**, 3114 (2002).
14. J. Markus and A. B. McBratney. *Progr. Environ. Sci.* **2** (4), 291 (2000).
15. T. A. Ioannidis and A. I. Zouboulis. *J. Hazard. Mater.* **B97**, 173 (2003).
16. T. C. Vaimakis and E. D. Economou. *Ind. Eng. Chem. Res.* **37**, 4306 (1998).
17. Deutsche Norm. *German Standard Methods for the Examination of Water, Wastewater and Sludge*, DIN 38414 (1984).
18. A. D. Eaton, L. S. Clesceri, A. E. Greenberg, M. A. H. Franson (Eds.). *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC (1995).
19. Z. Karaoglanov and B. Sagortschev. *Z. Anorg. Allg. Chem.* **207**, 129 (1932).
20. H. D. Lutz, K. Beckenkamp, S. Peter. *Spectrochim. Acta* **51A** (5), 755 (1995).
21. H. D. Lutz, K. Beckenkamp, T. Kellerson, H. Moller, S. Peter. *J. Solid State Chem.* **124**, 155 (1996).
22. Th. A. Ioannidis. *Treatment and Recycling of Solid Toxic Industrial Wastes Contaminated with Lead and Bromide*, Ph.D. thesis, Aristotle University of Thessaloniki (2004).
23. J. Viguri, A. Andres, R. Ibanez, C. Ruiz Puente, A. Irabien. *J. Hazard. Mater.* **A79**, 63 (2000).
24. E. J. Elzinga and D. L. Sparks. *Environ. Sci. Technol.* **36**, 4352 (2002).
25. Y. Xu and F. W. Schwartz. *J. Contam. Hydrol.* **15**, 187 (1994).
26. W. Stumn and J. J. Morgan. *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley, New York (1996).
27. T. C. Vaimakis and A. T. Sdoukos. *Thermochim. Acta* **277**, 107 (1996).
28. N. Senamaud, D. Bernache-Assollant, E. Champion, M. Heughebaert, C. Rey. *Solid State Ionics* **101**–**103**, 1357 (1997).
29. M. Ayati and H. E. Lundager Madsen. *J. Cryst. Growth* **208**, 579 (2000).
30. B. J. Melde and A. Stein. *Chem. Mater.* **14**, 3326 (2002).
31. N. V. Vagenas, A. Gatsouli, C. G. Kontoyannis. *Talanta* **59**, 831 (2003).
32. Y. F. Chou, W. A. Chiou, Y. Xu, J. C. Y. Dunn, B. M. Wu. *Biomaterials* **25**, 5323 (2004).
33. X. Chen, J. V. Wright, J. L. Conca, L. M. Peurrung. *Environ. Sci. Technol.* **31**, 624 (1997).
34. A. Godelitsas, J. M. Astilleros, K. Hallam, S. Harissopoulos, A. Putnis. *Environ. Sci. Technol.* **37**, 3351 (2003).
35. C. F. Baes and R. E. Mesmer, Jr. *The Hydrolysis of Cations*, John Wiley, New York (1976).
36. N. W. Perera, G. Hefter, P. M. Sipos. *Inorg. Chem.* **40**, 3974 (2001).
37. D. G. Kanellopoulou and P. G. Koutsoukos. *Langmuir* **19**, 5691 (2003).